JUN 10 2004

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COVER LETTER

DATE: June 10, 2004

TO: Philip Isorena, Chief of the Regulatory Unit, SWRCB

From: Jason Cashman

SUBJECT: SWRCB's Statewide General NPDES Permit for the Discharge of Aquatic Pesticides for Aquatic Weed Control in Waters of the United States, SIP Exception – Required Information

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Dear Mr. Isorena,

The application submitted herewith has been prepared on behalf of Woodbridge Irrigation District ("District") in order to fulfill the requirements set forth in the Statewide General NPDES Permit for the Discharge of Aquatic Pesticides for Aquatic Weed Control in Waters of the United States ("General Permit") to enable the District to obtain a Section 5.3 categorical exception.

To obtain a categorical exception from General Permit from the State Water Resources Control Board, the discharge must submit for approval the following information:

1. A detailed description of the proposed action, including the proposed method of completing the action (Attachment 1);
2. A time schedule (Attachment 2);
3. A discharge and receiving water quality monitoring plan (Attachment 3);
4. CEQA documentation (Attachment 4); and
5. Contingency plans (Attachment 5).

The District provides this information within its Application for the State Board's Policy for Implementation of Toxics Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California, Section 5.3 exception as Appendices 1 through 5.

If there are any questions, or if any additional information is needed, please contact either Dan Gallery or myself at our office at (916) 444-2880. We would appreciate the Board's prompt consideration of this matter.

Sincerely,

Jason P. Cashman

Jason P. Cashman
Law Offices of Daniel F. Gallery

cc: Woodbridge Irrigation District

Table of Contents

Attachment 1

Description of Woodbridge Irrigation District's Algae/Aquatic Weed Control Program

Woodbridge Irrigation District: Algae/Aquatic Weed Control Program

The District has an aggressive weed control program for controlling aquatic weeds in the canal and terrestrial weeds along the canal roads during the irrigation season. Aquatic weeds in a canal can reduce the ability of the canal to carry water and increase the amount of hydraulic head needed to push the water to the delivery points. These plants also consume large amounts of water that otherwise would be available for irrigation purposes.

The District has adopted a Quality Assurance Project Plan ("QAPP") for the monitoring of its algae and aquatic weed control program and discharges at spill points into the Sacramento-San Joaquin Delta and waters of the United States. The District's program monitors during the irrigation season and tests for the presence of herbicides that are used in controlling aquatic and terrestrial weeds. The plan also contains best management practices that are designed to reduce the chance of detectable chemicals from entering the canal system.

During it's 80 year history, Woodbridge Irrigation District has employed several methods to combat aquatic weeds, including: dewatering canals, mechanical cleaning of various types, and chemicals including Magnacide H (acrolein), Copper Sulfate and Rodeo (Glyphosate).

Woodbridge Irrigation District uses these chemicals to maintain the functionality of its distribution system. These products are necessary to ensure that design flows are maintained. Unchecked algae growth can actually adversely affect water quality to the point of foul odors, undesirable tastes, livestock and wildlife poisonings and declines in invertebrate and fish populations.

Attachment 2

Woodbridge Irrigation District's
Algae/Aquatic Weed Control Program – Time Schedule

Woodbridge Irrigation District: Algae/Aquatic Weed Control Program – Time Schedule

Woodbridge Irrigation District applies acrolein and copper sulfate throughout the irrigation season. Historically, the number of herbicide applications varies between three to six. The actual number of seasonal applications is determined on an as-needed basis.

Attachment 3

Woodbridge Irrigation District's
Algae/Aquatic Weed Control Program:
Quality Assurance Project Plan / Monitoring Plan

See Attachment 4: CEQA Documentation, Mitigated Negative Declaration, Appendix B

Attachment 4

Woodbridge Irrigation District's Algae/Aquatic Weed Control Program: CEQA Documentation

Form A

Notice of Completion & Environmental Document Transmittal

SCH # _____

Mail to: State Clearinghouse, PO Box 3044, Sacramento, CA 95812-3044 916/445-0613

Project Title: Woodbridge Irrigation District Algae/Aquatic Weed Control Program

Lead Agency: Woodbridge Irrigation District | Contact Person: Anders Christensen

Mailing Address: 18777 No. Lower Sacramento Road | Phone: 209-369-6808

City: Woodbridge, CA | Zip: 95258 | County: San Joaquin

Project Location: See Project Description

County: San Joaquin | City/Nearest Community: Woodbridge

Cross Streets: _____ | Zip Code: _____ | Total Acres: _____

Assessor's Parcel No. _____ | Section: _____ | Twp. _____ | Range: _____ | Base: _____

Within 2 Miles: State Hwy #: _____ | Waterways: _____

Airports: _____ | Railways: _____ | Schools: _____

Document Type:

CEQA: ☐ NOP ☐ Early Cons ☐ Neg Dec ☐ Draft EIR ☐ Supplement/Subsequent EIR (Prior SCH No.)_____ ☐ Other _____

NEPA: ☐ NOI ☐ EA ☐ Draft EIS ☐ FONSI

Other: ☐ Joint Document ☐ Final Document ☐ Other_____

Local Action Type:

☐ General Plan Update ☐ General Plan Amendment ☐ General Plan Element ☐ Community Plan

☐ Specific Plan ☐ Master Plan ☐ Planned Unit Development ☐ Site Plan

☐ Rezone ☐ Prezone ☐ Use Permit ☐ Land Division (Subdivision, etc.)

☐ Annexation ☐ Redevelopment ☐ Coastal Permit ☒ Other District adoption of Algae/Aquatic Weed Control Program

Development Type:

☐ Residential: *Units*_____ *Acres*_____

☐ Office: *Sq.ft.*_____ *Acres*_____ *Employees*_____

☐ Commercial: *Sq.ft.*_____ *Acres*_____ *Employees*_____

☐ Industrial: *Sq.ft.*_____ *Acres*_____ *Employees*_____

☐ Educational _____

☐ Recreational _____

☐ Water Facilities: *Type*_____ *MGD*_____

☐ Transportation: *Type*_____

☐ Mining: *Mineral*_____

☐ Power: *Type*_____ *Watts*_____

☐ Waste Treatment: *Type*_____

☐ Hazardous Waste: *Type*_____

☐ Other:_____

Funding (approx.): Federal $_____ State $_____ Total $_____

Project Issues Discussed in Document:

☒ Aesthetic/Visual
☐ Agricultural Land
☐ Air Quality
☐ Archeological/Historical
☐ Coastal Zone
☐ Drainage/Absorption
☐ Economic/Jobs
☐ Fiscal
☐ Flood Plain/Flooding
☐ Forest Land/Fire Hazard
☐ Geologic/Seismic
☐ Minerals
☐ Noise
☐ Population/Housing Balance
☒ Public Services/Facilities
☒ Recreation/Parks
☐ Schools/Universities
☐ Septic Systems
☐ Sewer Capacity
☐ Soil Erosion/Compaction/Grading
☐ Solid Waste
☒ Toxic/Hazardous
☐ Traffic/Circulation
☒ Vegetation
☒ Water Quality
☒ Water Supply/Groundwater
☒ Wetland/Riparian
☒ Wildlife
☐ Growth Inducing
☐ Landuse
☐ Cumulative Effects
☐ Other _____

Present Land Use/Zoning/General Plan Designation: Agricultural

Project Description: The District is planning the adoption of an Algae/Aquatic Weed Control Program for its use of aquatic herbicides containing chemicals in its canal system distributing irrigation water to farms served by the District, under controls and restrictions that would permit occasional variances in the event of any exceedances of the applicable water quality criteria for priority pollutants, to the extent allowed under the SWRCB draft 2004 General Permit requirements for a Policy for Implementation of Toxic Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California ("SIP"), Section 5.3 Exception. The District embraces a gross area of approximately agricultural 40,000 acres lying west of Highway 99, between Thornton and Stockton in San Joaquin County, and distributes an irrigation water supply from the Mokelumne River through an earthen canal system to approximately 12,000 acres of agricultural lands within the larger area. Any terminal spills from the canal system passing outlet control weirs discharge into waterways on the eastern edge of and tributary to the Sacramento San Joaquin Delta (Beaver Slough, West Main Canal to Sycamore Slough, Moffit Dam and South Main Canal to Calaveras River).

Notice of Preparation of and of Intent to Adopt Mitigated Negative Declaration
Woodbridge Irrigation District

1.0 Project Title: Algae/Aquatic Weed Control Program

2.0 Project Location: San Joaquin County, California

3.0 Project Description:
The Woodbridge Irrigation District provides irrigation water to its agricultural customers within its geographic boundaries. The District service area is adjacent *to* the unincorporated communities of Woodbridge and Thornton, and to the incorporated municipalities of Lodi and Stockton. The District obtains its water supply primarily from the Mokelumne River and diverts its water supply at the Woodbridge Diversion Dam.

The District has a general policy of not accepting drainage from agricultural return flows into its canal system. Any terminal spill from the District's canals passing outlet control weirs discharge into waterways on the eastern edge of and tributary to the Sacramento-San Joaquin Delta (Beaver Slough, West Main Canal to Sycamore Slough, Moffit Dam and South Main Canal at Calaveras River.)

3.1 Aquatic Herbicide History at the Woodbridge Irrigation District

The District has an aggressive weed control program for controlling aquatic weeds in the canals and terrestrial weeds along the canal roads. Aquatic weeds in a canal can reduce the ability of the canal to carry water and increase the amount of hydraulic head needed to push the water to the delivery points. These plants also consume large amounts of water that otherwise would be available for irrigation purposes.

Woodbridge Irrigation District uses aquatic herbicides (acrolein, copper sulfate, and glyphosate) to maintain the functionality of its distribution system. These products are necessary to ensure that design flows are maintained. Unchecked algae growth can actually adversely affect water quality to the point of foul odors, undesirable tastes, livestock and wildlife poisonings and declines in invertebrate and fish populations.

The District has adopted a Quality Assurance Project Plan ("QAPP") for the monitoring of its algae and aquatic weed control program and discharges at spill points into the Sacramento-San Joaquin Delta and waters of the United States.

Woodbridge Irrigation District has been and currently is operating its Algae/Aquatic Weed Control Program within the State Water Resource Control Board's Draft 2004 General Permit for the Discharge of Aquatic Pesticides requirements. The adoption of this Draft General Permit by the SWRCB is expected on March 18, 2004. The concentrations of aquatic pesticides leaving

Algae/Aquatic Weed Control Program

DRAFT
California Environmental Quality Act
Initial Study
And
Mitigated Negative Declaration

Woodbridge Irrigation District
18777 North Lower Sacramento Road
Woodbridge, California 95258
Contact: Anders Christensen: (209) 369-6808

TABLE OF CONTENTS

California Environmental Quality Act

Draft Initial Study & Mitigated Negative Declaration

1.0 INTRODUCTION

1.1 Introduction and Regulatory Guidance

This Initial Study and Mitigated Negative Declaration ("MND") was conducted for Woodbridge Irrigation District ("District") in order to comply with the 2004 General Permit requirements for a Policy for Implementation of Toxic Standards for Inland Surface Waters, Enclosed Bays, and Estuaries of California ("SIP"), Section 5.3 Exception. Section 5.3 of the SIP allows the Regional Water Quality Control Board ("RWQCB"), after compliance with the California Environmental Quality Act ("CEQA"), to approve short-term or seasonal exceptions from meeting the priority pollutant criteria/objectives if it is determined to be necessary to implement control measures for resource or pest management conducted by public agencies. The policy specifically refers to vector or weed control, pest eradication, and fishery management as bases for categorical exceptions.

Because Woodbridge Irrigation District is a public agency and because it conveys water, it is eligible for a categorical exception related to implementing control measures for weed control and pest eradication.

Requirements for a 5.3 Categorical Exception include compliance with CEQA, namely the preparation of CEQA documentation. The District is the Lead Agency for this Mitigated Negative Declaration and Initial Study.

Woodbridge Irrigation District has been and currently is operating its Algae/Aquatic Weed Control Program within the General Permit requirements. The concentrations of aquatic pesticides leaving the treatment area and entering the waters of the United States are below the General Permit maximum allowable levels (See Appendix D for the laboratory analysis of water samples collected from the termination point of the District's system). The District is applying for the exemption in the event that, in the future, it exceeds the limits set forth in the General Permit. However, the District will make every attempt to continue to comply with the General Permit requirements.

1.2 Purpose

The purpose of this document is to assess the environmental effects (impacts) of the proposed Woodbridge Irrigation District's Algae/Aquatic Weed Control Program as required by the California Environmental Quality Act and in compliance with the State CEQA Guidelines. This Initial Study/Mitigated Negative Declaration serves as an informational document to be used in the local planning and decision-making process. Woodbridge Irrigation District, the lead agency under CEQA, must consider the impacts

of the proposed project when determining whether to approve the project. This Initial Study/Mitigated Negative Declaration has been prepared because all significant impacts resulting from the Algae/Aquatic Weed Control Program would be reduced to less than significant levels through the implementation of mitigation measures. The mitigation measures discussed in this document are currently in use by Woodbridge Irrigation District to reduce potentially significant risks to the environment to less than significant levels.

2.0 INITIAL STUDY & MITIGATED NEGATIVE DECLARATION

This Initial Study provides justification for a Mitigated Negative Declaration for Woodbridge Irrigation District's Algae/Aquatic Weed Control Program. This program involves the application of aquatic herbicides into its canals and pipelines in order to control and/or eliminate unwanted vegetation which can reduce the ability of canals to transport water if left unchecked. This document has been prepared in a manner consistent with CEQA, California Public Resources Code Section 21000 et seq., and the CEQA Guidelines, California Code of Regulations Section 15000 et seq.

The purpose of an Initial Study is to determine if a project may have a significant effect on the environment. If it is determined that the project will have a significant effect upon the environment, an Environmental Impact Report must be prepared. However, if the Lead Agency determines that the project will not have a significant effect on the environment, a Negative Declaration may be prepared. CEQA Section 15070 states that a Negative Declaration shall be prepared for a project when either:

a) The Initial Study shows that there is no substantial evidence, in light of the whole record before the agency, that the proposed project may have a significant effect on the environment, or

b) The Initial Study identifies potentially significant effects, but

   (1) Revisions in the project plans or proposals made by or agreed to by the applicant before the proposed negative declaration is released for public review would avoid the effects or mitigate the effects to a point where clearly no significant effects would occur, and

   (2) There is no substantial evidence, in light of the whole record before the agency, that the proposed project as revised may have a significant effect on the environment.

If the revisions in 15070(b)(1) are adopted, then a Mitigated Negative Declaration is prepared.

2.1 CEQA Initial Study and Environmental Checklist Form

1.	**Project Title:**	Algae/Aquatic Weed Control Program
2.	**Lead Agency Name and Address:**	Woodbridge Irrigation District 18777 North Lower Sacramento Road Woodbridge, CA 95258
3.	**Contact Person and Phone Number:**	Anders Christensen, Manager/Secretary/Treasurer (209) 369-6808
4.	**Project Location:**	San Joaquin County
5.	**Applicants:**	Woodbridge Irrigation District 18777 North Lower Sacramento Road Woodbridge, CA 95258
6.	**General Plan:**	Ag/Res/Com
7.	**Zoning:**	Ag/Res/Com

8. Project and Process Description:

The Woodbridge Irrigation District provides irrigation and domestic water within its geographic boundaries, an area of approximately 40,442 total acres (63 square miles). The District is the supplier of irrigation water for approximately 13,000 acres presently receiving surface water within its water service area. Crops grown with District water include alfalfa, tomatoes, beans, grapes, corn, orchard fruit and nuts, landscaping, and vegetables. The District's current water service area constitutes approximately 4% of the area of San Joaquin County, west of the City of Lodi and north of the City of Stockton. The District service area includes the unincorporated communities of Woodbridge and Thornton, and small portions of the incorporated municipalities of Lodi and Stockton.

The District obtains its water supply primarily from the Mokelumne River. The District diverts its water supply from the Mokelumne River at the Woodbridge Diversion Dam under pre-1914 appropriative rights. These appropriative rights provide for the diversion of up to 300 CFS water at Woodbridge Dam. The District also has post-1914 water rights for the appropriation of 300 CFS from February 1 to October 31 for irrigation use, and for the diversion of an additional 114.4 CFS from May 1 to August 31 of each year and from November 1 of each year to January 31 of the succeeding year, for irrigation use. The combined pre-1914 and post-1914 water rights are limited in the aggregate to a maximum diversion of 414.4 CFS.

The District's water system consists of Woodbridge Diversion Dam, the Beaver Slough pump diversion, the District's Moffit Weir at Pixley Slough, diversion canal head-works, and a distribution system of over 100 miles of canals and pipelines. The distribution system includes approximately 18 miles of concrete lined canals or pipelines to minimize seepage losses and controlling weeds on adjacent canal rights-of-way.

The District has a general policy of not accepting drainage from agricultural return flows into its canal system. The District's terminal spill directs all drainage into the Sacramento-San Joaquin Delta.

Aquatic Herbicide History at the Woodbridge Irrigation District
The District has an aggressive weed control program for controlling aquatic weeds in the canal and terrestrial weeds along the canal roads. Aquatic weeds in a canal can reduce the ability of the canal to carry water and increase the amount of hydraulic head needed to push the water to the delivery points. These plants also consume large amounts of water that otherwise would be available for irrigation purposes.

The District has adopted a Quality Assurance Project Plan ("QAPP") for the monitoring of its algae and aquatic weed control program and discharges at spill points into the Sacramento-San Joaquin Delta and waters of the United States. The District's program monitors during the irrigation season and tests for the presence of herbicides that are used in controlling aquatic and terrestrial weeds. The plan also contains best management practices that are designed to reduce the chance of detectable chemicals from entering the canal system.

During it's 80 year history, Woodbridge Irrigation District has employed several methods to combat aquatic weeds, including: dewatering canals, mechanical cleaning of various types, and chemicals including Magnacide H (acrolein), Copper Sulfate and Rodeo (Glyphosate).

Woodbridge Irrigation District uses these chemicals to maintain the functionality of its distribution system. These products are necessary to ensure that design flows are maintained. Unchecked algae growth can actually adversely affect water quality to the point of foul odors, undesirable tastes, livestock and wildlife poisonings and declines in invertebrate and fish populations.

9. Surrounding Land Uses and Setting

The Woodbridge Irrigation District is located in San Joaquin County, California. The District's service area is bounded on the north by the Mokelumne River, on the east by the City of Lodi and State Highway 99, on the south by the City of Stockton and the Calaveras River and on the west by the easterly fringe of the Sacramento-San Joaquin Delta.

The land use in San Joaquin County varies from the urban cities of Stockton and Lodi to large tracts of farmland, wetlands, and rural residential property. The climate is arid-temperate, and the average rainfall is about 14 inches per year.

The Algae/Aquatic Weed Control Program is conducted in the irrigation system of the Woodbridge Irrigation District. That system consists of about 40,442 acres, including 18 miles of concrete lined canals or pipelines and 82 miles of earth ditches.

10. Other agencies whose approval is required

The SWRCB. Notice of application of aquatic herbicides is given to San Joaquin County and the California Department of Fish and Game.

3.0 EVIRONMENTAL CHECKLIST

Pursuant to Section 15603, CEQA Guidelines, the Woodbridge Irrigation District has utilized an Environmental Checklist to evaluate the potential environmental effects of the project. The checklist provides a determination of these potential impacts and includes the substantiation developed in support of the conclusions checked on the form.

The environmental factor checked below would be potentially affected by this project, involving at least one impact that is a "Potentially Significant Impact" as indicated by the checklist on the following pages.

☐	Aesthetics	☐	Land Use/Planning
☐	Agricultural Resources	☐	Mineral Resources
☐	Air Quality	☐	Noise
XX	Biological Resources	☐	Population/Housing
☐	Cultural Resources	☐	Public Services
☐	Geology/Soil	☐	Recreation
XX	Hazards & Hazardous Material	☐	Transportation/Traffic
XX	Hydrology & Water Quality	☐	Utilities/Service Systems
XX	Mandatory Findings of Significance		

Determination

On the basis of this initial evaluation:

☐ I find that the proposed project COULD NOT have a significant effect on the Environment, and a NEGATIVE DECLARATION will be prepared.

XX I find that although the proposed project could have a significant effect on the environment, there will not be a significant effect in this case because revisions in the project have been made by or agreed to by the project proponent. A MITIGATED NEGATIVE DECLARATION will be prepared.

☐ I find that the proposed project MAY have a significant effect on the environment, and an ENVIRONMENTAL IMPACT REPORT is required.

☐ I find that the proposed project MAY have a "potentially significant impact" or "potentially significant impact unless mitigated" impact on the environment, but at least one effect 1) has been adequately analyzed in an earlier document pursuant to applicable legal standards, and 2) has been addressed by mitigation measures based on the earlier analysis as described on attached sheets. An ENVIRONMENTAL IMPACT REPORT is required, but it must analyze only the effects that remain to be addressed.

☐ I find that although the proposed project could have a significant effect on the environment, because all potentially significant effects (a) have been analyzed adequately in an earlier EIR or NEGATIVE DECLARATION pursuant to applicable standards, and (b) have been avoided or mitigated pursuant to that earlier EIR or NEGATIVE DECLARATION, including revisions or mitigation measures that are imposed upon the proposed project, nothing further is required.

Anders Christensen — Signature

February 12, 2004 — Date

Anders Christensen — Printed Name

Woodbridge Irrigation Dist. — For

EVALUATION OF ENVIRONMENTAL IMPACTS

The following terminology is used in the Initial Study/Mitigated Negative Declaration to describe the levels of significance of impacts that would result from the proposed Algae/Aquatic Weed Control Program.

- A conclusion of NO IMPACT is appropriate when the analysis concludes that there would be no impact on a particular resource topic.
- An impact is considered LESS THAN SIGNIFICANT if the analysis concludes that an impact on a particular resource topic would not be significant (i.e., would not exceed the criteria or limits established by the 2004 General Permit).
- An impact is considered LESS THAN SIGNIFICANT WITH MITIGATION INCORPORATED if the analysis concludes that an impact to a particular resource topic would be significant (i.e., would exceed the criteria or limits established by the 2004 General Permit) but would be reduced to a less than significant level through the implementation of mitigation measures.

3.1 Aesthetics

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Have a substantial adverse effect on a scenic vista?				X
b) Substantially damage scenic resources, including, but not limited to, trees, rock outcroppings, and historic buildings within a state scenic highway?				X
c) Substantially degrade the existing visual character or quality of the site and its surroundings?				X
d) Create a new source of substantial light or glare which would adversely affect day or nighttime views in the area?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not have any adverse impact on scenic vistas because the irrigation water is running below the graded level of the surrounding ground.

b) The application and use of aquatic herbicides will not substantially damage scenic resources, including trees, rock outcroppings, and historic buildings within a state highway because the canal and canal banks have historically been maintained free of trees in order to maintain the functionality of the canal system. Additionally, the application of chemical herbicides will not affect rocks and there are no historic buildings or scenic highways in the vicinity of the canals and/or pipelines.

c) The application and use of aquatic herbicides will not substantially degrade the existing visual character or quality of the site or its surroundings because the herbicides are transparent. Further, the use of the herbicides will eliminate unsightly algal grown and improve the clarity of the water.

d) The application and use of aquatic herbicides will not create a new source of substantial light or glare which would adversely affect day or nighttime views in the area because the chemicals themselves do not emit light and the methods of application do not produce light.

3.2 Agriculture Resources

In determining whether impacts to agricultural resources are significant environmental effects, lead agencies may refer to the California Agricultural Land Evaluation and Site Assessment Model (1997) prepared by the California Dept. of Conservation as an optional model to use in assessing impacts on agriculture and farmland.

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the project:				
a) Covert Prime Farmland, Unique Farmland, or Farmland of Statewide Importance, as shown on the maps Prepared pursuant to the Farmland Mapping and Monitoring Program of the California Resources Agency, to non-agricultural use?				X
b) Conflict with existing zoning for agriculture use, or a Williamson Act contract?				X
c) Involve other changes in the existing environment which, due to their location or nature, could result in conversion of Farmland, to non-agricultural use?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not convert Prime Farmland, Unique Farmland, or Farmland of Statewide Importance, as shown on the maps prepared pursuant to the Farmland Mapping and Monitoring Program of the California Resource Agency, to non-agricultural uses because the use of these

herbicides is important to maintaining adequate water supplies and modes of delivery for farming.

b) The application and use of aquatic herbicides will not conflict with existing zoning for agriculture use, or a Williamson Act contract because the use of aquatic herbicides is designed to maintain adequate water supplies and delivery systems for agricultural uses.

c) The application and use of aquatic herbicides will not involve other changes in the existing environment which, due to their location or nature, could result in conversion of Farmland to non-agricultural uses because the use of aquatic herbicides is designed to maintain adequate water supplies and delivery systems for agricultural uses.

3.3 Air Quality

Where available, the significance criteria established by the applicable air quality management or air pollution control district may be relied upon to make the following determinations:

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Conflict with or obstruct implementation of the applicable air quality plan?				X
b) Violate any air quality standard or contribute substantially to an existing or projected air quality violation?				X
c) Result in a cumulatively considerable net increase of any criteria pollutant for which the project region is non-attainment under an applicable federal or state ambient air quality standard (including releasing emissions which exceed quantitative thresholds for ozone production)?				X
d) Expose sensitive receptors to substantial pollutant concentrations?				X
e) Create objectionable odors affecting a substantial number of people?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not conflict with or obstruct implementation of the applicable air quality plan because aquatic herbicides are not gaseous in nature. Further, since these herbicides are only applied approximately 4 to 5 times per year, vehicular emissions associated with the application process is kept at a minimum.

b) The application and use of aquatic herbicides will not violate any air quality standard or contribute substantially to an existing or projected air quality violation because the application process would involve only a few light to medium duty trucks to transport the herbicides to the treatment areas.

c) The application and use of aquatic herbicides will not result in a cumulatively considerable net increase of any criteria pollutant for which the project region is non-attainment under an applicable federal and state ambient air quality standard (including releasing emissions which exceed quantitative thresholds for ozone precursors) because only a few light to medium duty trucks would be used to transport the herbicides to the treatment areas approximately 4 to 5 times per year.

d) The application and use of aquatic herbicides will not expose sensitive receptors to substantial pollutant concentrations because these types or herbicides are designed for use in the aquatic environment and are not gaseous in nature.

e) The application and use of aquatic herbicides will not create objectionable odors affecting a substantial number of people because the use of these chemicals actually eliminates odoriferous compounds, such as those present algal blooms and the subsequent die-off, which emit noxious odors. The copper based herbicides may emit a slight ammonia odor during application, however this odor is only perceptible at the point the herbicide enters the water. Since this odor is only slight and restricted to a location not near sensitive receptors, no impact would occur to a substantial number of people.

3.4 Biological Resources

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Have a substantial adverse effect, either directly or through habitat modifications, on any species identified as a candidate, sensitive, or special status species in local or regional plans, policies, or regulations, or by the California Dept. of Fish and Game or U.S. Fish and Wildlife Service?		X		
b) Have a substantial adverse effect on any riparian habitat or other sensitive natural communities identified in local or regional plans, policies, regulations or by the California Department of Fish and Game or U.S. Fish and Wildlife Service?		X		
c) Have a substantial adverse effect on federally protected wetlands as defined by Section 404 of the Clean Water Act (including, but not limited to, marsh, vernal pool, coastal, etc.) through direct removal, filling, hydrological interruption, or other means?				X
d) Interfere substantially with the movement of any native resident or migratory fish or wildlife species or with established native resident or migratory wildlife corridors, or impede the use of native wildlife nursery sites?				X
e) Conflict with any local policies or ordinances protecting biological resources, such as a tree preservation policy or ordinance?				X
f) Conflict with the provisions of an adopted Habitat Conservation Plan, Natural Community Conservation Plan, or other approved local, regional, or state habitat conservation plan?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not have a substantial adverse effect, either directly or through habitat modifications, on any species identified

as a candidate, sensitive, or special status species in local or regional plans, policies, or regulations, or by the California Department of Fish and Game or U.S. Fish and Wildlife Service. The canal system is an artificial channel for the designed specifically for the transport of water. The application of aquatic herbicides merely sustains the current conditions and maintains the canal system as they were designed and constructed, therefore, no habitat modification would occur.

Further, the canal and water channels utilized and maintained by the District are not suitable habitat for threatened or endangered species such as the Red Legged Frog and the Giant Garter Snake. The habitat of the California Red Legged Frog is characterized by dense, shrubby riparian vegetation associated with deep, still or slow-moving water. (www.dfg.ca.gov) The shrubby riparian vegetation that is most suitable for the Red Legged Frog is provided by the arroyo willow, cattails and bulrushes. (Id.) Populations of Red Legged Frogs probably cannot be maintained in ephemeral streams in which surface water disappears. (Id.) Since the District dewaters the canals seasonally, populations of Red Legged Frogs cannot be maintained in the Districts waterways. (Id.) Further, juvenile frogs favor open, shallow aquatic habitats with dense submergents. (Id.) The District has historically maintained its waterways free from dense vegetation in order to ensure proper operation of the system. Therefore, the system would not be suitable to juvenile frogs since dense submerged vegetation does not exist in the District's waterways.

Additionally, the District has not identified any sensitive plant species in its canal or ditch system. Further, since the District's formation approximately 80 years ago, it has kept its canals and ditches free from vegetative growth. Therefore, the District's Algae/Aquatic Weed Control Program would not have any adverse effect on sensitive plant species.

The habitat of the Sacramento-San Joaquin Delta is suitable to the maintenance of California Red Legged Frog and the Giant Garter Snake. Since District water is discharged into the Delta, there exists a potential significant adverse impact upon the frog's and snake's habitat. However, the District has been and will continue to follow the mitigation measures described in Section 3.8 (Hydrology and Water Quality) to reduce the impacts to Red Legged Frogs to less than significant levels. Additionally, the California Department of Fish and Game has approved the District's Algae/Aquatic Weed Control Program conditioned on implementation of the following mitigation measures (See Appendix E for the Department of Fish and Game Approval Letter, February, 2003):

Mitigation Measures:

1. Aquatic herbicides are only applied to those ditches previously approved by the Department of Fish and Game.
2. Aquatic herbicides are not applied to natural stream channels.

3. Aquatic herbicides are not applied to ditches with direct discharges to natural streams.
4. Treated water, unless sufficiently detoxified, will not be discharged into any fish-bearing water of the State.
5. Detoxified water discharged into fish-bearing waters will not cause the dissolved oxygen concentration of the receiving water to drop below 5 mg/L.
6. In the event of fish loss, those losses will be reported immediately to the Department of Fish and Game.
7. Any fish that die as a result of treatment will be removed.
8. The District will obtain a permit from the County Agricultural Commissioner prior to possess or use of aquatic herbicides. All instructions on the container label will be strictly followed.
9. Aquatic herbicides will be applied by or under the supervision of a certified commercial applicator.
10. The Department of Fish and Game will be notified at least 24 hours prior to each application.

b) The application of aquatic herbicides has the potential to have a substantial adverse effect on any riparian habitat or other sensitive natural community identified in local or regional plans, policies, regulations or by the California Department of Fish and Game or U.S. Fish and Wildlife Service. The District's waters are discharged into the Sacramento-San Joaquin Delta. However, due to the District's adopted mitigation measures identified in Section 3.8 (Hydrology and Water Quality), the impacts to the Delta habitat will be reduced to less than significant levels. Additionally, the levels of acrolein, copper, and glyphosate present at the point where the District water discharges into the Delta, as shown by laboratory analysis, indicates that the District's operations will not have a significant adverse impact on Delta habitat.

Within the District's boundaries there will be no impact to riparian habitat because canals are not considered riparian habitat nor are canals sensitive natural communities.

c) The application of aquatic herbicides will not have a substantial adverse effect on federally protected wetlands as defined by Section 404 of the Clean Water Act (including, but not limited to, marsh, vernal pool, coastal, etc.) through direct removal, filling, hydrological interruption, or other means because the project does not involve removing or filling of a wetland and the project will not interrupt the hydrological process of a wetland.

d) The application and use of aquatic herbicides will not interfere substantially with the movement of any native resident or migratory fish or wildlife species or with established native resident or migratory wildlife corridors, or impede the use of native wildlife nursery sites because canals are not conducive to the

maintenance or the migration of fish or wildlife species due to the seasonal nature of the canal system and their physical characteristics.

e) The application and use of aquatic herbicides will not conflict with any local policies or ordinances protecting biological resources, such as a tree preservation policy or ordinance because the herbicides will be applies within the banks of the canals.

f) The application and use of aquatic herbicides will not conflict with the provisions of an adopted Habitat Conservation Plan, Natural Community Conservation Plan, or other approved local, regional or state habitat conservation plans. On May 22, 1995, the State Water Resource Control Board adopted a Bay-Delta Water Quality Control Plan establishing water quality standards necessary for the protection of fisheries and of the beneficial uses in the San Francisco Bay and Sacramento-San Joaquin Delta. Another plan is the Lower Mokelumne River Habitat Conservation Plan. The plan covers areas within the District's boundaries. However, the application of aquatic herbicides to the District's canals will not conflict with the provisions of either plan since the District applies the aquatic herbicides only to its canals and has been and will continue to follow the mitigation measures set forth in Section 3.8 (Hydrology and Water Quality). Further, canals and other artificial water channels are not considered habitat. Additionally, the California Department of Fish and Game has given the District approval for the application of aquatic herbicides to its canals and waterways.

3.5 Cultural Resources

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Cause a substantial adverse change in the significance of a historical resource as defined in § 15064.5?				X
b) Cause a substantial adverse change in the significance of an archaeological resources pursuant to §15064.5?				X
c) Directly or indirectly destroy a unique paleontological resource or site or unique geological feature?				X
d) Disturb any human remains, including those interred outside of formal cemeteries?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not cause a substantial adverse change in the significance of a historical resource as defined in § 15064.5 because the area of application of the aquatic herbicides is into the canals transporting water which are not considered a historical resource.

b) The application and use of aquatic herbicides will not cause a substantial adverse change in the significance of an archaeological resource pursuant to § 15064.5 because the water delivery systems used by the District are not considered an archaeological resource at this time.

c) The application and use of aquatic herbicides will not directly or indirectly destroy a unique paleontological resource or site or unique geologic feature because the water delivery systems that the herbicides are applied to are not considered a paleontological or unique geological feature.

d) The application and use of aquatic herbicides will not disturb any human remains, including those interred outside of formal cemeteries because canals and water delivery systems do not contain such remains.

3.6 Geology and Soils

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Expose people or structures to potential substantial adverse effects, including the risk of loss, injury, or death involving: i) Rupture of a known earthquake fault, as delineated on the most recent Alquist-Priolo Earthquake Fault Zoning Map issued by the State Geologist for the area or based on other substantial evidence of a known fault? ii) Strong seismic ground shaking? iii) Seismic-related ground failure, including liquefaction? iv) Landslides?				X X X X X
b) Result in substantial soil erosion or the loss of topsoil?				X
c) Be located on a geologic unit or soil that is unstable, or that would become unstable as a result of the project, and potentially result in on- or off-site landslide, lateral spreading, subsidence, liquefaction or collapse?				X
d) Be located on expansive soil, as defined in Table 18-1-B of the Uniform Building Code (1994), creating substantial risk to life or property?				X
e) Have soils incapable of adequately supporting the use of septic tanks or alternative waste water disposal systems where sewers are not available for the disposal of waste water?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not expose people or structures to potential substantial adverse effects, including the risk of loss, injury, or death involving:
   i) Rupture of a known earthquake fault
   ii) Strong seismic ground shaking
   iii) Seismic-related ground failure, including liquefaction

iv) Landslides, because the application of aquatic herbicides do not involve the construction of buildings or other structures that would expose persons to risk of injury or death.

b) The application and use of aquatic herbicides will not result in substantial soil erosion or the loss of topsoil because no new construction activities are involved during the process and the canals have already been constructed.

c) The application and use of aquatic herbicides to waters will not be located on a geologic unit or soil that is unstable, or that would become unstable as a result of the project, and potentially result in on- or off-site landslide, lateral spreading, subsidence, liquefaction or collapse because the project is limited to the application of herbicides directly to existing canals and such systems will not affect these factors.

d) The application and use of aquatic herbicides to irrigation water will not be located on expansive soil, as defined in Table 18-1-B of the Uniform Building Code (1994), creating substantial risks to life or property because no structures will be build as a result of the application program and the construction and maintenance of canals are not covered under the Uniform Building Code.

e) The application and use of aquatic herbicides to irrigation water will not have soils incapable of adequately supporting the use of septic tanks or alternative waste water disposal systems where sewers are not available for the disposal of waste water because the use of these herbicides are designed to help sustain agriculture by maintaining water delivery systems and these systems are not located near septic tanks or alternative waste water delivery systems.

3.7 Hazards and Hazardous Materials

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Create a significant hazard to the public or the environment through the routine transport, use, or disposal of hazardous materials?		X		
b) Create a significant hazard to the public or the environment through reasonably foreseeable upset and accident conditions involving the release of hazardous materials into the environment?		X		
c) Emit hazardous emissions or handle hazardous or acutely hazardous materials, substances, or waste within one-quarter mile of an existing or proposed school?		X		
d) Be located on a site which is included on a list of hazardous materials sites compiled pursuant to Government Code § 65962.5 and, as a result, would it create a significant hazard to the public or the environment?				X
e) For a project located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport, would the project result in a safety hazard for people residing or working in the project area?				X
f) For a project within the vicinity of a private airstrip, would the project result in a safety hazard for people residing or working in the project area?				X
g) Impair implementation of or physically interfere with an adopted emergency response plan or emergency evacuation plan?				X
h) Expose people or structures to a significant risk of loss, injury or death involving wildland fires, including where wildlands are adjacent to urbanized areas or where residences are intermixed with wildlands?				X

The Districts responses to the above issues are as follows:

a) The routine transport and usage of hazardous materials could potentially create a hazard to the public and the environment unless mitigation measures are employed. Woodbridge Irrigation District routinely uses aquatic herbicides Magnacide H (acrolein), copper sulfate, and Rodeo (glyphosate) to control aquatic weeds and vegetation. These chemicals when used according to the FIFRA label requirements are not expected to adversely affect the public, water quality or the surrounding environment. If an accidental spill or release does occur, the District has a Process Safety Management Guidelines for the Application, Storage, and Handling of Acrolein ("PSM") which outlines spill abatement measures to be employed. The District has also followed and will continue to follow its Quality Assurance Project Plan ("QAPP"). Since only small amounts of these chemicals are stored and transported to the application area, the above potential impacts are considered less than significant. Further, only applicators holding a valid Qualified Applicator's Certificate apply the herbicides. See Appendix A for the PSM and Appendix B for the QAPP. The District will implement the following mitigation measures to continue operating without a significant impact and reduce any future potential significant impacts to less than a significant level:

Mitigation Measures:

11. The District has adopted and follows a Process Safety Management Guildelines for the Application, Storage, and Handling of Acrolein and a Quality Assurance Project Plan. (Appendices A & B)
12. The District only transports one container of acrolein to the treatment area.
13. The District follows the FIFRA label requirements for the application and use of the aquatic herbicides.
14. Only applicators holding a valid Qualified Applicator's Certificate will apply the herbicides to the District's canals and water channels.

b) The Algae/Aquatic Weed Control Program involves the use of potentially hazardous materials (i.e. acrolein, copper sulfate, and glyphosate). Accidental spills involving the release of hazardous materials to the environment are reasonably foreseeable. However, these risks are minimized because the storage, transportation, and application of these herbicides are conducted according to applicable federal, state, and local laws. Following the applicable guidelines minimizes the risk of potential accidental spills of hazardous materials during the application process. Only applicators holding a valid Qualified Applicator's Certificate apply the herbicides. Further, due to the small quantities of the chemicals stored, transported and applied, the risk of a significant hazard to the public or the environment would be less than significant. See Appendix A & B for the PSM and QAPP. The District will implement the following mitigation measures to continue operating without a significant impact and reduce any future potential significant impacts to less than a significant level:

Mitigation Measures: Same as 3.7 (a)

c) The herbicide application program by Woodbridge Irrigation District is located within one-quarter mile of an existing school. However, this impact is considered to be less than significant due to Best Management Practices implemented as part of the District's Program, following the herbicide label requirements, and because only applicators licensed to handle the herbicides apply the chemicals to the waterway. See Appendix A & B for the PSM and QAPP. The District will implement the following mitigation measures to continue operating without a significant impact and reduce any future potential significant impacts to less than a significant level:

Mitigation Measures: Same as 3.7 (a)

d) The application and use of aquatic herbicides will not be located on a site which is included on a list of hazardous materials sites compiled pursuant to Government Code § 65962.5 and, as a result, would create a significant hazard to the public or the environment. The District has received a Risk Management Plan Exemption from San Joaquin County, Office of Emergency Services, because the District does not store quantities of herbicides at or above the Threshold Quantity. The inventory of acrolein on-site at any one time is not more than 370 lbs., which is below the Federal Threshold Quantity of 5,000 lbs and CalARP Threshold Quantity of 500 lbs. See Appendix C for a copy of the Risk Management Plan Exemption.

e) The applicant and use of aquatic herbicides will not result in a safety hazard for people residing or working in the project area, where the herbicide application would be located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport because no such airports or plans are located within or within two miles of the program area.

f) The application and use of aquatic herbicides will not result in a safety hazard for people residing or working in the project area where the project is located within the vicinity of a private airstrip because no private airstrips are located in the vicinity of the project area.

g) The application and use of aquatic herbicides will not impair implementation of or physically interfere with an adopted emergency response plan or emergency evacuation plan.

h) The application and use of aquatic herbicides will not expose people or structures to a significant risk of loss, injury or death involving wildland fires, including where wildlands are adjacent to urbanized areas or where residents are intermixed with wildlands.

3.8 Hydrology And Water Quality

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Violate water quality standards or waste water discharge requirements?		X		
b) Substantially deplete groundwater supplies or interfere substantially with groundwater recharge such that there would be a net deficit in aquifer volume or a lowering of the local groundwater table level (e.g., the production rate of pre-existing nearby wells would drop to a level which would not support existing land uses or planned uses for which permits have been granted?				X
c) Substantially alter the existing drainage pattern of the site or area, including through the alteration of the course of a stream or river, in a manner which would result in substantial erosion or siltation on- or off-site?				X
d) Substantially alter the existing drainage pattern of the site or area, including through the alteration of the course of a stream or river, or substantially increase the rate or amount of surface runoff in a manner which would result in flooding on- or off-site?				X
e) Create or contribute runoff water which would exceed the capacity of existing or planned stormwater drainage systems or provide substantial additional sources of polluted runoff?				X
f) Otherwise substantially degrade water quality?		X		
g) Place housing within a 100-year flood hazard area as mapped on a federal Flood Hazard Boundary or Flood Insurance Rate Map or other flood hazard delineation map?				X
h) Place within a 100-year flood hazard area structures which would impede or redirect flood flows?				X
i) Expose people or structures to a				X

significant risk of loss, injury or death involving flooding, including flooding as a result of the failure of a levee or dam?				
j) Inundation by seiche, tsunami, or mudflow?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides by the district has the potential to violate water quality standards or waste discharge requirements. The District's system has five (5) discharge points: one (1) into Beaver Slough and four (4) end up ultimately in the Sacramento-San Joaquin Delta. The District has gates at these locations that can be closed. Woodbridge Irrigation District plans to adhere to the water quality standards and discharge requirements of the Clean Water Act ("CWA") as they apply to herbicide applications into the waters of the United States. The District has regularly conducted water analyses on samples collected at the above mentioned discharge five (5) discharge points. The results of these laboratory analyses have shown that the concentrations of acrolein, copper and glyphosate have been below the maximum allowable limits set forth in the 2004 Draft General Permit. The analytical results for acrolein have been below the quality control limit (PQL). The concentration of copper has been below 0.01 mg/L. Further, glyphosate has been non-detectable (not present in the water in concentrations at or above the detection limits). Additionally, acrolein is broken down into its non-toxic constituents after 40 hours. See Appendix D for the Laboratory Analytical Data Sheets. Therefore, this project is currently in full compliance with the 2004 Draft General Permit and would not cause a significant impact to the environment.

The project involves the application of Magnacide H (acrolein), copper-based herbicides, and glyphosate to the District's canals in concentrations that temporarily exceed the California Toxics Rule water quality objectives within the treatment areas. The District will implement the following mitigation measures to continue operating without a significant impact and reduce any future potential significant impacts to less than a significant level:

Mitigation Measures:

15. The District will adhere to FIFRA and follow all label requirements for the application and use of aquatic herbicides.
16. Only certified applicators will apply the herbicides in a manner consistent with the label requirements.
17. Herbicide applications will occur only in those areas where weeds are present to minimize the amount of herbicides applied to the system.
18. Discharges of waters treated with herbicides to natural systems will be avoided when possible and otherwise minimized.

19. Waters treated with copper-based herbicides will be monitored for alkalinity and application rates be decreased to minimize potential toxic impacts.
20. The District will continue to follow its established BMPs. (See Appendices A & B)
21. The District will notify the California Department of Fish and Game and San Joaquin County prior to application of aquatic herbicides.

b) The application and use of aquatic herbicides will not substantially deplete groundwater supplies or interfere substantially with groundwater recharge such that there would be a net deficit in aquifer volume or a lowering of the local groundwater table level (e.g., the production rate of pre-existing nearby wells would drop to a level which would not support existing land uses or planned uses for which permits have been granted) because almost all the water treated comes from surface resources.

c) The application and use of aquatic herbicides will not substantially alter the existing drainage pattern of the site or area, including through the alteration of the course of a stream or river, in a manner which would result in substantial erosion or siltation on- or off-site because the application of herbicides is directly to canals which are below the surrounding grade and therefore do not cause erosion or siltation. Additionally, the herbicides are not applied to streams or rivers directly.

d) The application and use of aquatic herbicides will not substantially alter the existing drainage pattern of the site or area, including through alteration of the course of a stream or river, or substantially increase the rate or amount of surface runoff in a manner which would result in flooding on- or off-site because application of herbicides do not alter run-off or contribute to flooding. Further, these systems are constructed below the grade of the surrounding area.

e) The application and use of aquatic herbicides will not create or contribute to runoff water which would exceed the capacity of existing or planned stormwater drainage systems or provide substantial additional sources of polluted runoff because the water distribution system is not part of any stormwater drainage systems. Treated water is not allowed to runoff into stormwater drainage.

f) Since the Algae/Aquatic Weed Control Program by Woodbridge Irrigation District involves the direct application of herbicides into canals and waterways, a potential to substantially degrade water quality exists. Magnacide H (acrolein), copper-based aquatic herbicides, and Rodeo (glyphosate) are used to control and eradicate noxious weeds and vegetation found in the water distribution system. The District regularly tests the water leaving its system at the point where the District's water enters the Sacramento-San Joaquin Delta. These test show that the concentrations of acrolein, copper, and glyphosate have been below the maximum allowable concretions as set forth in the General Permit.

Therefore, this project is currently in full compliance with the General Permit and would not cause a significant impact to the environment. See Appendix D for the Laboratory Analytical Data Sheets. The mitigation measures discussed below will reduce this potentially significant impact to a less than significant level:

Mitigation Measures:

22. The District will use the minimum amount of herbicide necessary to effectively combat the weed problem.
23. The District will avoid discharging treated waters to natural waterways.

g) The Algae/Aquatic Weed Control Program will not place housing within a 100-year flood hazard area as mapped on a federal Flood Hazard Boundary of Flood Insurance Rate Map or other flood hazard delineation map. This project does not involve the construction of housing units within the District's boundaries.

h) The Algae/Aquatic Weed Control Program will not place within a 100-year flood hazard area structures which would impede or redirect flood flows. This project does not involve the construction of structures within the District's boundaries.

i) The application and use of aquatic herbicides will not expose people or structures to a significant risk of loss, injury or death involving flooding, including flooding as a result of the failure of a levee or dam. This project involves the application of aquatic herbicides into canals and waterways operated by Woodbridge Irrigation District and would not result in the above mentioned risks.

j) The application or treatment areas are not located in areas subject to seiche, tsunami, or mudflow.

3.9 Land Use And Planning

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Physically divide an established community?				X
b) Conflict with any applicable land use plan, policy, or regulation of an agency with jurisdiction over the project (including, but not limited to the general plan, specific plan, local coastal program, or zoning ordinance) adopted for the purpose of avoiding or mitigating an environmental effect?				X
c) Conflict with any applicable habitat conservation plan or natural community conservation plan?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not physically divide an established community. The canals and other water distribution channels are already constructed and do not divide communities.

b) The application and use of aquatic herbicides will not conflict with any applicable land use plan, policy, or regulation of an agency with jurisdiction over the project (including, but not limited to the general plan, specific plan, local coastal program, or zoning ordinance) adopted for the purpose of avoiding or mitigating an environmental effect because these canals and waterways into which the herbicides are applied have been in existence and operated for decades.

c) The application and use of aquatic herbicides will not conflict with any applicable habitat conservation plan or natural community conservation plan because any proposed habitat conservation plan would not prohibit the maintenance and use of these water delivery systems with aquatic herbicides.

3.10 Mineral Resources

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Result in the loss of availability of a known mineral resource that would be of value to the region and the residents of the state?				X
b) Result in the loss of availability of a locally-important mineral resource recovery site delineated on a local general plan or other land use plan?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not result in the loss of availability of a known mineral resource that would be of value to the region and the residents of the state. The project only involves the application of herbicides to existing canal and water distribution channels.

b) The application and use of the aquatic herbicides will not result in the loss of availability of a locally-important mineral resource recovery site delineated on a local general plan or other land use plan. The project only involves the application of herbicides to existing canals and water distribution channels.

3.11 Noise

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project Result In:				
a) Exposure of persons to or generation of noise levels in excess of standards established in the local general plan or noise ordinance, or applicable standards of other agencies?				X
b) Exposure of persons to or generation of excessive groundborne vibration or groundborne noise levels?				X
c) A substantial permanent or periodic increase in ambient noise levels in the project vicinity above levels existing without the project?				X
d) A substantial temporary or periodic increase in ambient noise levels in the project vicinity above levels existing without the project?				X
e) For a project located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport, would the project expose people residing or working in the project area to excessive noise levels?				X
f) For a project within the vicinity of a private airstrip, would the project expose people residing or working in the project area to excessive noise levels?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not result in exposure to or generation of noise levels in excess of standards established in the local general plan or noise ordinance, or applicable standards of other agencies. The application of herbicides occurs during daytime hours and only minimal noise would be associated with the application process, mainly the operation of light-duty trucks to transport the herbicides to the treatment locations. The ambient noise levels will not be increase as a result of the Algae/Aquatic Weed Control Program.

b) The application and use of aquatic herbicides will not result in the exposure of persons to or generation of excessive groundborne vibration or groundborne noise levels. The application of herbicides occurs during daytime hours and only minimal noise would be associated with the application process, mainly the operation of light-duty trucks to transport the herbicides to the treatment locations. Further, the Magnacide H (acrolein) is introduced into the canal through the use of pressurized gas which does not produce vibration. The ambient noise levels will not be increase as a result of the Algae/Aquatic Weed Control Program.

c) The application and use of aquatic herbicides will not result in a substantial permanent increase in ambient noise levels in the project vicinity above levels existing without the project. The application of herbicides occurs during daytime hours and only minimal noise would be associated with the application process, mainly the operation of light-duty trucks to transport the herbicides to the treatment locations. The ambient noise levels will not be increase as a result of the Algae/Aquatic Weed Control Program.

d) The application and use of aquatic herbicides will not result in a substantial temporary increase in ambient noise levels in the project vicinity above levels existing without the project. The application of herbicides occurs during daytime hours and only minimal noise would be associated with the application process, mainly the operation of light-duty trucks to transport the herbicides to the treatment locations. The ambient noise levels will not be increase as a result of the Algae/Aquatic Weed Control Program.

e) The application and use of aquatic herbicides will not expose people residing or working in the project area to excessive noise levels where the project is located within an airport land use plan or, where such a plan has not been adopted, within two miles of a public airport or public use airport because no public airport is located near the treatment areas.

f) The application and use of aquatic herbicides will not expose people residing or working in the project area to excessive noise levels for a project within the vicinity of a private airstrip because no private airstrips exist within the projects treatment areas.

3.12 Population And Housing

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Induce substantial population growth in an area, either directly (for example, by proposing new homes and businesses) or indirectly (for example, through extension of roads or other infrastructure)?				X
b) Displace substantial numbers of existing housing, necessitating the construction of replacement housing elsewhere?				X
c) Displace substantial numbers of people, necessitating the construction of replacement housing elsewhere?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides would not induce substantial population growth in an area, either directly or indirectly because the use of aquatic herbicides sustains agriculture by providing a stable source through channels free from excessive vegetative growth. Sustaining agriculture actually inhibits population growth in the District's boundaries.

b) The application and use of aquatic herbicides would not displace substantial numbers of existing housing, necessitating the construction of replacement housing elsewhere. The Algae/Aquatic Weed Control Program does not involve the construction of any canals or other water transportation channels that would displace housing.

c) The application and use of aquatic herbicides would not displace substantial numbers of people, necessitating the construction of replacement housing elsewhere because the herbicide program does not involve the construction of new infrastructure that would displace people.

3.13 Public Services

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the project result in substantial adverse physical impacts associated with the provision of new or physically altered government facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable services ratios, response times or other performance objectives for any of the public services:				
a) Fire Protection?				X
b) Police Protection?				X
c) Schools?				X
d) Parks?				X
e) Other Public Facilities?				X

The District's responses to the above issues are as follows:

a) The application of aquatic herbicides would not result in substantial adverse physical impacts associated with the provision of new or physically altered governmental facilities, needed for new or physically altered governmental facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable service ratios, response times or other performance objectives for fire protection because the maintenance of the canals and waterways with herbicides actually increases the amount of water available for fire protection.

b) The application of aquatic herbicides would not result in substantial adverse physical impacts associated with the provision of new or physically altered governmental facilities, needed for new or physically altered governmental facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable service ratios, response times or other performance objectives for fire protection because the canals have existed and have been maintained for years without any disruption to police protection.

c) The application of aquatic herbicides would not result in substantial adverse physical impacts associated with the provision of new or physically altered governmental facilities, needed for new or physically altered governmental facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable service ratios, response times or other

performance objectives for fire protection because the canals have existed and have been maintained for years without any disruption to police schools.

d) The application of aquatic herbicides would not result in substantial adverse physical impacts associated with the provision of new or physically altered governmental facilities, needed for new or physically altered governmental facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable service ratios, response times or other performance objectives for fire protection because the maintenance of the canals and waterways with herbicides actually increases the amount of water available for parks.

e) The application of aquatic herbicides would not result in substantial adverse physical impacts associated with the provision of new or physically altered governmental facilities, needed for new or physically altered governmental facilities, the construction of which could cause significant environmental impacts, in order to maintain acceptable service ratios, response times or other performance objectives for fire protection because the canals have existed and have been maintained for years without any disruption to other public facilities.

3.14 Recreation

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
a) Would the project increase the use of existing neighborhood and regional parks or other recreational facilities such that substantial physical deterioration of the facility would occur or be accelerated?				X
b) Does the project include recreational facilities or require the construction or expansion of recreational facilities which might have an adverse physical effect on the environment?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not increase the use of existing neighborhood and regional parks or other recreational facilities such that substantial deterioration of the facility would occur of be accelerated because the water distribution system into which the herbicides are applied have been in operation for years without significant adverse impacts to recreational

opportunities. The use of aquatic herbicides will improve recreational opportunities by improving the quality and quantity of water. Further, swimming and fishing are not allowed in the District's canals or ditches at any location. The District has displayed "No Trespassing" signs at several locations throughout its system. Therefore, recreational resources for swimming and fishing will not be adversely affected by the District's Algae/Aquatic Weed Control Program.

b) The application and use of aquatic herbicides does not involve the construction or expansion of recreational facilities which might have an adverse physical effect on the environment. The project scope involves only the application of aquatic herbicides to the canal and water channel system within the District.

3.15 Transportation / Traffic

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Cause an increase in traffic which is substantial in relation to the existing traffic load and capacity of the street system (i.e., result in a substantial increase in either the number of vehicle trips, the volume to capacity ratio on roads, or congestion at intersections)?				X
b) Exceed, either individually or cumulatively, a level of service standard established by the county congestion management agency for designated roads or highways?				X
c) Result in a change in air traffic patterns, including either an increase in traffic levels or a change in location that results in substantially safety risks?				X
d) Substantially increase hazards due to a design feature (e.g., sharp curves or dangerous intersections) or incompatible uses (e.g., farm equipment)?				X
e) Result in inadequate emergency access?				X
f) Result in inadequate parking capacity?				X
g) Conflict with adopted policies, plans, or programs supporting alternative transportation (e.g., bus turnouts, bicycle racks)?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides will not cause an increase in traffic which is substantial in relation to the existing traffic load and capacity of the street system(e.g., result in a substantial increase in either the number of vehicle trips, the volume to capacity ratio on roads, or congestion at intersections). The application of aquatic herbicides is has historically been conducted 3-6 times per year. Typically, only one vehicle is used to transport the herbicides to the treatment area. The use of one vehicle 3-6 time per year would not substantially increase the number of vehicle trips or increase congestion.

b) The application and use of aquatic herbicides will not exceed, either individually or cumulatively, a level of service standard established by the county congestion management agency for designed roads or highways. The application of aquatic herbicides is has historically been conducted 3-6 times per year. Typically, only one vehicle is used to transport the herbicides to the treatment area. Therefore, no impact to service standards would result from the use of aquatic herbicides in the canal system.

c) The application and use of aquatic herbicides will not result in a change in air traffic patterns, including either an increase in traffic levels or a change in location that results in substantial safety risks because this project is limited to the application of aquatic herbicides to the canal and water channel system of the District.

d) The application and use of aquatic herbicides will not substantially increase hazards due to a design feature (e.g., sharp curves or dangerous intersections) or incompatible uses (e.g., farm equipment) because the project does not involve the construction on new roads, etc.

e) The application and use of aquatic herbicides will not result in inadequate emergency access because the application of the herbicides does not block emergency routes or access points. The project is limited to the canal and water channel system.

f) The application and use of aquatic herbicides will not result in inadequate parking capacity because the project does not involve the construction of new facilities or the removal of parking areas.

g) The application and use of aquatic herbicides will not conflict with adopted policies, plans, or programs supporting alternative transportation (e.g., bus turnouts, bicycle racks) because the program is limited to the application of herbicides to the canal and water channel system of the District.

3.16 Utilities And Service Systems

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
Would the Project:				
a) Exceed wastewater treatment requirements of the applicable Regional Water Quality Control Board?				X
b) Require or result in the construction of new water or wastewater treatment facilities or expansion of existing facilities, the construction of which could cause significant environmental effects?				X
c) Require or result in the construction of new storm water drainage facilities or expansion of existing facilities, the construction of which could cause significant environmental effects?				X
d) Have sufficient water supplies available to serve the project from existing entitlements and resources, or are new or expanded entitlements needed?				X
e) Result in a determination by the wastewater treatment provider which serves or may serve the project that it has adequate capacity to serve the project's projected demand in addition to the provider's existing commitments?				X
f) Be served by a landfill with sufficient permitted capacity to accommodate the project's solid waste disposal needs?				X
g) Comply with federal, state, and local statutes and regulations related to solid waste?				X

The District's responses to the above issues are as follows:

a) The application and use of aquatic herbicides by the District will not exceed wastewater treatment requirements of the applicable Regional Water Quality Control Board because the treated water will not be routed to or treated in a wastewater treatment facility.

b) The application and use of aquatic herbicides will not require or result in the construction of new water or wastewater treatment facilities or expansion of existing facilities, the construction of which would cause significant environmental

effects because the treated water will not be routed to or treated in a wastewater treatment facility.

c) The application and use of aquatic herbicides will not require or result in the construction or new storm water drainage facilities or expansion of existing facilities, the construction of which could cause significant environmental effects because the treated water is not directed to any storm drain or storm water drainage facility.

d) The project does not require additional water. The project actually increases the amount of water available for beneficial use by controlling or eradicating noxious aquatic vegetation that consumes water. Therefore, no adverse impact would occur as a result of the project.

e) The application and use of aquatic herbicides will not result in a determination by the wastewater treatment provider which serves or may serve the project that it has adequate capacity to serve the project's projected demand in addition to the provider's existing demands because the treated water from the project will not be routed to or treated in a wastewater treatment facility.

f) The application and use of aquatic herbicides project will not be required to be served by a landfill with sufficient capacity to accommodate the project's solid waste disposal needs because the project only produces small volumes of used canisters or containers that may go to the landfill.

g) The application and use of aquatic herbicides will not cause non-compliance with federal, state or local statutes and regulations related to solid waste because the treated water is a liquid and will not be delivered to a landfill. Additionally, the disposal of all used containers will fully comply with all applicable federal, state, and local regulations. The empty herbicide containers are transported to their respective manufactures.

3.17 Mandatory Findings of Significance

	Potentially Significant Impact	Potentially Significant Unless Mitigation Measures Incorporated	Less Than Significant Impact	No Impact
a) Does the project have the potential to degrade the quality of the environment, substantially reduce the habitat of a fish or wildlife species, cause a fish or wildlife population to drop below self-sustaining levels, threaten to eliminate a plant or animal community, reduce the number or restrict the range of a rare or endangered plant or animal or eliminate important examples of the major periods of California history or prehistory?		X		
b) Does the project have impacts that are individually limited, but cumulatively considerable? ("Cumulatively considerable" means that the incremental effects of a project are considerable when viewed in connection with the effects of past projects, the effects of other current projects, and the effects of probable future projects)?			X	
c) Does the project have environmental effects which will cause substantial adverse effects on human beings, either directly or indirectly?		X		

The District's responses to the above issues are as follows:

a) The Algae/Aquatic Weed Control Program does have the potential to significantly degrade the quality of the environment by potentially impacting listed species of fish and wildlife or potentially impacting water quality.

However, the canal and water channel system of the district should not be considered suitable habitat or fish or other wildlife. The canals do not allow for normal fish migration and are seasonally dewatered. Additionally, the vegetation in and on the banks of the canals and channels have historically been controlled and maintained at low levels in order to keep the canals free from noxious weeds that restrict flow, foul pump and plug screens. These above factors indicate that the District's canal and water channel system is not suitable habitat for fish or wildlife.

The project involves the use and storage of copper containing chemicals, glyphosate, and acrolein which are considered hazardous materials. The District has and will continue to implement the mitigation measures discussed in Section 3.7 (Hazards and Hazardous Materials) to reduce the impacts to less than significant levels.

The Algae/Aquatic Weed Control Program involves the application of Magnacide H (acrolein), copper-based aquatic herbicides, and Rodeo (glyphosate) in concentrations that temporarily exceed the CTR water quality objectives within the treatment areas. However, the District tests its water at the point immediately prior to entering into the Sacramento-San Joaquin Delta. The results from these tests indicate that acrolein and copper concentrations are below those set by the General Permit. The District has been and is currently in full compliance with the General Permit. Therefore, the Aglae/Aquatic Weed Control Program will not have a significant effect on the quality of the environment. Further, the District has implemented and will continue to implement the mitigation measures discussed in Section 3.4 (Biological Resources) and Section 3.8 (Hydrology and Water Quality) to continue operating without a significant impact and reduce any future potential adverse impacts to less than significant levels.

b) The application and use of aquatic herbicides does not have impacts that are individually limited, but cumulatively considerable because the water leaving the District's system contains acrolein, copper, and glyphosate in concentrations below those set by the General Permit. The District has been and is currently in full compliance with the General Permit. Therefore, the Aglae/Aquatic Weed Control Program will not have a significant effect on the quality of the environment. The loading of acrolein, copper, and glyphosate to natural waterways as a result of this project will add to the herbicide loads from other similar activities conducted in the watershed. However, the additional loadings from this project are incremental and not cumulative considerable, as indicated by the laboratory analyses of District water leaving the system, and are therefore, not anticipated to have significant impacts.

c) The Algae/Aquatic Weed Control Program does have the potential to have environmental impacts which will cause substantial adverse effects on human being, either directly or indirectly. However, the District has adopted and uses the mitigation measures discussed in Section 3.7 (Hazards and Hazardous Materials) and Section 3.8 (Hydrology and Water Quality). The implementation of these mitigation measures will reduce the risk of adverse effects on human being to less than significant levels.

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5.0 LIST OF PREPARERS

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Appendix A

Project Safety Management (PSM) Guidelines for the Application, Storage and Handling of 370 lb. Acrolein Containers at the Woodbridge Irrigation District

PROCESS SAFETY MANAGEMENT GUIDELINES FOR THE APPLICATION, STORAGE AND HANDLING OF 370 LB. ACROLEIN CONTAINERS AT THE WOODBRIDGE IRRIGATION DISTRICT

Note: This model is for use of acrolein as an aquatic herbicide. It is not designed for use of acrolein as a rodenticide (this is under development).

PROCESS SAFETY MANAGEMENT OF ACROLEIN AT

WOODBRIDGE IRRIGATION DISTRICT

I. INTRODUCTION

The purpose of this plan is to prevent or minimize the consequences of catastrophic releases of acrolein (MAGNACIDE® H) into the work area or surrounding community. A catastrophic release is a major uncontrolled emission, fire, or explosion that presents serious danger to employees or the surrounding community. This plan has also been developed to comply with the Cal/OSHA General Industry Safety Order, Process Safety Management of Highly Hazardous Chemicals, 8 CCR 5189.

This plan addresses the application, storage, handling and transport of acrolein containers at the Woodbridge Irrigation District storage facility (facilities) and permanent application sites, as well as temporary application sites.

Woodbridge Irrigation District stores acrolein containers at general plant, and transports it to various application sites. Acrolein is used to control aquatic weed growth in designated sections of the canal system.

The District Manager is responsible for oversight of development, implementation and integration of all program elements outlined in this plan.

This plan will be located at the District office and will be available to all employees.

II. PLAN DEVELOPMENT

A. Employee Participation

The development of this plan is based on a multi-disciplined approach. Team members from the office and field will participate in plan development.

Members of the team will be involved in various aspects of plan development. Employee representatives include an acrolein applicator who will be consulted on the development of the checklists for the process hazard analysis. See attachment #1 for the list of participants and their roles.

III. PROCESS SAFETY INFORMATION

A. Chemical and Physical Properties of Acrolein (MAGNACIDE H)

Acrolein, also known as 2-Propenal, is an aldehyde. It is present between 92-96% pure in MAGNACIDE H. It is inhibited with hydroquinone (0.35%) and covered with a nitrogen blanket to prevent hazardous polymerization. Acrolein is acutely toxic, an inhalation and fire hazard. Some of the typical physical and chemical properties are listed below.

- CAS # 107-02-8
- clear, colorless liquid
- acrid and pungent odor, extremely irritating
- pH of 7
- flashpoint of -13F° (TCC)
- heavier than air
- can produce exothermic hazardous polymerization reaction

- can be neutralized with soda ash or sodium bisulfite (increasing the pH results in decreased half-life)
- immediately dangerous to life and health at 2 ppm
- OSHA permissible exposure limit (PEL), 0.1 ppm
- OSHA short term excursion limit (STEL), 0.3 ppm.

Additional information is located in the MSDS (see Attachment #2) and the MAGNACIDE H Herbicide Application and Safety Manual, further referred to as the Safety Manual.

B. Health Hazards

Acrolein vapor is a strong irritant (lachrymator) and is toxic at low concentrations. It is extremely irritating to the eyes, nose, throat and lungs. It can be detected at levels between 0.02 and 0.2 ppm. The vapor concentration tolerable to humans (0.1 to 1 ppm) serves as a warning of its presence. Pulmonary edema and permanent lung damage can result from overexposure to the vapor. Acrolein is immediately dangerous to life and health at 2 ppm. There is no emergency antidote for acrolein.

Developmental and reproductive studies have indicated no adverse effects in the test animals. Eye contact with acrolein liquid will produce severe damage. Skin contact with the liquid can produce skin irritations ranging from reddening to severe blistering.

Additional health hazard information can be found in the MSDS (attachment #2) and MAGNACIDE H Application and Safety Manual (attachment #3).

C. Fire and Reactivity Hazards and Other Hazards

Refer to MSDS and MAGNACIDE H Application and Safety Manual (pages 5 through 8).

D. Process Technology

Acrolein is stored and dispensed from pressurized containers containing approximately 53 gallons (370 lbs.) or 347 gallons (2450 lbs.) of inhibited acrolein. Inhibited acrolein means that hydroquinone is added to slow oxygen catalyzed polymerization. Additionally, the dead space at the top of the cylinder is filled with pure nitrogen. Acrolein is injected into canals by means of a pressurized nitrogen cylinder applying a specified pressure to the acrolein cylinder. The liquid acrolein is forced up a dip tube inside the cylinder and out to the canal via piping and hoses.

On pages 28 and 29 of the MAGNACIDE H Application and Safety Manual, is the Process and Instrument Diagram (P & ID) for the acrolein injection process. The equipment in the process primarily consists of the following:

- Nitrogen cylinder
- The MAGNACIDE H container (inhibited acrolein)
- Various shut off valves
- Nitrogen pressure regulator
- Various pressure indication gauges
- Flexible hose
- Flow regulating orifice and strainer
- Check valves (to prevent backflow)
- Submersible pump (optional, to aid in mixing)
- Diffuser (optional).

The precise metering of acrolein is accomplished by regulating the nitrogen pressure and by means of an orifice placed in the acrolein discharge piping. A table in the MAGNACIDE H Application and Safety Manual (page 21) is used to determine the proper nitrogen pressure and orifice size for a particular canal application. A pump or diffuser may be used to aid in the mixing of acrolein in water to avoid volatilization of the acrolein.

1. Process Chemistry

Once injected into water, acrolein is diluted to a maximum concentration of 15 ppm, per the manufacturer's directions. Acrolein degrades in a hydration reaction with water. This degradation begins the moment the product is injected into the water. The primary degradation product is 3-hydroxypropanal. 3-hydroxypropanal undergoes further degradation. EPA mandated studies utilizing radioactive-labeled acrolein indicate that the degraded acrolein adds to the naturally present carbon pool used by bacteria and is ultimately mineralized to carbon dioxide. Studies indicate that there is no bioaccumulation as a result of the use of acrolein. Any acrolein which binds to soil reacts with the organic material in the soil.

Acrolein's half life (the amount of time it takes for the initial treatment concentration to half), ranges from 5.5 to 30 hours depending on the conditions of treatment (i.e., temperature of water, weed condition, flow rate, etc.). The overall conclusion based on the half life information for acrolein, is that it is not persistent in the environment.

2. Maximum Intended Inventory

The maximum expected inventory of acrolein at the General Plant is 740 pounds. The maximum number of containers allowed on a dispensing truck is one (1). The dispensing truck should only be loaded with the number of containers which are needed for the day's applications.

3. Safe Upper and Lower Limits and Consequences of Deviations

a. **Maximum Allowable Concentration** in water is 15 ppm per manufacturer's directions. Deviation from this may result in volatilization of acrolein into the air which in extreme cases may require evacuation of the population in the affected area.

b. **Maximum Application Flowrates & Pressures** are indicated in the MAGNACIDE H Application and Safety Manual flow tables as being 65 gallons per hour at 60 psig. This is the maximum acrolein flow which could possibly be applied and comply with manufacturer recommendations. This flowrate results from a nitrogen pressure of 60 psig (maximum nitrogen operating pressure) and a 0.081" diameter orifice (Maximum Orifice Size). Exceeding the maximum nitrogen pressure would cause more acrolein to be injected into the canal than recommended. A nitrogen pressure of approximately 175 psig would cause the pressure relief valve to open, venting acrolein until the pressure is reduced to around 158 psig at which time the valve closes. The acrolein when vented through the pressure relief device would pose a serious hazard to anyone in the immediate vicinity.

c. **Maximum Cylinder/Skid Liquid Level** must never exceed the manufacturers labeled net weights--370 pounds in cylinders, 2450 pounds in skid tanks.

d. **Limits on Temperature** Acrolein autoignites at a temperature of 455°F. Care should be taken not to store acrolein near any heat source, or near any ignition source. As the temperature in the acrolein cylinder or skid increases, the pressure also increases. At a sustained temperature of approximately 150°F, the pressure in the cylinder may build up to 175 psig and cause acrolein to be vented to the atmosphere. In the worst case, where acrolein containers are subjected to a fire, the containers could explode violently. A very serious acrolein fueled fire could generate toxic vapors. Emergency evacuation of the General Plant facility and the general public in the vicinity may be required.

e. **Stability of Acrolein** Acrolein is chemically stable when a nitrogen blanket is maintained at all times. Acrolein will under go polymerization when exposed to oxygen, acids, or alkalis. Hydroquinone is added to acrolein to inhibit oxygen catalyzed polymerization. However, the inhibiting agent only slows the polymerization process rather than preventing it. Deviation from maintaining a nitrogen blanket on the acrolein may result in safety relief valve activation and possibly a cylinder explosion. Employees and the general public in the vicinity of a container explosion could be severely injured. Evacuation of the General Plant facility and of the general public in the vicinity may be required. To assure an adequate nitrogen supply, when the nitrogen cylinder pressure goes under 100 psig, a freshly charged nitrogen container shall replace the depleted container.

E. Process Equipment Information

1. Materials of Construction & Applicable Codes:

- Nitrogen Cylinder: Carbon Steel, pressure rating = 2265 psig, DOT specification 3AA, 49CFR 178.37.
- Acrolein Cylinder: Carbon Steel, wall thickness = 0.130", pressure rating = 240 psig, rupture disc rating = 175 psig, safety relief valve lifting pressure = 160 psig, DOT specification 4BW, 49CFR 178.61, cylinder shutoff valves are ½' ball valves, carbon steel body, stainless steel trim, and TFE seat & seals rated for 2000 psig at 70°F.
- Acrolein Skid Tank: Carbon Steel, wall thickness = 0.250", pressure rating = 150 psig, rupture disc rating = 175 psig, safety relief valve lifting pressure = 160 psig, DOT specification = DOT 51, 49CFR 178, skid shutoff valves are 1" and ½' ball valves.
- Piping:
  - Copper Pipe: ASTM B42
  - Red Brass Pipe: ASTM B43.
- Fittings:
  - Bronze Fittings: ANSI B16.15, 200 psig w.o.g. (use with copper or brass pipe).
- Elastomeric Hose: Shall be of a acrolein compatible material per the MAGNACIDE H Application and Safety Manual, page 31, minimum pressure rating = 500 psi.

2. Electrical Classification

Acrolein containers when in storage are classified as Class 1, Division 2 which means that acrolein containers do not release vapors under normal conditions. Any electrical equipment used in close vicinity to acrolein in an enclosed environment must be explosion proof. Electrical equipment used near acrolein in an outdoor environment may be ordinary, provided set back distances are observed. The recommended set back distances are:

- 2 feet in all directions of acrolein containers
- from grade to 18 inches above grade within 5 foot radius.

Note: The above set back distances apply to stationary containers and are not applicable to the transport vehicle's electrical system, during container transport, loading or unloading.

3. Design Codes & Standards

The storage and dispensing of acrolein at W.I.D. are performed in accordance with the following codes and standards:

- NFPA 70 (National Electric Code)
- NFPA 30 (Flammable and Combustible Liquids Code)
- 8 CCR 5189.

F. Mechanical Integrity of Equipment

The equipment used in the acrolein injection process is simple when compared to large industrial plants. A maintenance program involving documented inspections and testing of equipment is required by 8 CCR 5189.

1. Equipment Included in Maintenance Program

The following equipment if utilized is to be included in the maintenance program:

- Acrolein Cylinders/Skids (including all valves attached to cylinder/skids from BPCI)
- Nitrogen Cylinders
- Pressure Regulators
- Pressure Gauges
- Piping and Fittings
- Flexible Hoses
- Valves
- Orifices
- Pumps
- Truck Mounted Jib Crane
- Weight Scale.

Stringent Department of Transportation (DOT) design, inspection and testing specifications govern the fabrication, charging, and transportation of nitrogen and acrolein containers. Upon request by District Manager, documentation will be provided to Woodbridge Irrigation District of the various tests and inspections performed on these containers. These DOT tests and inspections performed by an independent inspection agency include the following:

- Verify chemical analysis of material of construction
- Inspect welds and fabrication
- Verify container markings
- Internal condition of container
- Verify threads meet specifications
- Verify heat treatment of materials

- Witness pressure tests
- Verify wall thickness requirements
- Verify volume and weight of container
- Pressure test each container and certify every five years
- Safety relief valve testing
- Furnish complete test results to purchaser upon request.

2. Inspection and Testing Requirements

The following describes various inspection and testing requirements. When the term "documented" inspection or test is used, this indicates that records are maintained. The records shall include the following information:

- Description of test or inspection
- Date of inspection or test
- Name of person performing function
- Serial number or other unmistakable identification
- Results of inspection or test.

When the term "check" is used, this indicates that a non-documented routine inspection or test will be performed.

a. Acrolein and Nitrogen Containers

The containers are regularly pressure tested by the manufacturer to conform to the DOT pressure testing requirements. The Woodbridge Irrigation District is to perform visual checks of these containers when received and when dispensed. Due to the pungent smell of acrolein even at low concentrations, any leaks would be obvious. Routine checks which should be performed on these containers are as follows:

- Upon receipt of acrolein and nitrogen containers:

Visually check containers for bulging, corrosion, or significant cuts or gouges. Also check the container shut-off and safety valves for any visual defects. Any container showing any significant defect should be rejected and returned to the supplier. The serial number of any rejected container should be documented. The serial number is engraved in the container and will be something like "SA00298 DT" for cylinders and "A18237" for skids. Also check the container to ensure that the weight is indicated.

- Upon use of acrolein and nitrogen containers:

Visually check containers for defects. Upon hooking up application equipment, check to ensure that the nitrogen cylinder has sufficient charge. The acrolein container should have a positive nitrogen charge.

The Superintendent will perform non-documented visual checks of the container and document any abnormalities of a given container taking down the serial number of the container and describing the abnormality. Containers will be

checked upon deliver and those rejected sent to the manufacture after writing down the serial number and describing the defect.

b. Pressure Gauges

- Annual Calibration:

Pressure gauges are critical in the proper application of acrolein. A faulty pressure gauge can lead an operator to believe that normal conditions exist when in fact a potentially dangerous situation may be present. Pressure gauges shall be permanently marked with a serial number and date of purchase. Each pressure gauge will be calibrated once a year. The date of last calibration will be marked on the pressure gauge. Any gauge which can not be properly calibrated will be discarded. Documented records of pressure gauge calibration will be kept on file.

- Routine Checks During Use:

A malfunctioning pressure gauge can often be spotted by an operator during use. If an operator suspects that a pressure gauge is defective, it should be documented, removed from service and calibrated or discarded as appropriate.

c. Flexible Hoses (Not Permanently Mounted)

Flexible hoses, especially ones made of elastomeric materials, have a relatively short service life when compared to metal pipe. This shorter life expectancy is due to factors such as dry rotting, sun degradation and flexing, abrasion and chinking during use. All flexible hoses shall be permanently marked with date of purchase. Hose material selection must be compatible with acrolein per the MAGNACIDE H Application and Safety Manual (page 31).

- Annual Pressure Test or Replacement:

Each flexible hose shall be either pressure tested once a year or discarded. A nitrogen pressure test of 150 psig shall be applied for 10 minutes. The criteria for passing will be no more than one (1) psig pressure loss during a 0 minute period. Passing hoses shall be marked to indicate the date of testing. The results of the test shall be documented and kept on file.

- Routine Visual Checks:

Before application, the operator will perform visual checks of hoses for cuts or damaged threads. Any hose with obvious damage shall be disposed of in a proper manner.

d. Permanently Mounted Flexible Hose in Rigid Conduit

At some acrolein injection sites, hoses may be installed for up to two years inside rigid conduit on grade from the application inlet point to the canal. Multiple hoses may be routed for redundancy in case one hose should leak or

clog. The rigid conduit acts as secondary containment which would drain acrolein into the canal.

- Two Year Pressure Test or Replacement:

A two year interval of testing or replacement is allowed on permanently affixed hoses in secondary containment conduit. At every canal dry-up or every two years (which ever is shorter), these hoses shall be pressure tested or replaced with new hoses. A nitrogen pressure test of 150 psig shall be applied for 10 minutes. The criteria for passing will be no more than one (1) psig pressure loss during a 10 minute period. Passing hoses shall be marked to indicate the date of testing. If hose replacement is selected, then the date of purchase and installation will be permanently affixed to the hose. The two year period shall begin from the date of installation of the new hose.

- Routine Visual Checks:

Before application, the operator will inspect the rigid secondary conduit for cuts or gouges. Any defective conduit will be repaired immediately.

e. **MAGNACIDE H Discharge Assembly**

The components which make up the acrolein discharge assembly include the following:

- Piping
- Fittings (tees, elbows, quick disconnects etc.)
- Valves downstream of container valves
- Check valves
- Orifice assembly.
- Annual Pressure Tests:

The acrolein assemblies shall be assembled as a fixed unit and only disassembled at the tank connection, hose connection or for purposes of changing orifices and cleaning strainers. Each component of the assembly will be match marked by means of painting to indicate that the components go together as an unit for purposes of pressure test records. The orifice assembly does not require painting since it must be serviced and possibly replaced on a frequent basis.

The assembly shall be pressure tested once a year with a nitrogen pressure of 150 psig for 10 minutes. During the pressure test the pressure gauges will be removed and the pipe connections capped. This is to protect the gauges from over pressurization and possible damage. The nitrogen pressure shall be applied from the cylinder connection fitting upstream of the check valve. The criteria for passing shall be no more than one (1) psig pressure loss during a 10 minute duration. If leakage occurs (which can be located by a soap test) and it can not be corrected by tightening a fitting, then the bad component shall be discarded and replaced with a new approved component. The test shall be repeated.

A second test shall be done to verify the proper function of the check valve. A nitrogen pressure of 30 psig shall be applied downstream of the check valve for one minute to verify that no nitrogen leaks past the check valve. The criteria for passing shall be no more than a one (1) psig pressure loss during the test. Check valves which fail shall be discarded and replaced.

After the acrolein assembly passes both tests, the assembly will be marked with a sticker indicating the date of test and who performed it.

- Routine Checks:

Operators shall routinely check the acrolein assemblies for signs of damage such as pipe bending, thread damage, etc. before use. After equipment hook-up, a soap test of fittings shall be conducted to verify that no leaks exist. If a leak is found in a component (such as an elbow) then it should be replaced immediately with a new component. The new component is to be soap tested after installation. The installation of the new component will be documented stating which component was replaced, the date of replacement, the serial number of the discharge assembly and who replaced the component. This replacement record will be placed in the filing system.

f. **Deep Well Pumps** (NOT APPLICABLE TO W.I.D.)

In some locations a deep well pump is utilized in the acrolein application process. The deep well pump steel pipe discharges into a square, concrete turnout structure in a waterfall like manner. A pipe from the bottom of the turnout structure then flows by gravity into the canal. The acrolein is injected by means of either a fixed or portable hose into the turnout structure where the turbulence aids in mixing. The concentrated acrolein/water mixture then flows into the canal where final dilution occurs.

- Routine Checks:

When using a deep well pump for mixing, normal application procedures and routine checks apply with respect to the equipment. The only unique check is the level of the canal relative to the discharge pipe outlet at the canal. Acrolein shall only be injected if the deep well pump outlet to the canal is equal to or less than the canal level. This avoids volatilization caused by direct air contact of the concentrated acrolein/water mixture before dilution in the canal.

g. **Truck Mounted Jib Crane/Hoisting Equipment** (NOT APPLICABLE TO W.I.D.)

The hoisting equipment should be tested per the requirements of the manufacturer and Cal/OSHA sections 4884 et seq. Cranes and hoisting equipment exceeding 3 tons capacity are to have a current Cal/OSHA certification as required by Section 5021 et seq. Records shall be kept on file. Per the requirements of the manufacturer and Cal/OSHA, various inspection reports and checklists will be used to inspect and check various aspects of the equipment before each use, monthly, and annually (depending on the component in question).

h. **Weight Scale**

If a scale is used to weigh containers in determining the remaining amount of acrolein, documented calibration of the scale will be performed once a year. Records shall be kept on file.

3. Training of Maintenance Personnel

The equipment used in the acrolein injection process is very basic and in general requires no complicated maintenance which would warrant special training. Most of the components in the process like piping hoses, fittings, containers, etc. have little or no moving parts and are simply replaced when a defect is found. To replace piping components, no special training is required since the parts are simply screwed together or joined by quick couplers.

IV. PROCESS HAZARD ANALYSIS

A. Methodology: Hazard and Operability Study (HAZOP)

The HAZOP method will be used to systematically identify, analyze and correct potential hazards associated with the storage, handling and movement of acrolein at the injection sites and General Plant facility. The HAZOP was developed by the team referenced in attachment #1 and the process hazard analysis will be performed by members of this team. See Attachment #4 for the HAZOP.

After completion of the process hazard analysis, the HAZOP will be reviewed and the findings reported to the [manager in charge of compliance] by a team member. The process hazard analysis findings worksheets (see Attachment #4) will be used to document the findings, recommendations, corrective actions and completion dates. It will also be used to document that the affected employees have been informed of the recommendations or actions. Once the worksheet is completed, a copy of the findings should be maintained in Attachment #4.

The [manager in charge of compliance] is responsible for ensuring that the recommendations are resolved in a timely manner and that the resolution is documented. The [manager in charge of compliance] must ensure that the affected employees are informed of the changes.

The hazard analysis must be updated and revalidated every 5 years by the [manager in charge of compliance] and other members of the team, to ensure that the process hazard analysis is consistent with the current process.

B. History, Facility Siting and Human Factors

Acrolein is used as an aquatic herbicide. It is stored at the General Plant facility. One (1) cylinder (52 gallons) is located at this site. Currently, there are approximately 12 employees located at this site; of these, 0 percent of employees work at other [District] locations during the day.

Currently there are 3 employees from Woodbridge Irrigation District that may handle acrolein. These employees will be trained as outlined in Section VI of this plan before any handling.

Acrolein is applied at one primary and four spot treatment sites. No acrolein is located at these sites.

Each year acrolein is applied from March through October. The material may be applied Monday through Friday, during daytime hours.

C. Engineering and Administrative Controls

To minimize the potential for catastrophic releases of acrolein, the amount of acrolein stored at the General Plant facility should be minimized. Also, to minimize the potential consequences of cylinder/skid failure, the distance of the storage area to other occupied buildings should be maximized.

D. Safety and Health Effects of Control Failure

Acrolein can produce a wide range of safety and health effects. Container rupture could release product into the air and may cause fire and explosion. Adverse health effects to employees or the general public in the immediate and adjacent areas could occur if exposed. Additional information on control failure can be found in Section III. B. Health Hazards, the MSDS and the MAGNACIDE H Application and Safety manual.

V. STANDARD OPERATING PROCEDURES AND SAFE WORK PRACTICES

The operating procedures and work practices are outlined on pages 23 through 26 in the MAGNACIDE H Application and Safety Manual.

VI. TRAINING

A. Initial Training

Each employee involved in handling acrolein, and new employees prior to handling acrolein, will be trained in an overview of the process and in the operating procedures for acrolein. The training will include emphasis on the health and safety hazards, emergency operations including shutdown and safe work practices.

B. Refresher Training

Refresher training will be provided at least every 3 years or more often if necessary. The training will assure that the employee understands and adheres to the current operating procedures. The [manager in charge of compliance] will discuss and determine with the employees, the frequency of the refresher training.

C. Training Documentation

Training records will be maintained by the Superintendent. The records will include the name of the employee, the training date and the trainer's names. A copy of the means of verifying that the employees understand the training will also be included in the documentation. This may be a copy of a quiz completed by the employee or other documentation from the Superintendent indicating the employee has demonstrated understanding of the process through hands-on-training. Training documentation will be retained in attachment #5.

VII. CONTRACTORS/VISITORS

Contractors (or visitors) working in the acrolein storage area (or areas adjacent to it) and any application areas must be evaluated through the [District's] Contractor's Safety Program.

Contractors and visitors must be informed of the potential safety and health hazards associated with the process. The contractors must also be informed of the emergency action plan and it contents. The contractor's entrance and exit from the facility must be controlled.

The contractor will be responsible for complying with the requirements of the Cal/OSHA PSM regulation, 8 CCR 5189.

VIII. PRE-START-UP REVIEW

For new or modified systems, prior to introduction of acrolein, a pre-startup safety review will be conducted when the modification is significant enough to require change in the process safety information. The review will be conducted by appropriate personnel and other support groups when appropriate.

The review shall consist of at least the following: review of equipment specifications; that safety, operating, maintenance, and emergency procedures are in place and adequate; and a process hazard analysis performed for the new or modified systems as a whole. The employees must be trained on the new or modified system.

IX. MANAGEMENT OF CHANGE

Prior to any change or modification in technology, equipment, standard operating procedures or the facility, a review of the change must be conducted by representatives from [identify group responsible]. Where appropriate, other departments may be called upon to review the changes. [This does not include replacements-in-kind.]

The review will consider the following:

- Technical basis for the proposed change
- Impact of change on safety and health
- Modifications to operating procedures
- Necessary time period for the change and
- Authorization requirements for the proposed change.

Employees involved in handling acrolein will be informed and trained in the change prior to start-up. Process safety information and operating procedures may need to be updated accordingly.

X. INCIDENT ANALYSIS

Each incident which results in, or could reasonably have resulted in, a catastrophic release of acrolein, must be investigated promptly, but no later than 48 hours following the incident. Woodbridge Irrigation District will establish an incident investigation team consisting of at least one person knowledgeable in the acrolein process (including a contract employee if the incident involved work of the contractor) and other persons with appropriate knowledge and experience to thoroughly investigate and analyze the incident.

A report shall be prepared by the Superintendent at the conclusion of the investigation and should include at a minimum the following:

- Date of incident
- Date investigation began
- Description of incident
- The factors that contributed to the incident and

- Any recommendations resulting from the investigation.

The report shall also establish a corrective action plan, completion dates and documentation of the corrective actions. All effected employees shall review the report. The incident report must be maintained on file for at least five years.

XI. EMERGENCY PLANNING AND RESPONSE

The Emergency Response Plan for the Woodbridge Irrigation District is located at the General Plant facility. This plan must be reviewed by all employees involved with the storage, handling and movement of acrolein. Other employees working at the site must be made aware of the evacuation routes contained in this plan.

XII. COMPLIANCE AUDITS

An audit will be conducted on the process safety management of acrolein by the [designated person] at least once every three years to verify that the procedures and practices developed under the program standard are adequate and are being followed. The audit team shall include personnel from [identify group], and others as deemed appropriate by both parties.

A report will be developed with findings, recommendations and a corrective action plan. [Designated person] is responsible for developing and implementing the corrective action. The last two audit reports will be retained by [designated person]. A sample audit checklist is included under Attachment #6.

ATTACHMENT #1

EMPLOYEE PARTICIPANTS

LIST OF EMPLOYEE PARTICIPANTS

Employee Name Anders Christensen — PSM Role

Title District Manager

A. Oversight of development implementation and intergration of all program elements outlined in this plan.

B. Team Leader.

LIST OF EMPLOYEE PARTICIPANTS

Employee Name Jim Shults — PSM Role

Title District Superintendent

A. Plan development team member.

B. Program research and development team member.

C. Multi-disciplined approached coordinator.

D. Applicator.

E. Development of checklists for the process hazard analysis.

LIST OF EMPLOYEE PARTICIPANTS

Employee Name Jaime Cantu PSM Role

Title Vegetation Manager

A. Plan development team member.

B. Team member totally familiar with all aspects of applicating storage handling and storing Acrolein Cylinders at Woodbridge Irrigation District.

LIST OF EMPLOYEE PARTICIPANTS

Employee Name Paul Agdeppa PSM Role
Title Shop Foremen

A. Plan development team member.

B. Team member totally familiar with all aspects of applicating storage handling and storing Acrolein Cylinders at Woodbridge Irrigation District.

ATTACHMENT #2

ACROLEIN MSDS

MAGNACIDE(R) H HERBICIDE

Caution Code 4-3-3

ID: 94980103

1 - SECTION I - IDENTITY

BAKER PERFORMANCE CHEMICALS, INC.
A Baker Hughes Company
3900 ESSEX LANE, P.O. BOX 27714
HOUSTON, TX 77227-7714

EMERGENCY TELEPHONE NUMBERS:
CHEMTREC: 1-800-424-9300
BPCI: 1-800-231-3606
TELEPHONE NUMBER FOR INFORMATION:
713-599-7400

CHEMICAL NAME: Acrolein, Inhibited

CHEMICAL FAMILY: Aldehyde

2 - SECTION II - REGULATORY CLASSIFICATION

ENVIRONMENTAL	OCCUPATIONAL	TRANSPORTATION
RQ= 0.15 Gallons (Acrolein)	OSHA Non-Hazardous: No	Not Regulated: No
TPQ= 77 Gallons (Acrolein)	OSHA Hazardous: Yes	Regulated: Yes
SARA S313: Yes	X Acute	Acrolein, Inhibited,
Acrolein - 92% Minimum	NA Chronic	6.1, (3), UN 1092, I,
	X Fire	Toxic-Inhalation
	NA Pressure	Hazard, Zone A, Marine
	X Reactive	Pollutant, RQ

EPA REGISTRATION NO. 10707-9

This product is subject to regulation under the US Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and is therefore exempt from US Toxic Substance Control Act (TSCA) Inventory listing requirements.

3 - SECTION III - HAZARDOUS INGREDIENTS

HAZARDOUS COMPONENT	CAS #	PEL(OSHA)* TWA	PEL(OSHA)* STEL	PEL(OSHA)* A/L	TLV(ACGIH)* TWA	TLV(ACGIH)* STEL	MFG* REC, TWA
Acrolein (92 Wt% Min)	107-02-8	0.1	0.3		0.1	0.3	

*ppm unless otherwise indicated; (C) denotes ceiling limit

4 - SECTION IV - PHYSICAL & CHEMICAL PROPERTIES

Specific Gravity @60F: Approx 0.848 (H2O=1)

pH: Not Applicable

Density, lb/gal: Approx 7.06

Viscosity (Method): 0.43 cps at 32 F (Absolute)

Vapor Density (Air=1): 1.93

Appearance and Odor: Clear, colorless liquid with aldehyde odor

Solubility: 22% by Wt. in water at 68 F

Stability: Stable

Freezing Point: -124F

Pour Point: Not Determined

Flash Point (Method): -13F (TCC)

Percent Organic Compounds: 100%

Auto-Ignition Temperature: 428F (HSDB)

MAGNACIDE(R) H HERBICIDE

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DS ID: 94980103

4 - SECTION IV - PHYSICAL & CHEMICAL PROPERTIES (continued)

Lower Flammable Limit (% by Volume): 2.8% (HSDB)

Upper Flammable Limit (% by Volume): 31% (HSDB)

Boiling Point: 127 F Vapor Pressure: 8.6 psi (Reid) at 100F

Conditions to Avoid: Oxidizers; heat, sparks, or open flames; amines; caustics; acids; ammonia

Haz. Decomp. Prod: Carbon monoxide; carbon dioxide; and/or peroxides

Hazardous Polymerization: May occur

FIRE CONTROL PROCEDURES: Use foam, dry chemical, CO2, water fog or spray. Do not enter a fire area without proper protective equipment, including NIOSH/MSHA approved, self-contained breathing apparatus. Cool exposed containers with water spray. Avoid vapors.

FIRE HAZARDS: Extremely flammable. Vapors form explosive mixtures with air. Fight fire from safe distance or from protected location. Use water to keep exposed containers cool. If vapors or liquid are not ignited, use water spray to disperse. Use self-contained breathing apparatus. Fumes are toxic. Use fully protective and chemical resistant clothing. For additional information see MAGNACIDE H HERBICIDE Application and Safety Manual.

- SECTION V - HEALTH HAZARDS

EFFECTS OF OVEREXPOSURE: Irritation of the eyes, throat, and skin, reddening or blistering of the skin; headaches, acute distress in affected areas; cessation of breathing. There is no emergency antidote for MAGNACIDE H HERBICIDE.

OTHER INFORMATION:

Acrolein Toxicity Information:
Inh - Rat - LC50 = 26 ppm/1H
Inh - Rat - LC50 = 8.31 ppm/4H
Orl - Rat - LD50 = 29 mg/kg
Skn - Rbt - LD50 = 231 mg/kg

MAGNACIDE H has been tested for developmental, reproductive and chronic health effects. Results from developmental studies (Ref.1,2) indicated this material did not cause teratogenic effects in rats or rabbits at doses that caused maternal toxicity. A two-generation reproductive study (Ref.3) in rats did not reveal any evidence of reproductive toxicity in either sex from any treatment group (maximum dose = 7.2 mg/kg). A second two-generation reproductive study in rats (Ref.7) also did not reveal any evidence of reproductive toxicity in either sex from any treatment group. (Maximum dose = 6 mg/kg).

In a 12-month chronic toxicity test in dogs (Ref.4), the highest dose (2 mg/kg) tested resulted in changes in blood chemistry, but no compound-related tumors or lesions were observed. An 18-month oncogenicity study in the mouse (Ref.5) did not reveal any compound-related tumors or lesions; the highest dose tested (4.5 mg/kg) resulted in increased mortality in the test group. A 24-month chronic toxicity/oncogenicity study in the rat (Ref.6) also did not reveal any compound related tumors or lesions. The high dose, 2.5 mg/kg caused an increased mortality in the test group. No indications of cancer were found in any of the chronic tests.

AQUATIC TOXICITY DATA:
Holmesimysis Costata 96HR LC50: 0.67 mg/L

MAGNACIDE(R) H HERBICIDE

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5 - SECTION V - HEALTH HAZARDS (continued)

TARGET ORGANS (29 CFR 1910.1200-APPENDIX A)

Pulmonary Agents (Lung)
Eye Hazard
Cutaneous Hazard (Skin)

6 - SECTION VI - EMERGENCY & FIRST AID PROCEDURES

EYE CONTACT: Flush eyes immediately with large amounts of water for at least 15 minutes. Immediately afterward, transport the patient to the nearest physician. Keep patient prone and quiet.

SKIN CONTACT: Remove the patient from the vicinity of the exposure to prevent any further exposure to the toxicant. If MAGNACIDE H HERBICIDE is spilled on the clothing or skin, remove the affected clothing IMMEDIATELY and wash the skin thoroughly with large amounts of water. Treat exposed area as a chemical burn. Get immediate medical attention.

INHALATION: Wearing appropriate protective equipment, immediately move victim out of the exposure area and start CPR if breathing has stopped. Keep patient prone and quiet. Get immediate medical attention. (NOTE: Persons exposed to MAGNACIDE H HERBICIDE vapors may have a delayed reaction and experience severe irritation of the respiratory tract. Therefore, it is advisable to keep persons who have been exposed to high concentrations of MAGNACIDE H HERBICIDE under observation for 24 hours following exposure.)

INGESTION: DO NOT INDUCE VOMITING. Drink promptly one to two glasses of milk, egg whites, or gelatin solution. If these are not available, use water. Avoid alcohol. NEVER GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS PERSON. Get immediate medical attention. Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression, and convulsion may be needed.

7 - SECTION VII - PROTECTIVE EQUIPMENT RECOMMENDATIONS

VENTILATION: The use of mechanical ventilation is recommended whenever this product is used in a confined space, is heated above ambient temperatures, or is agitated. Where engineering controls are not feasible, assure use is in an area where there is natural air movement.

RESPIRATORY	CHEMICAL RESISTANT APPAREL	EYE/FACE
X AS NEEDED:	X AS NEEDED:	X AS NEEDED:
Air Supplied (SCBA)	X Gloves - Butyl Rubber	X Chemical Splash Goggles
X Air Purifying	X Clothing	Full Face Shield
X Full Facepiece	X Tyvek Polyethylene Suit	
Half Facepiece	Neoprene Boots	
X Cartridge or Cannister		
Acid Gas		
X Organic Vapor		
Ammonia		

MAGNACIDE(R) H HERBICIDE

ution Code 4-3-3

MSDS ID: 94980103

7 - SECTION VII - PROTECTIVE EQUIPMENT RECOMMENDATIONS (continued)

As per NIOSH, full-facepiece air-purifying respirators may be worn to protect personnel up to 2 ppm (IDLH) acrolein. The air purifying respirators should have organic vapor cartridge(s) or canister and should have a protection factor of 50.

Exposure levels of unknown concentrations or greater than 2 ppm acrolein require the use of full-facepiece positive pressure supplied-air breathing apparatus with a protection factor of 10,000.

Under normal operating conditions, no excursions above the regulated (recommended) exposure levels should occur. However, if used at elevated temperatures (fire), lower atmospheric pressure (high altitudes) or any other physical conditions that may increase the inhalation exposure, respiratory protective equipment as described above, should be worn. Also, due to individual susceptibility and sensitivity, before respirators are used, a full medical evaluation should be performed per 29 CFR 1910.134(b)(10).

A thorough review of the job task (job safety analysis) by a competent safety professional should be conducted to determine the appropriate level of protection. See 29 CFR 1910, Subpart I and 29 CFR 1910.133 for further information.

8 - SECTION VIII - SPILL & LEAK PROCEDURES

Don appropriate protective clothing and respiratory protection prior to entering a spill/leak area. Eliminate ignition sources. Approach area upwind if possible. Shut off leak if it can be done safely. MAGNACIDE H HERBICIDE spills can be deactivated into a stable polymer by spraying with a 5-10% solution of sodium carbonate (soda ash) or solid carbonate may be added followed by dilution with water. Alternately, a 10% solution of sodium bisulfite may be added resulting in deactivation of the MAGNACIDE H HERBICIDE. CAUTION: Apply sodium bisulfite only in its liquid form) If RQ (reportable quantity) is exceeded, report to National Spill Response Office 1-800-424-8802 Also in some jurisdictions , spills or leaks of any hazardous materials are reportable. Consult local lead agencies for further information. Continue to observe precautions.

WASTE DISPOSAL METHOD(S): Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal Law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance. Dispose of all wastes and/or containers in accordance with federal, state, and local regulations.

REQUIREMENTS FOR TRANSPORTATION, HANDLING AND STORAGE: Transport, handle and store in accordance with OSHA Regulation 1910.106 and applicable DOT regulations.

When using MAGNACIDE H HERBICIDE, all electrical equipment should meet the requirements of Section 500 of the National Electrical Code for that that application. Electrical equipment should also be properly grounded.

Full tanks of MAGNACIDE H HERBICIDE should be stored in an open or well ventilated area away from all other chemicals. No alkalies or oxidizing materials should be near. Recommend that all electrical equipment should be of Class 1 - Division 2 type and properly grounded. Do not reuse empty container. Return empty containers to Baker Performance Chemicals Incorporated.

8 - SECTION VIII - SPILL & LEAK PROCEDURES (continued)

NOTE: The information on this MSDS is based on data which is considered to be accurate. BPCI, however, makes no guarantees or warranty, either expressed or implied of the accuracy or completeness of this information.

The conditions or methods of handling, storage, use and disposal of the product are beyond our control and may be beyond our knowledge. For this and other reasons, we do not assume responsibility and expressly disclaim liability for loss, damage or expense arising out of or in any way connected with the handling, storage, use or disposal of this product.

This MSDS was prepared and is to be used for this product. If the product is used as a component in another product, this MSDS information may not be applicable.

By: Jack Lowell Date: 05/10/96 Supercedes: 04/10/96
Regulatory Information Specialist

9 - SECTION IX - REFERENCES

REFERENCES:

1. Parent, Richard A., Halina E. Caravello, Mildred S. Christian, and Alan M. Hoberman. Developmental Toxicity of Acrolein in New Zealand White Rabbits. Fundamental and Applied Toxicology. 20, 248-256 (1993).

2. Parent, Richard A., Halina E. Caravello, Marilyn F. Balmer, Thomas E. Shellenberger, and James E. Long. One-year Toxicity of Orally Adminstered Acrolein to the Beagle Dog. Journal of Applied Toxicology, Vol. 12(5), 311-316 (1992).

3. Parent, Richard A., Halina E. Caravello, and James E. Long. Two-year Toxicity and Carcinogenicity Study of Acrolein in Rats. Journal of Applied Toxicology, Vol. 12(5), 131-139 (1992).

4. Parent, Richard A., Halina E. Caravello, and Alan M. Hoberman. Reproductive Study of Acrolein on Two Generations of Rats. Fundamental and Applied Toxicology. 19, 228-2237 (1992).

5. Parent, Richard A., Halina E. Caravello, and James E. Long. Oncogenicity Study of Acrolein in Mice. Journal of the American College of Toxicology. 10(6), 647-659 (1991).

6. Smith, Ann M., Rebecca A. Doane, and Martin F. Kovacs, Jr. Metabolic Fate of [Carbon-14]Acrolein under Aerobic and Anaerobic Aquatic Conditions, Journal of Agricultural and Food Chemistry. Vol. 43(9), 2497-2503 (1995).

ATTACHMENT #3

MAGNACIDE H APPLICATION & SAFETY MANUAL

MAGNACIDE® H HERBICIDE

APPLICATION AND SAFETY MANUAL

EPA Reg. No. 10707-9

Revised: 4/97
Supersedes: 6/94

MAGNACIDE® H HERBICIDE

APPLICATION AND SAFETY MANUAL

Baker Crop Protection Chemicals, A Division of Baker Performance Chemicals Incorporated makes no warranty of merchantability, fitness for any purpose or otherwise, expressed or implied, concerning this product or its uses which extend beyond the use of the product under normal conditions in accord with the statements made in this manual.

EPA Reg. No. 10707-9

Revised: 4/97

Supersedes: 6/94

PLEASE SIGN AND RETURN

The attached MAGNACIDE® H Herbicide Application & Safety Manual contains directions for use and is part of the EPA registered labelling. Federal law requires that this handbook be in the possession of the applicator. Please acknowledge receipt of this handbook by signing below and returning this page to the address listed below.

I also acknowledge that I have successfully completed a MAGNACIDE H Safety and Application training program and fully understand the techniques presented.

Baker Crop Protection Chemicals
A Division of Baker Performance Chemicals Incorporated
P.O. Box 11192
Bakersfield, CA 93389

_____ _____

(Signature) (Date)

_____

(Title or Capacity)

_____

(Firm or Organization)

RESTRICTED USE PESTICIDE

FOR RETAIL SALE TO AND USE ONLY BY CERTIFIED APPLICATORS OR PERSONS UNDER THEIR DIRECT SUPERVISION AND ONLY FOR THOSE USES COVERED BY THE CERTIFIED APPLICATOR'S CERTIFICATION.

The attached information is supplied by:

_____ _____

(Baker Crop Protection Chemicals Representative) (Date)

TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

INTRODUCTION

This manual provides information on the proper application and handling of MAGNACIDE H HERBICIDE. MAGNACIDE H is registered with the U.S. Environmental Protection Agency (EPA) under Registration Number: 10707-9 for the control of submersed and floating weeds and algae in irrigation canals. The legal uses of MAGNACIDE H are limited to those listed on the EPA registered product label and this manual.

Because of its toxicity by inhalation, the EPA has classified MAGNACIDE H as a RESTRICTED USE PESTICIDE for retail sale to, and use only by, certified applicators or persons under their direct supervision and only for those uses covered by the certified applicator's certification. The various states each have differing requirements concerning record keeping for restricted use pesticides. Please contact the appropriate agency in your state for further information.

MAGNACIDE H controls submersed and floating vegetation in irrigation canals. Since 1956 hundreds of field trials have been conducted in the United States using MAGNACIDE H (active ingredient: acrolein, inhibited) in cooperation with public and private agencies. In addition, MAGNACIDE H has been widely used for commercial applications since 1959.

Effective dosages range from 1 part per million (ppm, parts of MAGNACIDE H per 1,000,000 parts water) to 15 ppm. In irrigation canals, submersed weed control is obtained at these dosages with application times ranging from 15 minutes to 8 hours (see MAGNACIDE H Concentration Table, page 23). All typical submersed aquatic weed species and algae appear to be susceptible. Floating forms such as watercress, water hyacinth and water primrose are typically not completely controlled at label rates. Emergent species, such as cattails and tules, are not affected.

Although acrolein, the active ingredient in MAGNACIDE H, is flammable, highly reactive chemically, and a lachrymator, the process of controlling submerged weeds with this product can be carried out effectively. Specialized application equipment permits introduction of MAGNACIDE H with minimal handling. MAGNACIDE H is supplied in DOT Specification pressurized containers. It is forced directly through a metering device into the irrigation canal, using nitrogen gas.

MAGNACIDE H is available in cylinders (370 lbs. net) or portable skid tanks (four sizes: 2300, 2450, 2500, and 3000 lbs. net) which meet DOT specifications for inhibited acrolein. All orders are F.O.B. Taft, California. Round trip freight charges for the containers are included in the product billing. Empty containers should be returned collect to Taft, California.

Those interested in the commercial application of MAGNACIDE H should contact:

Baker Crop Protection Chemicals
P.O. Box 11192
Bakersfield, CA 93389

Telephone: (805) 763-5137

Fax: (805) 765-6046

CONTROLLING SUBMERSED AQUATIC VEGETATION WITH MAGNACIDE H HERBICIDE

Introduction

Aquatic vegetation is a serious pest in many waterways of the world. This is particularly true in irrigation canals where weeds and algae reduce flow below that of the designed capacity of the channel. Unhampered weed growth causes the water level to rise, thus increasing the chance of overflow and levee breaks. Weeds collect silt and debris, necessitating periodic costly cleanouts. Occasionally these weeds break loose, clogging weirs, siphons and other canal structures. Control of this vegetation is a costly, but necessary part of the maintenance of these systems. The process of controlling submersed aquatic vegetation with MAGNACIDE H as described in this manual is an effective means of overcoming many of these problems.

Mode of Action on Plants

MAGNACIDE H is a general cell toxicant which reacts with various vital enzyme systems. The dead plant tissues gradually disintegrate and float downstream, without releasing any large masses of vegetation to clog canal structures. The weeds disintegrate slowly and clear out over a period of 3 or 4 days to 2 weeks, depending on the temperature. The time for restoration of the canal to full capacity will, of course, depend on the rate at which the weeds die and disintegrate. However, some increase in capacity may be apparent in a few hours, as the weeds become flaccid.

Weed Specificity

Although MAGNACIDE H appears to be toxic to all submersed weeds and algae, no special studies have been made to determine the relative susceptibility of the various species. However, among pondweeds, forms such as Zannichellia sp. and Potamogeton crispus were more easily controlled than the forms which also have floating leaves such as P. nodosus and P. illinoiensis. The latter type are best controlled when immature.

The following species have been controlled by recommended label use rates:

Algae:

Anabaena flos-aquae	(blue-green algae)
Chara sp.	(stoneworts)
Cladophora sp.	(green algae)
Cladophora glomerata	(green algae)
Hydrodictyon reticulatum	
Navicilla pelliculosa	(freshwater diatom)
Selenastrum capricornutum	(green algae)
Skeletonema costatum	(marine diatom)
Spirogyra sp.	(green algae)

Submersed Aquatic Weeds:

Callitriche sp.	(water starwort)
Ceratophyllum demersum	(coontail)
Elodea canadensis	(waterweed)
Heteranthera dubia	(waterstargrass)
Lemna gibba	(duckweed)
Potamogeton crispus	(curlyleaf pondweed)
Potamogeton foliosus	(leafy pondweed)
Potamogeton illinoiensis	(pondweed)
Potamogeton nodosus	(American pondweed)
Potamogeton obtusifolius	(pondweed)
Potamogeton pectinatus	(sago pondweed)
Potamogeton richardsonni	(richardson pondweed)
Najas sp.	(naiad)
Zannichellia palustris	(horned pondweed)

PRECAUTIONARY STATEMENTS

HAZARDS TO HUMANS AND DOMESTIC ANIMALS

DANGER **POISON**

EXTREMELY FLAMMABLE AND IRRITATING VAPOR AND LIQUID. POISONOUS BY INHALATION, SKIN CONTACT OR SWALLOWING. DO NOT BREATHE VAPOR. CORROSIVE: CAUSES EYE DAMAGE AND SKIN BURNS. DO NOT GET IN EYES, ON SKIN OR ON CLOTHING.

Wear goggles and butyl rubber gloves during handling. If spilled on clothing, gloves, or shoes, remove them immediately and wash thoroughly with soap and water before reuse. Use with adequate ventilation. Keep available at all time a full face air purifying respirator jointly approved by the Mine Safety and Health Administration and the National Institute of Occupational Safety and Health (NIOSH).

ENVIRONMENTAL HAZARDS STATEMENT

This product will kill fish and wildlife. Keep out of lakes, streams or ponds. Fish, shrimp and crabs will be killed at application rates recommended. Do not apply where they are important resources. Do not apply to water drainage areas where runoff or flooding will contaminate ponds, lakes, streams, tidal marshes and estuaries. Do not contaminate water by cleaning of equipment or disposal of wastes. Notify your state Fish and Game Agency before applying this product. Use only as specified. Do not release treated water for six days after application into any fish bearing waters or where it will drain into them.

RECOMMENDATIONS FOR PROPER HANDLING OF MAGNACIDE H

This section has been developed to inform the applicator of the recommended handling methods for MAGNACIDE H. It summarizes the importance of proper storage, chemically compatible hardware, use of safety equipment, disposal, fire control, first aid and other safety related issues. All persons who handle MAGNACIDE H should be trained thoroughly in correct operation techniques. They should be completely familiar with its properties and with proper emergency procedures. Handling instructions and safety precautions should be available in all areas where it is used or stored.

Physical and Chemical Properties

MAGNACIDE H is a formulation containing a minimum of 92% (by weight) acrolein as the active ingredient. Some of the typical physical and chemical properties are listed below.

Formula	(CH2=CH-CHO)
Molecular weight	56.06
Appearance	clear, colorless liquid
Odor	aldehydic (extremely irritating)
Specific gravity at 60° F	0.847
Pounds per gallon at 60° F	7.06
Boiling point (@760 mmHg)	127° F
Freezing point	-124° F
Vapor density	1.93 (air = 1.0)
Flash point	
Tag open cup	-20° F (approx.)
Tag closed cup	-13° F (approx.)
Flammability limits in air	
Lower limit	2.8% (by volume)
Upper limit	31.0% (by volume)
Solubility at 68° F	
Acrolein in water	22% by weight
Water in acrolein	7% by weight
Vapor pressure at 100° F	8.6 psia
Coefficient of expansion at 59° F	0.000762 per degree F
Viscosity at 32° F (Abs.)	0.43 cps
Threshold limit value (OSHA)	0.1 ppm

FIRE AND POLYMERIZATION HAZARDS

MAGNACIDE H is a highly volatile liquid. In certain combinations with air (see table on previous page), vapors can have an explosive potential if ignition sources are present. Keep away from all sources of heat, spark and flame.

Liquid MAGNACIDE H is highly chemically reactive and readily forms polymers evolving tremendous heat. Contamination with air, alkalies, or strong acids can initiate polymerization. Contamination with all foreign materials must be avoided. If the product is stored or handled improperly, the polymerization may proceed with sufficient violence to rupture the container.

MAGNACIDE H polymerizes slowly in the presence of air. Therefore, all containers are packaged with a blanket of nitrogen to exclude air. To avoid the possibility of air contamination during use, MAGNACIDE H must be pressured from the container with oxygen-free nitrogen only. In addition, hydroquinone is added to inhibit oxygen catalyzed polymerization. However, hydroquinone does not inhibit polymerization catalyzed by alkalies and strong acids.

HEALTH HAZARDS

MAGNACIDE H vapor is a strong irritant (lachrymator) and is toxic in high concentrations. It is extremely irritating to the eyes, nose, throat and lungs. However, it is practically impossible to remain voluntarily in a vapor-contaminated atmosphere long enough to produce serious physiological effects because of its high lachrymatory activity. The vapor concentration tolerable to man (0.1 - 1 ppm in air) serves as a warning of its presence and is far below the minimal lethal concentration. Chronic toxicity studies have not revealed any cumulative effects. However, severe overexposure to the vapor can result in serious injury to the lungs. Additional information is found in the **"Toxicity"** section.

Eye contact with MAGNACIDE H liquid will produce severe damage; the chemical must be removed immediately by flushing with large quantities of water. Skin contact with liquid MAGNACIDE H can cause skin irritations ranging from simple reddening of the skin to severe blistering. (See "Statement of Practical Treatment" section for additional information).

PERSONAL SAFETY EQUIPMENT AND USE

Routine Personal Safety Wear

The applicator, to protect himself from an accidental splash or spray, must wear chemical splash goggles and butyl rubber gloves. It is of paramount importance that splash goggles be worn to prevent permanent eye damage.

Keep available at all times a full face air purifying respirator jointly approved by the Mine Safety and Health Administration (MSHA) and National Institute of Occupational Safety and Health. The respirator must be available for use if irritation from MAGNACIDE H vapors is experienced. The eyes, nose and throat can be mildly to severely irritated depending on the concentration of the vapor. NOTE: Applicators will find that when vapors are present, vapors will enter both the vented and non-vented types of splash goggles. Splash goggles are for protection from liquid chemical only, not vapor. This being the case, the applicator will have to use a full face air purifying respirator to protect himself from eye and respiratory irritation.

Applicators should also have fresh water available in case of accidental irritation to the eyes or skin from MAGNACIDE H liquid or vapors. In addition, the applicator should have a ten (10) pound dry chemical fire extinguisher at his disposal when working with MAGNACIDE H. All of the equipment mentioned above should be provided for the applicator's use during each application to comply with OSHA standards 1910.132 (a) and 1910.151 (c).

SPILL CONTROL PROCEDURE

General Information

MAGNACIDE H spills can be deactivated using sodium carbonate (soda ash). This will polymerize the spill forming a hard odorless polymer. Sodium carbonate is added to the spill in powdered form followed by dilution with water. The deactivated polymer can then be placed in marked containers for disposal in an approved industrial waste disposal facility. Never flush MAGNACIDE H into sewers or natural waterways as this can result in biological upset of treatment systems or kill fish in waterways.

Recommended Procedure For Handling Spills

1. Evacuate all nonessential personnel to an upwind area.

2. All decontamination personnel must wear self-contained breathing apparatus and appropriate protective clothing.

3. Contain spill by diking with dirt.

4. Add sodium carbonate (soda ash) to the spill in powdered form. Follow by dilution with water.

5. When deactivation is complete, scoop the polymer in properly marked containers for disposal at an approved industrial waste disposal facility in compliance with state and/or federal requirements.

6. All personnel responding to a spill of MAGNACIDE H must have completed the appropriate training as outlined in 29 CFR 1910.120 (q).

RECOMMENDED FIRE CONTROL

Pursuant to federal regulations, states require that the appropriate fire department be notified of the location where MAGNACIDE H is stored.

MAGNACIDE H is highly flammable and produces toxic vapors. All professional fire fighting personnel must wear self-contained breathing apparatus and protective clothing.

Carbon dioxide or dry chemical extinguishers can be used on small fires. Alcohol-type foam is recommended for large fires. If the fire can be tolerated without endangering additional personnel or property, then it should be left to burn itself out.

Water spray may be effective if used in large quantities, at least 20 volumes of water per volume of MAGNACIDE H. Use water spray to help disperse vapors and cool containers.

Note: At elevated temperatures, such as in fire conditions, there is the possibility of violent rupture of MAGNACIDE H containers.

MAGNACIDE H STORAGE

All containers of MAGNACIDE H should be stored in an open or well ventilated area, away from all other chemicals. No alkalies or oxidizing materials should be near. Any electrical equipment should be Class 1 - Division 2 type and properly grounded. Do not reuse empty container. Return empty containers to Baker Performance Chemicals Incorporated.

DISPOSAL

Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal Law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

STATEMENTS OF PRACTICAL TREATMENT

MAGNACIDE H is irritating to the eyes, nose, and throat; the resulting irritation is ordinarily recognized by most people at nonhazardous levels in a short period of time. This practically precludes the possibility of prolonged, voluntary exposure to the vapor in harmful concentrations. It is virtually impossible for a person to ingest a harmful quantity due to its extreme irritating effect.

Symptoms:

Irritation of the eyes, throat, and skin; reddening or blistering of the skin; headaches; acute distress in affected areas; cessation of breathing. There is no emergency antidote for MAGNACIDE H.

If Inhaled:

Get victim into fresh air immediately and start artificial respiration if breathing has stopped. Keep patient prone and quiet. NOTE: Persons exposed to MAGNACIDE H vapors may have a delayed reaction and experience severe irritation of the respiratory tract. Therefore, it is advisable to keep persons who have been exposed to high concentrations of MAGNACIDE H under observation for 24 hours following exposure.

If on Skin:

First, remove patient from the vicinity of the chemical to prevent any further exposure. If MAGNACIDE H is spilled on the clothing or skin, remove the affected clothing immediately and wash the skin thoroughly with soap and water. Treat exposed area as a chemical burn.

If in Eyes:

If the material has been splashed into the eyes, wash immediately with large amounts of fresh water for at least 15 minutes. For eyes, get medical attention.

If Swallowed:

DO NOT INDUCE VOMITING. Drink promptly a large quantity of milk, egg whites, gelatin solution or if these are not available, drink large quantities of water. Avoid alcohol. Call a physician immediately. Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression and convulsion may be needed. NEVER give anything by mouth to an unconscious person.

In the event of any type of overexposure to MAGNACIDE H requiring medical attention, this manual should accompany the patient to the physician.

DIRECTIONS FOR USE

It is a violation of Federal Law to use this product in a manner inconsistent with its labelling.

GUIDE FOR MAGNACIDE H APPLICATION FROM CYLINDERS AND PORTABLE SKID TANKS

Introduction

Information contained in the following pages of this manual will assist the applicator in determining: (1) the proper size orifice through which he should apply MAGNACIDE H; (2) the nitrogen application pressure which he should use; and (3) the proper setup and shut down of the MAGNACIDE H Application Equipment as distributed by Baker Crop Protection Chemicals (BCPC).

MAGNACIDE H is forced from the container with oxygen-free nitrogen gas and introduced directly into the canal over a period of 15 minutes to 8 hours to form a wave of treated water. Because of its high activity against submersed vegetation, concentrations in the range of 1 - 15 ppm are required for control. As the wave proceeds down the canal, it acts like a chemical dragline, destroying weeds as it moves.

The amount of MAGNACIDE H required is primarily determined by the amount of water flow in the canal, although velocity, weed density, water temperature and quality must also be considered. Canal flow is generally stated in cubic feet per second (cfs) and the amount of material used can be expressed in terms of this value. As an example, if MAGNACIDE H is recommended at 1 gallon/cfs, it means that for a canal flowing 10 cfs a total of 10 gallons of material will be needed.

Since MAGNACIDE H is added over a time interval, a wave of treated water is formed that moves downstream, bathing the weeds in herbicide. The amount of herbicide the weeds receive is, therefore, determined by (1) its concentration in the water and (2) the time required for the treated water to pass over the plants. In fast flowing canals (linear velocity greater than 2.5 ft/sec), masses of vegetation may be compacted or bent by the water; channeling will occur preventing the free movement of the treated water through the weeds. The same situation may prevail in canals heavily infested with weed growth. Consequently, all plants may not receive their proportionate share of the available herbicide and control will be less effective. Therefore, in canals flowing faster than 2.5 ft/sec, the dosages may have to be increased (not to exceed 15 ppm) or the time period of treatment extended.

MAGNACIDE H APPLICATION GUIDE

To determine the proper orifice size and nitrogen pressure setting one must know:

1. The weed growth condition of the canal: Naturally the more severe the weed growth condition the more MAGNACIDE H will be required for control. Use the Magna condition code below to determine the weed growth condition and gallons of MAGNACIDE H per cubic foot per second (cfs).

WEED GROWTH CONDITION CHART

Condition Code		MAGNACIDE H per cfs
A. Little algae and pondweed less than 6" long	=	0.17 gallons per cfs
B. Algae (non-floating) and pondweed less than 12" long	=	0.25 gallons per cfs
C. Algae (some floating) and pondweed 12 - 24" long	=	0.50 gallons per cfs
D. Algae (some floating) and mature pondweed (over 24" long)	=	1.0 gallons per cfs
E. Choked condition	=	1.50 gallons per cfs

NOTE: Water temperatures also affect the amount of MAGNACIDE H required for effective treatment. MAGNACIDE H is less soluble in cooler water and plant reactivity is lowered. The above conditions are for temperatures above 60° F. Correct the amount of MAGNACIDE H required for effective treatment as follows:

Water Temperatures	Increase Amount of MAGNACIDE H
60° F - 55° F	20%
55° F - 50° F	50%
50° F or below	100%

2. Canal Rate of Flow: The volume of water that passes a particular reference section in a unit of time. Usually designated as cubic feet per second (cfs). Calculated as mean depth in feet times mean width in feet times the linear velocity in feet per second.

3. Determine the temperature of the canal water to be treated.

4. Application Time: Normal application times will range from 15 minutes to 8 hours. Items to be considered in selecting an application time are:

   a. Contact time: Since MAGNACIDE H is a contact herbicide, consider the velocity of the canal. In fast flowing canals (2 mph or more) extend the application time to insure good contact.

   b. Concentration of MAGNACIDE H in parts per million (ppm) may be controlled by adjusting the application time. Concentrations should not exceed 15 ppm. See MAGNACIDE H Concentration Table, page 23.

After you have determined the above 4 items you can calculate the orifice size and nitrogen pressure setting.

Method I

Example A:
1. Weed growth condition: Some algae and pondweed 10 inches in length.
2. Canal rate of flow is 50 cfs.
3. Temperature of 65° F.
4. Application time 3 hours.

Step 1

From Weed Growth Condition Chart we determine a condition **B** or 0.25 gallons of MAGNACIDE H per cfs. **NOTE:** Temperature is above 60° F.

Step 2

Determine total gallons of MAGNACIDE H required:
Multiply canal rate of flow (cfs) by weed growth condition code (MAGNACIDE H per cfs) to find the total gallons of MAGNACIDE H required.

50 cfs X 0.25 gallons MAGNACIDE H/cfs = 12.5 total gallons of MAGNACIDE H

Step 3

Determine gallons of MAGNACIDE H per hour. Divide total gallons of MAGNACIDE H by application time to find gallons of MAGNACIDE H per hour.

12.5 total gallons MAGNACIDE H/3 hours = 4.2 gph of MAGNACIDE H

Step 4

Determine orifice size and nitrogen pressure setting. Go to Orifice Flow Table MAGNACIDE H Gallons Per Hour, page 22. Locate the gallons per hour of MAGNACIDE H, or the closest number in the table. Read to the left to find the orifice size and read up to find the nitrogen pressure setting. We determine 4.1 gph is the closest number to 4.2 gph and locate the orifice size and pressure setting of:

Orifice Size, Inches	Pressure Setting, psig
0.025	25 psig

Example B:

1. Weed growth condition: Floating algae and floating pondweed 12 - 24" long.
2. Canal rate of flow 120 cfs.
3. Temperature 57° F.
4. Application time 4 hours.

Step 1

From Weed Growth Condition Chart we determine condition **C** or 0.50 gallons of MAGNACIDE H per cfs. **NOTE:** Temperature of 57° F will increase rate by 20%.

Step 2

Determine total gallons of MAGNACIDE H required. Multiply canal rate of flow (cfs) by weed growth condition code (MAGNACIDE H per cfs) to find the total gallons of MAGNACIDE H. Due to temperature below 60° F we will increase the total gallons of MAGNACIDE H by 20%.

120 cfs X 0.50 gallons of MAGNACIDE H per cfs = 60 gallons MAGNACIDE H

60 gallons MAGNACIDE H X 0.20 (for water temperature) = 12 gallons

60 gallons + 12 gallons = 72 total gallons MAGNACIDE H required

Step 3

Determine gallons of MAGNACIDE H per hour: Divide total gallons MAGNACIDE H by the application time to find gallons of MAGNACIDE H per hour.

72 total gallons MAGNACIDE H/4 hours = 18 gph of MAGNACIDE H

Step 4

Determine orifice size and nitrogen pressure setting. Go to Orifice Flow Table, page 22, locate the gallons per hour of MAGNACIDE H, or the closest number on the table. Read to the left to find the orifice size and read up to find the nitrogen pressure setting. We determine 18.5 gph is the closest number to 18 gph and locate the orifice size and pressure setting:

Orifice Size, Inches	Pressure Setting, psig
0.045	50 psig

Method II

Alternatively, the gallons per hour of MAGNACIDE H may be determined as follows:

Example A:

1. Weed growth condition: Some algae and pondweed 10" in length.
2. Canal rate of flow 50 cfs
3. Temperature of 65° F.
4. Application time of 3 hours.

Step 1

From Weed Growth Condition Chart we determine a condition **B** or 0.25 gallons MAGNACIDE H per cfs. **NOTE:** Temperature is above 60° F.

Step 2

Go to weed condition code **B**, page 18. Under **"Flow in Canal (cfs)"** column read down to 50 cfs. Then read across to your right and intersect the 3 hour column. We find 4.2 gallons per hour (gph).

Step 3

Determine orifice size and nitrogen pressure setting: Go to Orifice Flow Table on page 22. Locate the gallons per hour of MAGNACIDE H, or the closest number on the table. Read to the left to find the orifice size and read up to find the nitrogen pressure setting. We determine 4.1 gph is the closest number to 4.2 gph and locate the orifice size and nitrogen pressure setting of:

Orifice Size, Inches	Pressure Setting, psig
0.025	25 psig

NOTE: If the water temperature had been 57° F, it would have been necessary to increase the gph rate by 20%.

	4.2	gph
X	0.20	(water temperature correction)
	0.840	gph additional MAGNACIDE H
+	4.2	gph
	5.0	gph MAGNACIDE H

Preventive Maintenance Program

It has been determined through various field studies that the most effective and economical method of aquatic weed control is obtained by utilization of a preventive maintenance program. This program consists of :

1. Making a series of MAGNACIDE H applications over the irrigation season so that the aquatic weeds are never allowed to reach a "problem" condition.

2. The first MAGNACIDE H application should be made as soon as aquatic weed growth appears (weed growth conditions **A** or **B**, p. 12). This will normally occur 3 - 6 weeks after the canal receives a constant supply of water.

3. The second and subsequent applications should be made at two to three week intervals, depending upon the regrowth of the aquatic weeds. Regrowth will depend on several variables such as water and atmospheric temperatures, species of aquatic plant, turbidity of water, water quality, and sunlight conditions.

4. By utilizing the preventive maintenance program, the irrigation system will be kept free of weeds throughout the irrigation season, solving water delivery problems and minimizing off-season maintenance created by aquatic weeds.

5. The treated water is much easier to contain or control when the preventive maintenance program is used.

WEED CONDITION CODE A

Little Algae and Pondweed Less Than 6" Long (0.17 gallon/cfs)

Flow in Canal (cfs)	1 Hour GPH	2 Hours GPH	3 Hours GPH	4 Hours GPH
5	0.83	-	-	-
10	1.7	0.83	-	-
20	3.3	1.7	-	-
30	5.0	2.5	-	-
40	6.6	3.3	2.3	1.76
50	8.3	4.2	2.8	2.1
60	10.0	5.0	3.3	2.6
70	11.6	5.8	4.0	3.0
80	13.3	6.6	4.5	3.4
90	15.0	7.5	5.0	3.8
100	16.6	8.3	5.6	4.2
200	33.2	16.6	11.0	8.3
300	50.0	25.0	16.7	12.5
400	66.4	33.2	22.4	16.6
500	83.0	41.5	27.6	20.8
600	100.0	50.0	33.3	25.0
700	116.2	58.1	39.0	29.0
800	132.8	66.4	44.5	33.3
900	150.0	75.0	50.0	37.5
1000	166.0	83.0	55.5	41.5

WEED CONDITION CODE B

Algae (not floating) and Pondweed Less Than 12" Long (0.25 gallon/cfs)

Flow in Canal (cfs)	1 Hour GPH	2 Hours GPH	3 Hours GPH	4 Hours GPH
5	1.25	0.63	-	-
10	2.5	1.25	0.83	0.63
20	5.0	2.5	1.7	1.25
30	7.5	3.8	2.5	1.9
40	10.0	5.0	3.3	2.5
50	12.5	6.3	4.2	3.1
60	15.0	7.5	5.0	3.8
70	17.5	8.8	5.8	4.4
80	20.0	10.0	6.7	5.0
90	22.5	11.3	7.5	5.6
100	25.0	12.5	8.3	6.2
200	50.0	25.0	16.6	12.5
300	75.0	37.5	25.0	19.0
400	100.0	50.0	33.3	25.0
500	125.0	62.5	41.6	31.0
600	150.0	75.0	50.0	38.0
700	175.0	87.5	59.0	44.0
800	200.0	100.0	67.0	50.0
900	225.0	112.5	75.0	55.5
1000	250.0	125.0	83.0	62.5

WEED CONDITION CODE C

Algae (some floating) and Pondweed 12 - 24" Long (0.50 gallon/cfs)

Flow in Canal (cfs)	2 Hours GPH	3 Hours GPH	4 Hours GPH	6 Hours GPH
5	1.25	0.83	0.63	-
10	2.5	1.76	1.3	0.83
20	5.0	3.3	2.5	1.7
30	7.5	5.0	3.8	2.5
40	10.0	6.7	5.0	3.3
50	12.5	8.3	6.3	4.2
60	15.0	10.0	7.5	5.0
70	17.5	11.7	8.8	5.8
80	20.0	13.3	10.0	6.7
90	22.5	15.0	11.1	7.5
100	25.0	16.7	12.5	8.4
200	50.0	33.3	25.0	16.6
300	75.0	50.0	37.5	25.0
400	100.0	66.7	50.0	33.3
500	125.0	83.3	62.5	41.7
600	150.0	100.0	75.0	50.0
700	175.0	117.0	88.0	58.0
800	200.0	133.0	100.0	67.0
900	225.0	150.0	111.0	75.0
1000	250.0	167.0	125.0	84.0

WEED CONDITION CODE D

Algae (some floating) and Mature Pondweed over 24" Long (1.0 gallon/cfs)

Flow in Canal (cfs)	3 Hours GPH	4 Hours GPH	6 Hours GPH	8 Hours GPH
5	1.7	1.25	0.83	-
10	3.3	2.5	1.7	1.25
20	6.7	5.0	3.3	2.5
30	10.0	7.5	5.0	3.8
40	13.3	10.0	6.7	5.0
50	16.7	12.5	8.3	6.3
60	20.0	15.0	10.0	7.5
70	23.3	17.5	11.7	8.8
80	26.7	20.0	13.3	10.0
90	30.0	22.5	15.0	11.3
100	33.3	25.0	16.7	12.5
200	67.0	50.0	33.3	25.0
300	100.0	75.0	50.0	37.5
400	133.0	100.0	66.7	50.0
500	167.0	125.0	83.3	62.5
600	200.0	150.0	100.0	75.0
700	233.0	175.0	117.0	87.5
800	267.0	200.0	133.0	100.0
900	300.0	225.0	150.0	112.5
1000	333.0	250.0	167.0	125.0

WEED CONDITION CODE E

Choked Condition
(1.5 gallons/cfs)

Flow in Canal (cfs)	4 Hours GPH	6 Hours GPH	8 Hours GPH
5	1.9	1.3	0.9
10	3.8	2.5	1.9
20	7.5	5.0	3.8
30	11.5	7.5	5.8
40	15.0	10.0	7.5
50	19.0	12.5	9.5
60	22.5	15.0	11.3
70	26.5	17.5	13.3
80	30.0	20.0	15.0
90	33.3	22.5	16.7
100	37.5	25.0	18.8
200	75.0	50.0	37.5
300	103.0	75.0	51.5
400	150.0	100.0	75.0
500	188.0	125.0	94.0
600	225.0	150.0	112.5
700	264.0	175.0	132.0
800	300.0	200.0	150.0
900	333.0	225.0	166.5
1000	375.0	250.0	187.5

ORIFICE FLOW TABLE (GPH)

Regulator Pressure (PSIG)

Orifice Size (Inches)	6 GPH	8 GPH	10 GPH	15 GPH	20 GPH	25 GPH	30 GPH	40 GPH	50 GPH	60 GPH
0.014	0.65	0.72	0.85	1.05	1.2	1.3	1.4	1.6	1.9	2.1
0.016	0.85	0.98	1.05	1.3	1.5	1.7	1.9	2.2	2.4	2.6
0.020	1.3	1.5	1.6	2.1	2.4	2.7	2.8	3.3	3.7	4.0
0.025	2.1	2.3	2.6	3.2	3.7	4.1	4.5	5.1	5.9	6.3
0.030	2.8	3.3	3.7	4.6	5.3	5.9	6.4	7.3	8.5	9.2
0.035	3.9	4.5	5.1	6.2	7.2	7.9	9.2	10.5	11.1	12.5
0.045	6.4	7.0	8.5	10.5	11.8	13.1	14.2	16.5	18.5	21.0
0.055	9.8	11.1	12.4	15.0	17.0	20.0	22.0	25.0	27.0	30.0
0.070	15.0	17.0	21.0	25.0	28.0	32.0	35.0	40.0	46.0	49.0
0.081	21.0	24.0	27.0	33.0	38.0	42.0	47.0	53.0	60.0	65.0

MAGNACIDE H CONCENTRATIONS

Flowing Irrigation Canals

Concentration in ppm at Various Gallon/cfs Rates

Application Time	Weed Condition A	Weed Condition B	Weed Condition C	Weed Condition D	Weed Condition E
	Gal/cfs 0.16	Gal/cfs 0.25	Gal/cfs 0.50	Gal/cfs 1.0	Gal/cfs 1.50
	ppm	ppm	ppm	ppm	ppm
30 minutes	10.0	-	-	-	-
1 hour	5.0	7.8	-	-	-
2 hours	2.6	3.9	7.8	-	-
3 hours	1.7	2.6	5.2	10.4	-
4 hours	1.3	2.0	3.9	7.9	11.8
6 hours		1.3	2.6	5.2	7.9
8 hours		1.0	1.9	3.9	5.9

The concentration of MAGNACIDE H should not exceed 15 ppm. The concentration in ppm is calculated as follows:

$$\frac{\text{dosage (gal/cfs)} \times 1884}{\text{application time (minutes)}} = \text{ppm (MAGNACIDE H Concentration)}$$

Alternately, the treating rate can be calculated using the following formula:

Gallons per Hour (gph) MAGNACIDE H = cfs X .032 X MAGNACIDE H (in ppm)

Based on the weed growth conditions at the time of treatment, choose the application time and concentration appropriate from above chart. Insert the flow rate and ppm into the equation and calculate the gallons per hour of MAGNACIDE H required.

APPLICATION FROM CYLINDERS AND SKID TANKS

GENERAL INSTRUCTIONS

Never hookup or breakdown container equipment alone. Once the application equipment is in place, and the treatment is in progress, an applicator should monitor the treatment if the containers are not secured. If the containers are secured (e.g., locked enclosures), the applicator need only to check on the treatment periodically (at least every two hours).

Know your procedures thoroughly; rehearse them if necessary before the job. Use only specified equipment as provided by BCPC.

Turn all valves cautiously, insuring that there are no leaks and that all hardware is working properly.

Insure that you have fresh wash water available, either in a fixed or portable supply for personal emergency use.

Maintain accurate records of all MAGNACIDE H applications including:

1. Date
2. Time application started and stopped
3. Location
4. Flow of canal (cfs)
5. Orifice size and pressure setting
6. Parts per million concentration of MAGNACIDE H
7. Amount of MAGNACIDE H injected

Application Instructions: (Refer to **Application Equipment Setup** drawing, page 30 and **MAGNACIDE H Application Kit** drawing, page 31.)

1. Calculate proper orifice size and regulator pressure setting using the appropriate tables shown in Guide for MAGNACIDE H Application, pages 11 to 23.

2. Install orifice in orifice assembly (18). Make sure the screen filter is **clean** and **in place.** Wrap threads on orifice assembly with two layers of Teflon tape to insure that good seal is obtained. Wrap the threaded portions (13) of the nitrogen (blue) (A) and MAGNACIDE H (orange) (B) assemblies with two layers of Teflon tape to insure that a good seal is obtained.

3. Check MAGNACIDE H cylinder/skid valves, Nitrogen (blue) (C) and MAGNACIDE H (orange) (D) to insure that they are in the closed and secured position. Check valve of MAGNACIDE H purging assembly (blue) (11) and bleed valve (blue) (6) to insure they are closed.

NOTE:

Put on chemical splash goggles, butyl rubber gloves, and have air purifying respirator assembled and wash water available before proceeding to Step 4.

4. Remove the plugs from the Nitrogen (blue) (C) and MAGNACIDE H (orange) (D) valves. Remove any Teflon tape that may be in the nitrogen or MAGNACIDE H valves. This tape could restrict flow of MAGNACIDE H and the desired application rate would not be obtained. Connect the nitrogen assembly (blue) (A) to the nitrogen valve (blue) (C) and MAGNACIDE H assembly (orange) (B) to the MAGNACIDE H valve (orange) (D).

NOTE:

If irritating vapors are present, put on an air purifying respirator before proceeding to Step 5. (See section on safety equipment.)

Secure nitrogen tank to prevent it from falling over. **DO NOT** lay tank down on its side.

5. Connect nitrogen regulator (1) to nitrogen tank. Only oxygen-free nitrogen should be used. By definition, "oxygen-free" nitrogen is nitrogen which contains less than 5 ppm oxygen. Oxygen will slowly consume the hydroquinone (inhibitor) and leave the MAGNACIDE H susceptible to polymerization (self-destruction).

6. Connect nitrogen line (5) to regulator (4) and to the nitrogen assembly (blue) (A) on the cylinder/skid.

7. Connect MAGNACIDE H injection hose (20) to the MAGNACIDE H assembly at the orifice outlet. To insure against leaks, wrap the threads with two layers of Teflon tape. A weight **must** be attached to the end of the injection hose (21) to insure that the hose remains submerged. Drop the weighted end of the injection hose into the canal.

NOTE:

Before proceeding to Step 8, adjust the nitrogen regulator handle (G) fully out, counterclockwise, before opening the nitrogen tank valve (F). Personal injury and/or damage to the regulator can result if this is not done correctly.

8. Open blue nitrogen valve (C) on cylinder/skid slowly. Read cylinder/skid pressure regulator gauge (7). If reading is greater than desired pressure setting for application (Step 1), the excess pressure must be bled off. Connect the MAGNACIDE H injection hose (20) to the bleed off valve (blue) (6). Bleed the cylinder/skid pressure down below the desired application pressure. After bleeding down, the hose can be purged with nitrogen by closing the cylinder/skid blue nitrogen valve (C), opening the nitrogen tank valve (F) and setting the low pressure gauge (7) for 30 seconds. Close the bleed off valve (6) **and** remove the MAGNACIDE H hose (20). Reconnect hose to MAGNACIDE H assembly (orange) (B).

9. Open nitrogen tank valve (F) and set pressure (G) as determined in Step 1 on nitrogen regulator, using bleed valve (6) as necessary. Check for leaks.

10. Open cylinder/skid blue nitrogen valve (C). The cylinder/skid will pressurize with nitrogen to the desired setting. Check for leaks.

11. Open orange MAGNACIDE H cylinder/skid valve (D) slowly. You should observe MAGNACIDE H flowing through the injection hose.

12. Check for leaks on the orange MAGNACIDE H assembly (B) and hose (20). If a leak is detected, close the orange MAGNACIDE H valve (D). In most cases the leak can be repaired by tightening the threaded connections on the orange MAGNACIDE H assembly and hose.

NOTE:

Your fullface air purifying respirator should be worn during any repairs of MAGNACIDE H leaks. The orange MAGNACIDE H assembly and injection hose may need to be disassembled and retaped with Teflon tape to repair the leak. Follow shutdown steps 3, 4, 5, 6, and 7 to purge MAGNACIDE H from assembly and hose before disassembly of injection equipment.

Repair leak and follow application steps 4, 6, 7, 8, 9, 10, 11, and 12.

13. Readjust regulator (G) pressure to set pressure as established in step 1.

14. Make note of time that application began, to determine duration of application.

15. Periodically during application check MAGNACIDE H application equipment to insure that equipment is functioning properly.

16. Monitor the nitrogen usage such that the remaining nitrogen pressure never drops below 100 psi during the application. This, in addition to the check valve will prevent any backflow of MAGNACIDE H vapors into the nitrogen cylinder.

SHUTDOWN PROCEDURE

NOTE:

Put on splash goggles and butyl rubber gloves, have air purifying respirator assembled and wash water available before proceeding to step 1.

1. Close MAGNACIDE H cylinder/skid valve (D) slowly.

2. Close blue cylinder/skid valve (C) slowly and secure the valve handle.

3. Remove nitrogen hose from nitrogen assembly (blue) (A).

4. Connect nitrogen quick coupler (8) to the blue purge valve on orange MAGNACIDE H assembly (B). Adjust regulator (G) 10 psi higher than the previously set application pressure. Open handle on purge valve (11). Nitrogen will immediately flow through the application hose and bubbles will be seen in the canal. Let nitrogen flow for at least 30 seconds to purge all MAGNACIDE H out of injection hose. Check any coils for remaining chemical.

5. Open and close orange MAGNACIDE H valve (D) several times to force all MAGNACIDE H in chemical assembly and valve back into container.

6. Close orange MAGNACIDE H valve (D) and secure. Close purge valve (11).

7. Remove nitrogen quick coupler (8) from purge valve (9).

8. Close nitrogen tank valve (F).

9. Bleed pressure from nitrogen line with bleed valve (6) on regulator.

10. Disconnect regulator (1) from nitrogen tank. Wrap regulator in a protective covering to prevent damage.

11. Replace nitrogen tank valve stem cover.

12. Remove nitrogen assembly (blue) (A) from cylinder/skid valve (C) and install valve plug.

13. Disconnect orange MAGNACIDE H assembly (B) and hose (20) from the cylinder/skid and install valve plug.

14. Secure cylinder/skid cover.

15. Wash assemblies and application hose with fresh water to remove any remaining traces of MAGNACIDE H.

16. Remove splash goggles and gloves.

17. Spray the inside of all quick coupler connections with silicone spray. This will insure that the check valves and O rings in the quick couplers will function properly.

18. Store all equipment properly. Make sure that splash goggles are stored separately from application equipment to prevent contamination.

MAGNACIDE H APPLICATION SETUP INDEX (PAGE 30)

A. Nitrogen assembly (blue)
B. MAGNACIDE H assembly (orange)
C. MAGNACIDE H cylinder nitrogen intake valve
D. MAGNACIDE H cylinder MAGNACIDE H discharge valve
E. MAGNACIDE H dip tube (delivers chemical from bottom of cylinder to assembly B)
F. Nitrogen tank valve
G. Nitrogen regulator pressure handle
H. Nitrogen tank high pressure (psi) gauge

1. Nitrogen regulator
5. Nitrogen hose
6. Nitrogen bleeder valve (blue)
7. Nitrogen low pressure (psi) gauge
8. Nitrogen hose female quick coupler (blue)
9, 11. MAGNACIDE H purging assembly (blue), containing nitrogen quick coupler valve and adjacent needle valve
18. Orifice assembly (orange) containing orifice plate and screen filter

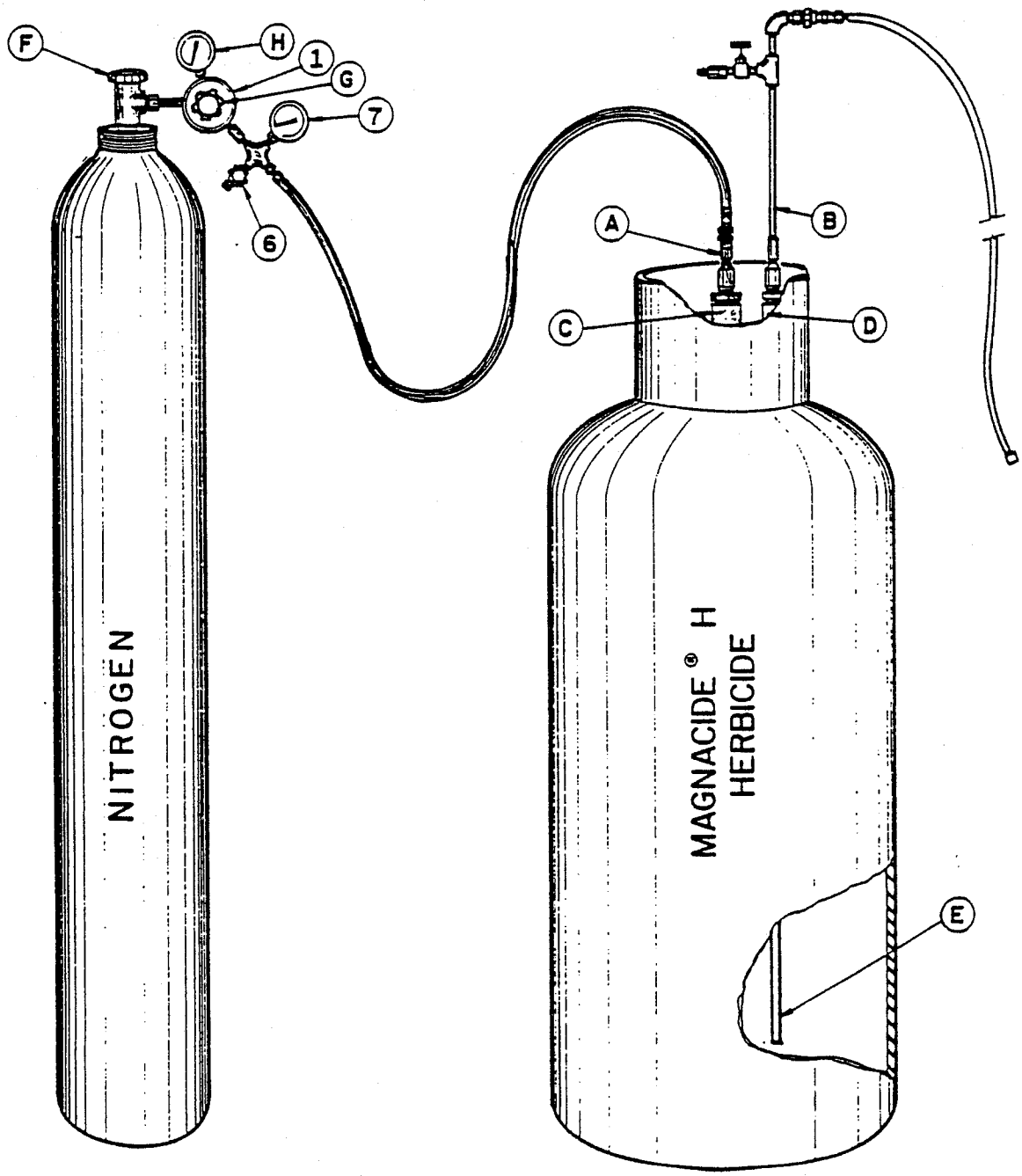
20. MAGNACIDE H injection hose

MAGNACIDE H APPLICATION KIT LIST (PAGE 31)

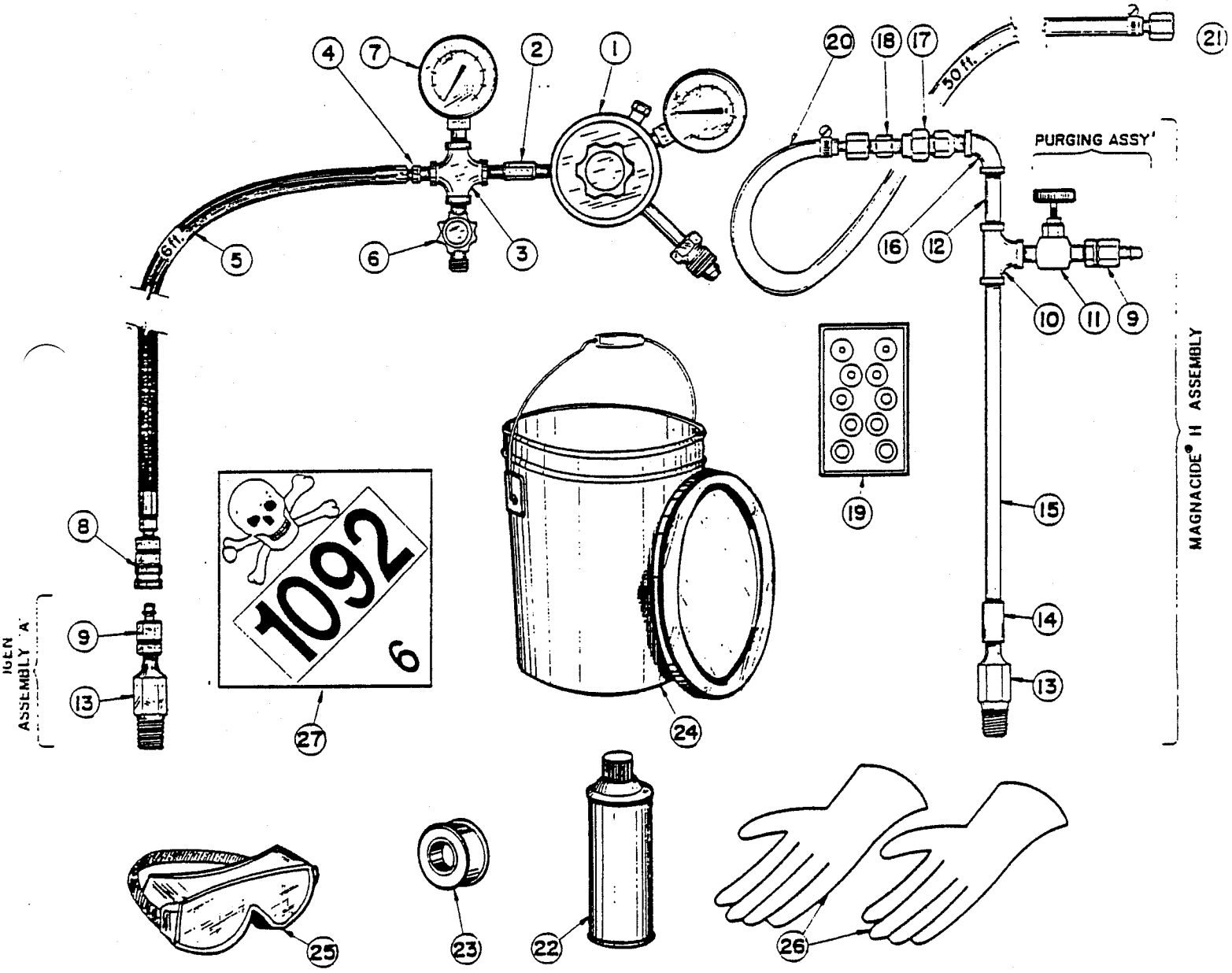
1. Nitrogen regulator with high pressure gauge
2. Check valve
3. Tee
4. Nitrogen hose adapter
5. Nitrogen hose
6. Bleeder valve
7. Low pressure nitrogen gauge
8. Nitrogen hose female quick coupler
9, 13. Nitrogen assembly (A)
9 - 18. MAGNACIDE H assembly with attached purging assembly
17 - 18. Orifice assembly with screen filter
19. One set of orifice plates
20. 50' MAGNACIDE H injection hose
21. Hose stem
22. Silicone spray
23. Teflon tape
24. Plastic 6 - gallon bucket with lid
25. Goggles

26. Butyl rubber gloves
27. Placards

MAGNACIDE® H APPLICATION SET -UP



MAGNACIDE® H APPLICATION KIT



EQUIPMENT AND HARDWARE

All hardware used in a MAGNACIDE H system must be chemically compatible. This means that the materials used in the system must not cause a reaction with the MAGNACIDE H or be dissolved or deteriorated by it. If the materials are not compatible, either the materials will be degraded or the MAGNACIDE H will itself degrade, resulting in a polymerization reaction. A polymerization reaction will release heat and pressure and could rupture the container, causing possible damage to personnel or property.

All parts used in the MAGNACIDE H Application Kit have been thoroughly tested for their compatibility with our product. No substitutions should be made without prior discussion with your technical sales representative.

In addition, all equipment and hardware must be free from all traces of contaminants, especially alkalies (such as ammonia and caustics) and acids. Contamination of MAGNACIDE H with these substances can cause vessels, piping and other hardware to rupture.

The following table list materials which have been tested for compatibility with MAGNACIDE H:

COMPATIBLE AND INCOMPATIBLE MATERIALS WITH MAGNACIDE H

HARDWARE OR ASSEMBLY PARTS	COMPATIBLE MATERIALS	INCOMPATIBLE MATERIALS
METALS	Carbon Steel Stainless Steel, 304/316 Copper Brass	Galvanized Material Cadmium Zinc
GASKETS, HOSES, TUBING	Ethylene propylene Rubber (EPR) Ethylene propylene and diene (EPDM) Natural rubber Thiokol 262T Teflon® Silastic 180 Butyl Rubber Polyethylene Garlock 7021 Ethylene Vinyl Acetate (EVA)	Viton Buna-N Neoprene Rubber Chemigum (raw) Hycar (raw) GARS Rubber (raw)
VALVE & PUMP PACKING	Garlock 233 Teflon® Durametallic 10 Raybestos-Manhattan 1845	Garlock 237 Thorndyke Garlock 31 Packing-Lubricant Garlock 927 Plastallic
PIPE THREAD SEALING COMPOUNDS	Permacel Ribbon Tape (Teflon® Tape) Duraplastic 22 White Lead in Linseed Oil Garlock 929 Compounds Approved for LP or Propane Gas	Portland Cement in Linseed Oil
KARBATES FOR MECHANICAL SEALS	Karbate 12 Karbate 18	Karbate 11
VALVE LUBRICANTS	Nordcoseal 654	Nordcoseal 755 Nordcoseal 357 Nordcoseal 546
PUMP & DIAPHRAGMS	Teflon®	Rubber Base Materials

TRANSPORTING MAGNACIDE H CONTAINERS

Transportation of hazardous chemicals is regulated by the U.S. Department of Transportation (DOT). The DOT requirements for transporting MAGNACIDE H (acrolein, inhibited) are as follows:

1. Transporting vehicle must be placarded when hauling full, partial or empty containers. Required placards are **Toxic 1092** and **Flammable Liquid**, available at cost through Baker Crop Protection Chemicals. All four sides of the transporting vehicle must have placards displayed.

2. Driver must carry correct shipping papers at all times, to include: The correctly worded bill-of-lading supplied by BCPC or commercial freight line, material safety data sheet on MAGNACIDE H, and Chemtrec emergency response information (supplied with bill-of-lading).

3. Bills-of-lading should be corrected after applications to show only the poundage remaining in the container.

4. Bills-of-lading for transportation of empty containers are available from your technical sales representative or BCPC headquarters.

5. Special drivers license requirements are in effect for transporting hazardous materials. For details, contact the Department of Motor Vehicles in your state.

RETURN OF EMPTY MAGNACIDE H CONTAINERS

Empty containers are to be returned, freight collect, to:

Baker Performance Chemicals Incorporated
19815 South Lake Road
Taft, California 93268

Please Note: No partly used containers should be returned to BCPC without prior notification. For information concerning the return of partly used containers contact:

Baker Crop Protection Chemicals
Telephone: (805) 763-5137

Normally, no credit will be issued for unused material returned from opened cylinders or skid tanks.

Prepare empty containers for shipment as follows:

1. Relieve container pressure down to 15 - 25 psig. This is normally accomplished by venting into the irrigation system during treatment.
2. Replace plugs in the inlet and outlet valves and tighten securely.
3. Fasten down valve handles securely with wire.
4. Close lid and secure with wire or latch.
5. Containers should be transported upright. Alert the carrier to tie down containers to prevent overturning during travel.

The DOT has special shipping paper requirements for shipment of empty containers which previously contained a hazardous material. Properly worded bills-of-lading for empty containers are available through your technical sales representative or BCPC headquarters. Trucks transporting empty containers must be placarded. It is the responsibility of the shipper to provide necessary placards.

APPENDIX A

Water Measurement Equivalents

Discharge or Rate of Flow	The volume of water that passes a particular reference section in a unit of time. Usually designated as cubic feet per second or miner's inches.
1 cfs	1 cubic foot per second, (mean depth (ft) X mean width (ft) X linear velocity (ft/sec)).
Miner's Inch	The quantity of water which will flow through an orifice one inch square under a stated head which varies from 4 to 6 1/2 inches in different localities.
Acre Foot	A commonly employed unit of volume defined as that quantity of water required to cover one acre of land to a depth of one foot or 43,560 cubic feet.
Atmospheric Pressure	15 pounds per square inch (at sea level) which will support a column of mercury (Hg) 30 inches high, i.e. one (1) psi = 2" Hg (.43 psi per foot of drop below surface level).
1 cfs	450 gallons per minute.
1 cfs	50 miner's inches in Idaho, Kansas, Nebraska, New Mexico, North Dakota, South Dakota, Northern California, Washington and Utah.
1 cfs	40 miner's inches in Arizona, Southern California, Montana and Oregon.
1 cfs	38.4 miner's inches in Colorado.
1 cfs flowing 1 hour	1 acre inch.
1 cfs in 12 hours	1 acre foot.
14 cfs flowing 2 hours	2.31 acre foot.
1 fluid gallon per cfs in 30 minutes	74 ppm.
1 cu. ft. of water at 25° C	62.2 lbs., 7.48 gallons.
1 gallon water	8.34 lbs.
0.001%	10 ppm.
1 acre foot of water	2.7 million lbs.
2.7 lbs. product/acre ft.	1 ppm MAGNACIDE H
1 lb. product/million gallons	0.12 ppm MAGNACIDE H
8 1/3 lb. product/million gallons	1 ppm
1 acre	43,560 sq. ft., 4,840 sq. yds.
1 mile	5,280 feet, 1,760 yards
1 kilometer	0.62 miles
1 inch	2.54 cm = 25.4mm
1 ounce	28.35 grams
1 gram	0.0353 ounces
1 lb.	453.59 grams
1 fluid oz.	29.57 ml
1 pint	473.2 ml
1 gal. (U.S.)	0.823 gal. (British)
1 mph	88 ft/min. = 1.5 ft./sec.

APPENDIX B

MAGNACIDE H HERBICIDE MONITOR

The MAGNACIDE H monitor is a hand held colorimeter designed to quickly and easily determine the concentration of MAGNACIDE H Herbicide in irrigation waters. The instrument's compact size and easy operating procedures make it a handy tool for measuring MAGNACIDE H levels in even the most remote irrigation canals.

A simple test determines the parts per million (ppm) of chemical present in the treated water with an accuracy of 0.1 ppm. The monitor readily measures the concentration of MAGNACIDE H in the range of 0.1 to 5.0 ppm and with a dilution, also monitors levels above 5.0 ppm. Test results are read directly off the monitor's scale, thus eliminating the need for complicated calculations.

The MAGNACIDE H monitor is furnished in a kit with all necessary equipment to conduct a number of tests. For additional information on the MAGNACIDE H monitor, please contact your Baker Crop Protection Chemicals technical sales representative.

APPENDIX C

TOXICITY

Results of toxicological studies are summarized below:

The acute oral toxicity (LD_{50}) of MAGNACIDE H for rats is approximately 29 mg/kg. The acute dermal LD_{50} of undiluted MAGNACIDE H in rabbits is 231.4 mg/kg.

In a subacute study conducted with male and female rats for 90 days, MAGNACIDE H was added to the drinking water at 0, 5, 13, 32, 80 and 200 ppm. Growth of both sexes was equal or better than the controls. Food efficiency was equivalent to the controls at all levels. Water consumption was reduced by 1/3 at the 200 ppm level for the first 3 weeks, but by the 12th week the animals had apparently adapted to the odor and the taste of the MAGNACIDE H. There were no hematological, organ weight or pathological changes that could be attributed to the ingestion of MAGNACIDE H.

In a study of skin absorption, rabbits were immersed, except for the head for one hour in 20 or 100 ppm. At 100 ppm, one rabbit appeared weakened, but returned to normal in 24 hours.

Lactating dairy cows were given MAGNACIDE H in their drinking water at levels of 30, 60 or 90 ppm for 24 hours. There were no adverse effects at 30 and 60 ppm on body weight, water intake, feed and water consumption, and milk and butterfat productions. No off-flavor was imparted to the milk. At 90 ppm, the only noticeable effect was 1/4 - 1/3 drop in water and hay consumption with a transitory drop in weight. However, all factors measured returned to normal the following day.

Data on vapor toxicity show that MAGNACIDE H vapor exerts its main action on the eyes and mucous membranes of the respiratory tract; severe exposure may produce serious injury to the lungs. A table of sensory response values is given below.

Atmospheric Concentration ppm	Duration of Exposure	Probable Human Response
0.25	5 minutes	Moderate irritation
1.0	5 minutes	Painful irritation
1.0	2 - 3 minutes	Eye & nose irritation
5.5	20 seconds	Painful eye & nose irritant
5.5	1 minute	Practically intolerable
153.0	10 minutes	May be fatal

MAGNACIDE H is not an insidious chemical, as the low levels of recognition (0.1 to 1.0 ppm in air) serves as a warning of its presence. There is no documentary evidence to indicate that MAGNACIDE H produces cumulative toxicological effects; its toxicity is derived apparently from the intense local irritation which it produces.

RESTRICTED USE PESTICIDE

DUE TO A HIGH ACUTE TOXICITY

For retail sale to and use only by Certified Applicators or persons under their direct supervision and only for those uses covered by the Certified Applicator's certification.

BPCI BAKER CROP PROTECTION CHEMICALS

A Division of Baker Performance Chemicals Inc.

MAGNACIDE® H HERBICIDE (Acrolein, Inhibited)

CONTENTS UNDER PRESSURE

EPA Reg. No. 10707-9 EPA Est. 10707-CA-5

ACTIVE INGREDIENT	BY WEIGHT
Acrolein	92%
INERT INGREDIENTS	8%
TOTAL	100%

This product contains the toxic inert ingredient hydroquinone.
(MAGNACIDE® H Herbicide contains 6.5 pounds of active ingredient per gallon.)

DANGER POISON

KEEP OUT OF REACH OF CHILDREN

PRECAUTIONARY STATEMENTS
HAZARDS TO HUMANS AND DOMESTIC ANIMALS

DANGER

EXTREMELY FLAMMABLE AND IRRITATING VAPOR AND LIQUID. POISONOUS BY INHALATION, SKIN CONTACT OR SWALLOWING. DO NOT BREATHE VAPOR. Corrosive. Causes eye and skin damage. DO NOT GET IN EYES OR ON SKIN OR ON CLOTHING. KEEP AWAY FROM FIRE, SPARKS AND HEATED SURFACES.

Wear goggles and rubber gloves during handling. If spilled on clothing, gloves, or shoes, remove them immediately and wash thoroughly before reuse. Use with adequate ventilation. Keep available at all times a mask or pesticide respirator jointly approved by the Mine Safety and Health Administration and the National Institute of Occupational Safety and Health (NIOSH).

ENVIRONMENTAL HAZARDS

This product is toxic to fish and wildlife. Keep out of lakes, streams or ponds. Fish, shrimp and crabs will be killed at application rates recommended. Do not apply where they are important resources. Do not apply to water drainage areas where runoff or flooding will contaminate ponds, lakes, streams, tidal marshes and estuaries. Do not contaminate water by cleaning of equipment or disposal of wastes. Notify your State Fish and Game Agency before applying this product. Use only as specified.

PHYSICAL OR CHEMICAL HAZARDS

DANGER: Acrolein, the active ingredient in MAGNACIDE H Herbicide is highly reactive chemically and readily forms polymers. If alkalies (such as ammonia and caustic) or strong acids are brought in contact with MAGNACIDE H Herbicide in a closed system, the Herbicide can polymerize with sufficient violence to rupture the container. Do not apply with equipment used for acids and alkalies. Contamination of MAGNACIDE H Herbicide with any foreign matter must be avoided.

A supply of sodium carbonate (soda ash) should be readily available for deactivating spilled MAGNACIDE H. All spills should be confined and deactivated before disposal. See the MAGNACIDE H Herbicide Application and Safety Manual for additional information.

STATEMENT OF PRACTICAL TREATMENT

CALL A PHYSICIAN IMMEDIATELY IN ALL CASES OF SUSPECTED POISONING

IF IN EYES: hold eyelids open and flush with water for 15 minutes. Get medical attention.

IF ON SKIN: wash with plenty of soap and water. Get medical attention.

IF SWALLOWED: do not induce vomiting. Drink promptly a large quantity of milk, egg whites, gelatin solution or if these are not available, drink large quantities of water. Avoid alcohol. Call a physician immediately. Probable mucosal damage may contraindicate the use of gastric lavage. Measures against circulatory shock, respiratory depression and convulsion may be needed. NEVER GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS PERSON.

IF INHALED, get victim into fresh air immediately and give artificial respiration if breathing has stopped.

NOTE TO PHYSICIANS

WARNING SIGNS AND SYMPTOMS: Liquid MAGNACIDE H Herbicide is absorbed by the skin and is particularly irritating to any lesion and to the eyes. The vapors act principally on the mucous membranes of the eyes and respiratory tract. Because of the extreme lachrymatory warning effect, the concentration tolerable by man is far below the minimum lethal concentration.

TREATMENT: Treat exposed area as a chemical burn. Thoroughly flush the eyes with water and treat symptomatically. Persons exposed to MAGNACIDE H Herbicide vapors have a delayed reaction and experience irritation of the respiratory tract. In severe cases, this may progress to pulmonary edema. Therefore, it is advisable to keep persons exposed to MAGNACIDE H Herbicide under observation for 24 hours following exposure.

DIRECTIONS FOR USE

It is a violation of Federal Law to use this product in a manner inconsistent with its labeling. MAGNACIDE H Herbicide is a water soluble material for the control of submersed and floating weeds and algae in irrigation canals. This material must only be applied in accordance with direction in the MAGNACIDE H Herbicide Application and Safety Manual by a certified applicator or under a certified applicator's supervision. Do not permit dairy animals to drink treated water. Do not use where waters will flow into potential sources of drinking water. Do not release treated water for 6 days after application into any fish bearing waters or where it will drain into them.

STORAGE AND DISPOSAL

STORAGE OF MAGNACIDE H TANKS

Full tanks of acrolein should be stored in an open or well ventilated area, away from *all* other chemicals. No alkalies or oxidizing materials should be near. Any electrical equipment should be Class 1 - Division 2 type and properly grounded. Do not reuse empty container. Return empty containers to Baker Performance Chemicals, Incorporated.

DISPOSAL

Pesticide wastes are acutely hazardous. Improper disposal of excess pesticide, spray mixture, or rinsate is a violation of Federal Law. If these wastes cannot be disposed of by use according to label instructions, contact your State Pesticide or Environmental Control Agency, or the Hazardous Waste representative at the nearest EPA Regional Office for guidance.

NOTICE OF WARRANTY

BAKER PERFORMANCE CHEMICALS INCORPORATED MAKES NO WARRANTY OF MERCHANTABILITY FITNESS FOR ANY PURPOSE, OR OTHERWISE, EXPRESSED OR IMPLIED concerning this product or its uses which extend beyond the use of the product under normal conditions in accord with the statements made on this label.

NET WEIGHTS

Cylinder-370 lbs. Skid Tank-2450 lbs.

MANUFACTURED BY: BAKER PERFORMANCE CHEMICALS, INCORPORATED 3900 Essex Lane, Houston, Texas 77027

PG0497

ATTACHMENT #4

PROCESS HAZARD ANALYSIS (HAZOP)

APPLICATION, STORAGE & HANDLING

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Receiving of shipment
Intention: Delivery vehicle enters facility property and maneuvers to the loading dock, storage area, or other designated off-load area in such a way as to facilitate safe and efficient off-load of Acrolein containers.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Vehicle cannot enter the facility				
Vehicle goes to the wrong area				
Vehicle goes too close to the storage area				
Vehicle badly situated for off-load				
Vehicle moves during off-load				
Container arrives on vehicle up-ended				
Container arrives on vehicle damaged/leaking				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Receiving of shipment
Intention: Delivery vehicle enters facility property and maneuvers to the loading dock, storage area, or other designated off-load area in such a way as to facilitate safe and efficient off-load of Acrolein containers.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container arrives over-pressurized				
Container arrives under-pressurized				
Container arrives empty				
Container does not pass visual inspection				
Container off-loaded by carrier driver prior to inspection				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Off-load of Acrolein container from delivery vehicle.
Intention: The Acrolein container is removed from the delivery vehicle and placed on the loading dock or other area designated for off-load.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container is not removed from vehicle				
Container is struck/ crushed by off-load equipment (forklift, etc.)				
Container is dropped from delivery vehicle				
Container is dropped from off-load equipment				
Container is knocked over				
Container/fittings are damaged during offload				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Placement of Acrolein container in storage area.
Intention: The Acrolein container is moved from the off-load area to the permanent storage area and properly secured.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container is left in off-load area				
Container is moved to a temporary storage area				
Container is not properly secured in storage area				
Container is damaged in route to storage area				
Container strikes other containers already in storage				
Container is placed in the empty container storage area				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Storage of the Acrolein container.
Intention: The Acrolein container is safely stored, secured, and protected from hazards.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container is opened either accidentally or purposely				
Container exposed to high temperatures or open flame				
Container exposed to extremely cold temperatures				
Container exposed to electrical discharge: power lines, lightning				
Container struck by shrapnel from exploding tanks/container				
Container exposed to forces of nature: Tornado, earthquake, etc.				
Container punctured				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Storage of the Acrolein container.
Intention: The Acrolein container is safely stored, secured, and protected from hazards.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container material fails/ ruptures				
Container fittings damaged				
Container storage area flooded				
Container over pressurized				
Container under pressurized				
Container improperly secured				
Container improperly grounded				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Storage of the Acrolein container.
Intention: The Acrolein container is safely stored, secured, and protected from hazards.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container struck/crushed by forklift/truck or other vehicle				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Retrieval of Acrolein container from the storage area.
Intention: The Acrolein container is moved from the storage area to the loading area.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container is left in storage area				
Container is moved to a temporary storage area				
Securing/grounding devices not removed prior to moving				
Container is damaged/ punctured en route to loading area				
Container strikes other containers already in storage				
Container is placed in the empty container storage area				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of _____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Acrolein container held on the loading dock awaiting shipment.
Intention: Acrolein container is safely stored temporarily in loading area, and is prepared for shipment.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container is opened either accidentally or purposely				
Container exposed to high temperatures or open flame				
Container exposed to extremely cold temperatures				
Container exposed to electrical discharge: power lines, lightning				
Container exposed to corrosive chemical in loading area				
Container exposed to forces of nature: Tornado, earthquake, etc.				
Container punctured				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Acrolein container held on the loading dock awaiting shipment.
Intention: Acrolein container is safely stored temporarily in loading area, and is prepared for shipment.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container material fails/ ruptures				
Container fittings damaged				
Loading area flooded				
Container over pressurized				
Container under pressurized				
Container struck/crushed by forklift/truck or other vehicle				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope: Placement of Acrolein container on carrier vehicle.
Intention: The Acrolein container is moved from the loading area, placed on the carrier vehicle and properly secured.

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions
Container dropped during loading				
Container not properly secured on carrier vehicle				
Carrier vehicle moves during loading				
Container/fittings damaged during loading				
Container punctured/ leaking				
Container not properly segregated from other chemicals on vehicle				

_____ Facility PHA HAZOP WORKSHEET

Process Hazard Analysis for storage and handling of ____ lb. Acrolein containers at the _____Facility. Date:_____/_____/_____

Scope:
Intention:

Deviation from Intention	Possible Causes	Possible Consequences	Safeguards	Suggested Actions

ATTACHMENT #5

TRAINING RECORDS

ATTACHMENT #6

AUDIT GUIDELINE

PSM Element: EMPLOYEE PARTICIPATION

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program Written program exists for implementing the employee participation requirements of the OSHA rule					
Training Not required					
Implementation *Specific activities necessary to implement this element are not specified in the rule. Provide a list in the Notes column of any implementation activities found*					
Communication Employees and their representatives are consulted on the conduct and development of PHAs and on the development of other elements of PSM					
Employees and their representatives are provided access to PHAs and to all other information required to be developed under the OSHA rule					
Documentation *Specific documentation necessary for this element is not specified in the rule. Provide a list in the Notes column of any documentation found*					

4-16-1

PSM Element: PROCESS SAFETY INFORMATION

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
CHEMICAL HAZARDS **Written Program** *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
CHEMICAL HAZARDS **Training** *Training that is required in chemical hazards is specified in the Training and Mechanical Integrity elements*					
CHEMICAL HAZARDS **Implementation** Compilation of chemical information is complete before conducting any PHA required by the OSHA rule. (MSDSs, meeting the requirements of 29 CFR 1910.1200, may be used to the extent they contain the required documentation)					
If a change covered by the Management of Change element (in the OSHA rule) results in a change in process safety information, the chemical information is updated accordingly					
CHEMICAL HAZARDS **Communication** The compilation of written chemical information enables the employer and the employees involved in operating the process to identify and understand the hazards posed by those processes involving highly hazardous chemicals					

4-16-2

PSM Element: PROCESS SAFETY INFORMATION (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
CHEMICAL HAZARDS **Documentation** The following chemical information is compiled: • Toxicity data • Permissible exposure limits • Physical data • Reactivity data • Corrosivity data • Thermal and chemical stability data • Chemical incompatibility data					
PROCESS TECHNOLOGY **Written Program** *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
PROCESS TECHNOLOGY **Training** *Training that is required in process technology is specified in the Training and Mechanical Integrity elements*					
PROCESS TECHNOLOGY **Implementation** Compilation of process technology information is complete before conducting any PHA required by the OSHA rule. (Where the original technical information no longer exists, such information may be developed in conjunction with the PHA in sufficient detail to support the analysis)					
If a change covered by the Management of Change element (in the OSHA rule) results in a change in process safety information, the process technology information is updated accordingly					

4-16-3

PSM Element: PROCESS SAFETY INFORMATION (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
PROCESS TECHNOLOGY **Communication** The compilation of written process technology information enables the employer and the employees involved in operating the process to identify and understand the hazards posed by those processes involving highly hazardous chemicals					
PROCESS TECHNOLOGY **Documentation** The following process technology information is compiled:					
• Block flow diagrams or simplified process flow diagrams					
• Process chemistry					
• Maximum intended inventories (of chemicals)					
• Safe upper and lower limits for temperatures, pressures, flowrates, compositions, etc.					
• An evaluation of consequences, including those affecting the safety and health of employees					

4-16-4

PSM Element: PROCESS SAFETY INFORMATION (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
PROCESS EQUIPMENT **Written Program** *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
PROCESS EQUIPMENT **Training** *Training that is required regarding process equipment is specified in the Training and Mechanical Integrity elements*					
PROCESS EQUIPMENT **Implementation** Compilation of process equipment information is complete before conducting any PHA required by the OSHA rule					
If a change covered by the Management of Change element (in the OSHA rule) results in a change in process safety information, the process equipment information is updated accordingly					
PROCESS EQUIPMENT **Communication** The compilation of written process equipment information enables the employer and the employees involved in operating the process to identify and understand the hazards posed by those processes involving highly hazardous chemicals					
PROCESS EQUIPMENT **Documentation** The following process equipment information is compiled: • Materials of construction					
• Piping and instrumentation diagrams (P&IDs)					

4-16-5

PSM Element: PROCESS SAFETY INFORMATION (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
• Electrical classifications (of equipment)					
• Relief system design (and design basis)					
• Ventilation system design					
• Design codes and standards employed					
• Material and energy balances (for processes built after May 26, 1992)					
• Safety systems (e.g., interlocks, detection or suppression systems)					
Documentation is provided to indicate equipment complies with recognized and generally accepted good engineering practices. (The documentation should also specify the design codes and standards employed)					
For existing equipment designed and constructed in accordance with codes, standards, or practices that are no longer in general use, the employer has determined and documented that the equipment is designed, maintained, inspected, tested, and operated in a safe manner					

4-16-6

PSM Element: PROCESS HAZARD ANALYSIS

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training *No specific training requirements are specified by the rule; however, knowledge of PHA techniques is required. Provide a list in the Notes column of any PHA training identified during the audit*					
Implementation Initial PHAs are performed. (PHAs completed after May 26, 1987, and meeting all the technical issue requirements are acceptable as initial PHAs)					
The PHAs are appropriate to the complexity of the process and identify, evaluate, and control the hazards involved in the process					
The priority order for conducting PHAs is determined based on a rationale that considers (1) extent of the process hazards, (2) number of potentially affected employees, (3) age of the process, and (4) operating history of the process					
Initial PHAs are completed as soon as possible, but no later than the following schedule: 25% of the initial PHAs completed by May 26, 1994; 50% by May 26, 1995; 75% by May 26, 1996; and all by May 26, 1997					

4-16-7

PSM Element: PROCESS HAZARD ANALYSIS (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Implementation (cont'd) The PHA uses one or more of the following methods (that are appropriate to determine and evaluate the hazards of the process being analyzed): • What-If • Checklist • What-If/Checklist • Hazard and Operability (HAZOP) Analysis • Failure Modes and Effects Analysis (FMEA) • Fault Tree Analysis • An appropriate equivalent method					
The PHA method selected addresses the following: • Hazards of the process • Previous incidents which had a likely potential for catastrophic consequences • Engineering and administrative controls applicable to the hazards and their interrelationships, such as appropriate application of detection methods to provide early warning of releases. (Acceptable detection methods might include process monitoring and control instrumentation with alarms, and detection hardware such as hydrocarbon sensors) • Consequences of failure of these controls • Facility siting • Human factors • Qualitative evaluation of a range of the possible safety and health effects of failure of controls on employees in the workplace					

4-16-8

PSM Element: PROCESS HAZARD ANALYSIS (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Implementation (cont'd) The PHA is performed by a team with expertise in engineering and process operations, with at least one individual who has experience and knowledge specific to the process being evaluated, and with one individual knowledgeable in the specific PHA method being used					
The team's findings and recommendations are promptly addressed and resolved in a timely manner					
Actions are completed as soon as possible					
At least every 5 years after completion of the initial PHA, PHAs are updated and revalidated by a team (meeting the above requirements) to assure the PHA is consistent with the current process					
Communication The actions taken in response to the findings of the PHA are communicated to all affected personnel (e.g., operations, maintenance)					
Documentation The priority order for conducting PHAs is documented					
The resolution to recommendations from PHAs is documented					
Actions to be taken from PHAs are documented					
A written schedule of when the PHA actions are to be completed is developed					
PHAs (including updates and revalidated PHAs) as well as the documented resolution of recommendations are retained for the life of the process					

4-16-9

PSM Element: OPERATING PROCEDURES

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training *Training in the operating procedures is specified in the Training element. It may be desirable to provide training on how to write operating procedures*					
Implementation Written operating procedures, which address all the documentation requirements, are implemented					
Operating procedures are reviewed as often as necessary to assure that they reflect current operating practice, including changes that result from changes in process chemicals, technology, and equipment, and changes to facilities					
Operating procedures are certified annually (to make sure they are current and accurate)					
Safe work practices are developed and implemented to provide for the control of hazards during operations (such as lockout/tagout, confined space entry, process equipment opening, and control of entrance into a facility by maintenance, contractor, laboratory, or other support personnel). These practices apply to employees and contractor employees					
If a change covered by the Management of Change element (of the OSHA rule) results in a change in the operating procedures or practices, the procedures or practices are updated accordingly					
Communication Operating procedures are readily accessible to employees who work in or maintain a process					

4-16-10

PSM Element: OPERATING PROCEDURES (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Documentation Written operating procedures (that provide clear instructions for safely conducting activities involved in each covered process consistent with the process safety information) exist and address at least the following: ***OPERATING MODES:*** • Initial startup • Normal operation • Temporary operations (as the need arises) • Emergency shutdown (including conditions under which to require a shutdown and assignment of shutdown responsibility to qualified operators to ensure the shutdown is executed in a safe and timely manner) • Emergency operations • Normal shutdown • Startup (following a turnaround or after an emergency shutdown)					
OPERATING LIMITS: • Consequences of deviations (from operating limits) • Steps necessary to correct and/or avoid deviations (from operating limits)					
SAFETY AND HEALTH CONSIDERATIONS: • Properties and hazards of chemicals used in the process • Precautions necessary to prevent exposure (including administrative and engineering controls and personal protective equipment) • Control measures to be taken if physical contact or airborne exposure occurs • Quality control for raw materials and control of hazardous chemical inventory levels • Any special or unique hazards					
SAFETY SYSTEMS AND THEIR FUNCTIONS					

4-16-11

PSM Element: TRAINING

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training This entire element involves training of operating personnel. It may also be desirable to provide training for trainers					
Implementation *INITIAL TRAINING:* Employees (presently involved in operating a process or before being involved in operating a newly assigned process) are trained in the following areas: • An overview of the process • Operating procedures • Safety and health hazards Training emphasizes: • Emergency operations, including shutdown • Safe work procedures applicable to the employee's job tasks (Instead of initial training for employees already involved in operating a process on May 26, 1992, the employer certifies in writing that the employee has the required knowledge, skills, and abilities to safely carry out the duties and responsibilities as specified in the operating procedures)					
Employer ascertains that each employee involved in operating a process has received and understood the training					

4-16-12

PSM Element: TRAINING (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Implementation (cont'd) ***REFRESHER TRAINING:*** Refresher training is provided at least every 3 years, and more often if necessary, to each employee involved in operating a process to assure that the employee understands and adheres to the current operating procedures of the process. (The employer, by consulting the employees involved in operating the process, determines the appropriate frequency of refresher training)					
Communication Employees are made aware when initial and refresher training is required and are consulted concerning frequency of refresher training (required at least every 3 years)					
Documentation ***INITIAL AND REFRESHER TRAINING:*** An employee record exists that contains the identity of the employee, the date of the training, and the means used to verify that the employee understood the training					
Instead of initial training (for those employees already involved in operating a process on May 26, 1992) a certification record exists that indicates the employee has the required knowledge, skills, and abilities to safely carry out the duties and responsibilities as specified in the operating procedures					

4-16-13

PSM Element: CONTRACTORS*

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training ***EMPLOYER RESPONSIBILITIES:*** Not required					
CONTRACT EMPLOYER RESPONSIBILITIES: Contract employer assures that each contract employee is trained in the work practices necessary to safely perform his/her job					
Contract employer assures that each contract employee is instructed in the known fire, explosion, or toxic release hazards related to his/her job and the process, and the applicable provisions of the emergency action plan					
Implementation ***EMPLOYER RESPONSIBILITIES:*** When selecting a contractor, employer obtains and evaluates information regarding the contract employer's safety performance and programs					
Employer develops and implements safe and consistent work practices to control the entrance, exit, and presence of contractor personnel in the covered process areas. (Safe work practices also address such activities as lockout/tagout and opening process equipment or piping)					
Employer periodically evaluates the safety performance of contractors in fulfilling their obligations					

4-16-14

* This element applies to contractors performing maintenance or repair, turnaround, major renovation, or specialty work on or adjacent to a covered process. This element does <u>not</u> apply to contractors providing incidental services that do not influence process safety (such as janitorial work, food and drink services, laundry, delivery, or other supply services).

PSM Element: CONTRACTORS (cont'd)*

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Implementation (cont.) ***CONTRACT EMPLOYER RESPONSIBILITIES:*** Contract employer assures that each contract employee follows the safety rules of the facility (including the safe work practices)					
Communication ***EMPLOYER RESPONSIBILITIES:*** Employer informs contract employers of known fire, explosion, or toxic release hazards					
Employer explains to the contract employers the applicable provisions of the emergency action plan					
CONTRACT EMPLOYER RESPONSIBILITIES: Contract employer advises the employer of any unique hazards presented by or found during the contract employer's work					
Documentation ***EMPLOYER RESPONSIBILITIES:*** Employer maintains a contract employee injury and illness log related to the contractor's work in process areas					
CONTRACT EMPLOYER RESPONSIBILITIES: The contract employer documents that each contract employee has received and understood the training required by the OSHA rule. The contract employer prepares a record that contains the identity of the contract employee, the date of training, and the means used to verify that the employee understood the training					

4-16-15

* This element applies to contractors performing maintenance or repair, turnaround, major renovation, or specialty work on or adjacent to a covered process. This element does <u>not</u> apply to contractors providing incidental services that do not influence process safety (such as janitorial work, food and drink services, laundry, delivery, or other supply services).

PSM Element: PRE-STARTUP SAFETY REVIEW

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training Not required					
Implementation Before introduction of hazardous materials into new or modified (when the modification is significant enough to require a change in the process safety information) processes, a pre-startup safety review is conducted that confirms the following: • Construction and equipment are in accordance with design specifications • Safety, operating, maintenance, and emergency procedures are in place and are adequate • For new facilities, a PHA has been performed and the recommendations have been resolved or implemented before startup • Modified facilities meet the requirements contained in the Management of Change provision of the OSHA rule • Training of each employee involved in operating a process has been completed					
Communication Not required					
Documentation *A requirement for documentation of the PSSR is not specifically stated in the rule, but is recommended to provide evidence of the completion of a PSSR*					

4-16-16

PSM Element: MECHANICAL INTEGRITY*

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program Written procedures are established to maintain the ongoing integrity of process equipment					
Training ***(for Process Maintenance Activities)*** Each employee involved in maintaining the ongoing integrity of process equipment is trained in an overview of that process and its hazards and in the procedures applicable to the employee's job tasks to assure that the employee can perform the job tasks in a safe manner					
Implementation *WRITTEN PROCEDURES:* Written procedures are followed to maintain the ongoing integrity of process equipment					
INSPECTION AND TESTING: Inspections and tests are performed on process equipment using recognized and generally accepted good engineering practices					
Frequency of inspections and tests of process equipment are consistent with applicable manufacturers' recommendations and good engineering practices, and more frequently if determined to be necessary by prior operating experience					
Implementation *EQUIPMENT DEFICIENCIES:* Deficiencies in equipment that are outside acceptable limits (as defined by the process safety information) are corrected before further use or in a safe and timely manner when necessary means are taken to assure safe operation					

4-16-17

* This element applies to the following process equipment: (1) pressure vessels and storage tanks, (2) piping systems (including piping components such as valves), (3) relief and vent systems and devices, (4) emergency shutdown systems, (5) controls (including monitoring devices and sensors, alarms, and interlocks), (6) pumps, and other equipment specified by the facility employer.

PSM Element: MECHANICAL INTEGRITY (cont'd)*

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
QUALITY ASSURANCE: In construction of new plants and equipment, the equipment as it is fabricated is assured to be suitable for the process application for which the equipment will be used					
Appropriate checks and inspections are performed to assure that equipment is installed properly and consistent with design specifications and the manufacturer's instructions					
Maintenance materials, spare parts, and equipment are assured to be suitable for the process application for which they will be used					
Communication Not required					
Documentation Each inspection and test performed on process equipment is documented. The documentation identifies: • Date of the inspection or test • Name of the person who performed the inspection or test • Serial number or other identifier of the equipment on which the inspection or test was performed • Description of the inspection or test performed • Results of the inspection or test					

4-16-18

* This element applies to the following process equipment: (1) pressure vessels and storage tanks, (2) piping systems (including piping components such as valves), (3) relief and vent systems and devices, (4) emergency shutdown systems, (5) controls (including monitoring devices and sensors, alarms, and interlocks), (6) pumps, and other equipment specified by the facility employer.

PSM Element: HOT WORK PERMIT

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training *Training in hot work permits as one of the safe work practices is required in the Training and Mechanical Integrity elements*					
Implementation A hot work permit is issued for hot work operations conducted on or near a covered process					
Communication Not required					
Documentation The hot work permit documents: • That the fire prevention and protection requirements in 29 CFR 1910.252(a) have been implemented before beginning the hot work operations • Date(s) authorized for hot work • Object on which the hot work is to be performed					
The permit is kept on file until completion of the hot work operations					

4-16-19

PSM Element: MANAGEMENT OF CHANGE

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program Written procedures exist to manage changes (except for "replacements in kind") to process chemicals, technology, equipment, and procedures and changes to facilities that affect a covered process					
Training Prior to startup of the process or affected part of the process, employees involved in operating a process and maintenance and contract employees whose job tasks will be affected by change in the process are *trained* in the change (in the process)					
Implementation Written procedures are followed in managing changes (except for "replacements in kind") to process chemicals, technology, equipment, and procedures, and changes to facilities that affect a covered process					
Prior to any change, the procedures assure that the following considerations are addressed: • Technical basis for the change • Impact of the change on safety and health • Modifications to operating procedures • Necessary time period for the change • Authorization requirements for the change					
Communication Prior to startup of the process or affected part of the process, employees involved in operating a process and maintenance and contract employees whose job tasks will be affected by a change in the process are *informed* of the change (in the process)					
Documentation Process safety information and operating procedures affected by the change are updated accordingly					

4-16-20

PSM Element: MANAGEMENT OF CHANGE (cont'd.)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Documentation (cont'd) Change control documentation is not required, but is recommended to provide evidence of the completion of the management of change requirements					

4-16-21

PSM Element: INCIDENT INVESTIGATION

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training *No specific training requirements are stated by the rule; however, provide a list in the Notes column of any training that ensures that incident investigation teams are knowledgeable in investigation techniques (see Implementation requirements)*					
Implementation Each incident is investigated that resulted in or could reasonably have resulted in a catastrophic release of a highly hazardous chemical in the workplace					
An incident investigation is initiated as promptly as possible, but not later than 48 hours, following the incident					
An incident investigation team is established consisting of at least one person knowledgeable in the process, a contract employee (if the incident involved the contractor's work), and other persons with appropriate knowledge and experience to thoroughly investigate and analyze the incident					
A system is established for promptly addressing and resolving the incident investigation report findings and recommendations					
Communication The incident investigation report is reviewed with all affected personnel whose work assignments are relevant to the incident findings, including contract employees where applicable					

4-16-22

PSM Element: INCIDENT INVESTIGATION (cont'd.)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Documentation An incident report is prepared at the conclusion of the investigation and includes at a minimum: • Date of the incident • Date the investigation began • A description of the incident • Factors that contributed to the incident • Any recommendations resulting from the investigation					
Resolutions and corrective actions are documented					
Incident investigation reports are retained for 5 years					

4-16-23

PSM Element: EMERGENCY PLANNING AND RESPONSE

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program Emergency action plan for the entire plant exists (in accordance with the provisions of 29 CFR 1910.38[a]): • Emergency escape procedures and escape route assignments (for different types of emergencies) • Procedures to be followed by employees who remain to operate critical plant operations before they evacuate • Procedures to account for all employees after emergency evacuation is complete • Rescue and medical duties for those employees who are to perform them • The preferred means for reporting fires and other emergencies • Names or regular job titles of people or departments who can be contacted for further information or explanation of duties under the plan • The types of evacuation to be used in emergency circumstances					
The emergency action plan also includes procedures to handle small releases					
Training Before implementing the emergency action plan, a sufficient number of persons are designated and trained to assist in the safe and orderly emergency evacuation of employees					
Employer reviews the plan with each employee covered by the plan at the following times: • Initially when the plan is developed • Whenever the employee's responsibilities or designated actions under the plan change • Whenever the plan is changed					

4-16-24

PSM Element: EMERGENCY PLANNING AND RESPONSE (cont'd)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Training (cont'd) Employer reviews with each employee upon initial assignment those parts of the plan which the employee must know to protect the employee in the event of an emergency					
Implementation Emergency drills are conducted to evaluate the readiness of emergency response and facility personnel					
If applicable, employer addresses requirements contained in 29 CFR 1910.120(a), (p), and (q) (HAZWOPER)					
Communication An employee alarm system is established (which complies with 29 CFR 1910.165)					
If the employee alarm system is used for alerting fire brigade members, or for other purposes, a distinctive signal for each purpose is used					
The written plan is kept at the workplace and made available for employee review. (For employers with 10 or fewer employees, the plan may be communicated orally to employees and the employer need not maintain a written plan)					
Documentation Emergency action plan is written (except for employers with 10 or fewer employees)					

4-16-25

PSM Element: COMPLIANCE AUDITS

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program *No requirement for a written program is specified in the rule. Provide a list in the Notes column of any pertinent written programs found*					
Training *No specific training requirements are stated by the rule. Provide a list in the Notes column of any practices found that help ensure the audit team is qualified to perform an effective audit*					
Implementation Compliance with the provisions of this PSM element are evaluated at least every 3 years to verify that the procedures and practices developed under the OSHA rule are adequate and are being followed					
The compliance audit is conducted by at least one person knowledgeable in the process					
Appropriate responses to each of the findings of the compliance audit are promptly determined					
Communication *No specific requirements are specified in the rule; however, note if any practices are found that communicate the results of PSM audits to employees in the affected areas*					

4-16-26

PSM Element: COMPLIANCE SAFETY AUDITS (cont'd.)

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Documentation The employer certifies that compliance has been evaluated					
A report of the findings of the audit is developed					
Appropriate responses to each of the findings of the compliance audit are documented					
Deficiencies that have been corrected are documented					
Two most recent compliance audit reports are retained					

4-16-27

PSM Element: TRADE SECRETS

Technical Areas	PSM Compliance Status			Information Source	Notes/Comments
	None	Partial	Complete		
Written Program Not required					
Training Not required					
Implementation Not required					
Communication Without regard to the possible trade secret status of such information, employers must make all information necessary for compliance with the OSHA rule available to those persons (1) compiling process safety information, (2) developing PHAs and operating procedures, and (3) involved in incident investigations, emergency planning and response, and compliance audits					
Employers are allowed to require persons to whom the information is made available to enter into confidentiality agreements (to not disclose the information as set forth in HAZCOM regulation 29 CFR 1910.1200)					
Employees and their designated representatives have access to trade secret information (contained within the PHAs and other documents required to be developed by the OSHA rule) subject to 29 CFR 1910.1200(i) (1) through (12)					
Documentation Not required (*unless* confidentiality agreements to prevent the disclosure of this information are used)					

4-16-28

Appendix B

Quality Assurance Project Plan (QAPP)

QUALITY ASSURANCE PROJECT PLAN

(QAPP)

Quality Assurance Project Plan (QAPP)
List of Attachments

Attachment	Title	Description
A	SOP (Standard Operating Procedures) 01	procedures for sampling
B	Health and Safety Plan	safety procedures
C	Example Field Data Sheets/Field Data Sheet Form	data collection form
D	Laboratory Method Detection Limits Studies	Method 547 Method 8260B Method 200.7
E	Laboratory Quality Assurance Manual	
F	Example Data Review Checklist & Example Data Review Checklist	
Figure 3.1	Study Area, and Sample Sites	map & list of sites

QUALITY ASSURANCE PROJECT PLAN

(QAPP)

For the

Algae/Aquatic Weed Control Program

MONITORING Acrolein and Copper Sulfate
in Woodbridge Irrigation District Canal System

Prepared by: James Shults

1.0 APPROVAL PAGE

This quality assurance project plan (QAPP) was prepared by James Shults. This document provides common framework of quality assurance practices designed to be followed for this program.

This document will be periodically reviewed and revised by CVRWQCB staff and the Woodbridge Irrigation District to update analytical procedures and program information. All revisions of this QAPP must be approved by the Executive Officer of the Regional Water Quality Control Board.

Gary M. Carlton
Executive Officer

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2.0 INTRODUCTION

This Quality Assurance Project Plan (QAPP) presents the organization, functions, procedures, and specific quality assurance (QA) and quality control (QC) activities for collecting and analyzing samples under the Algae/Aquatic Weed Control Program in the Woodbridge Irrigation District's canal system. The primary users of this QAPP include the staff performing laboratory analyses and fieldwork for this program. Guidelines used to develop the specifications and procedures in this plan are presented here:

- U.S. EPA Guidance on Quality Assurance Project Plans Final (U.S. EPA QA/G-5)(February 1998);
- WID Best Management Practices (BMP) for application of acrolein and copper sulfate.

o QAPP Objective and Use

The goal of the procedures and specifications established in this QAPP is to provide references, standardized procedures and quality control elements and acceptance criteria for the sampling, analysis and data review procedures required for the acrolein and copper sulfate monitoring in the Woodbridge Irrigation District Canal System.. This QAPP also establishes QA procedures for reviewing and documenting compliance with field and analytical procedures.

o Project Planning Documents

This QAPP is the primary planning document needed for monitoring acrolein and copper sulfate under this program; the QAPP details the specific activities and standard field procedures and specifications for this program. The QAPP and the standard operating procedures (SOPs) Woodbridge and Dellavalle Laboratory, Inc. present the site-specific data quality objectives (DQOs) and sampling plans that identify sampling locations, number of samples, field procedures and analytical methods to be used.

A health and safety plan (HASP) prepared by Woodbridge Irrigation District should also be prepared for this sampling effort to establish the safety procedures and the level of personal protective equipment (PPE) required. This ensures that field activities are conducted in a manner that protects personnel performing the work and others in the vicinity.

3.0 SITE DESCRIPTION AND HISTORY

The Woodbridge Irrigation District delivers irrigation water to 13,000 acres of agricultural land in Northern San Joaquin County out of a gross acreage of 40,000 acres. The system has been in operation since 1891 and consists of 100 miles of canals and

pipelines. The prime water supply is the Mokelumne River diversion at Woodbridge which can supply all of the District lands with a gravity water supply. The District owns Woodbridge Diversion Dam which creates the head necessary for the gravity system. In most years, 60,000 acre feet is available from the Mokelumne subject to agreements with East Bay Municipal Utility District. The approximate range of flows from the diversion into the District's canal system is from 75 CFS to 350 CFS with a summer peak flow of 414.4 CFS. The District can also supplement its Mokelumne river supply with water from Beaver Slough near Thornton at the rate of 18 CFS.

3.1 Site(s) Description

The Districts canal system and project area is located on the east side of the Delta in an area generally stretching east of Interstate Highway 5 to State Highway 99 and south of the Mokelumne River and north of the Calaveras river near Stockton. The area is adjacent to the Cities of Lodi, Stockton and Thornton, California. Most of the area is flat agricultural lands with a broad range of diverse crops.

Figure 3-1 shows the study area and the sampling sites.

Figure 3-1 Study Area and Sampling Sites is included in the back of the QAAP.

3.2 Type of Contaminants Reported

The application of aquatic weed control chemicals including acrolien and copper sulfate is made at the prime location of the Woodbridge Irrigation District's headworks at Woodbridge but four other spot treatment sites have been designated in the Woodbridge Best Management Practices Plan on the South Main Canal, the Northwest Main Canal, the West Main Canal, and at the Beaver Slough Diversion pumping station. At these locations acrolein or copper sulfate crystals for control of algae and submersed weeds can be applied. Figure 3-1 provides a map showing these application locations.

4.0 PROGRAM ORGANIZATION AND RESPONSIBILITIES

4.1 Woodbridge Irrigation District

The Woodbridge Irrigation District is the operator for the District's canal system and as such has applied aquatic chemicals to for purposes of keeping the District's canal waters clean. The organizational chart shown below shows the key persons involved in this effort:

WID Organizational Chart

Name	Position	Responsibility
Anders Christensen	General Manager	Directly responsible for all programs and reports to the District Board of Directors.
James Shults	Superintendent	A Qualified Applicator (QC 41526 and specifically applies the chemicals and overseas the program

The California Regional Water Quality Control Board primary functions are as follows:

- Conduct initials audit of the laboratory and the field procedures
- Conduct annual audit of field and laboratory programs
- Conduct data validation on 10 % of the data on a quarterly basis

4.2 Subcontract Laboratory

The laboratory is responsible for testing (not collection) of the District's waters for the aquatic herbicides acrolein and copper sulfate.

Dellavalle Organizational Chart

Name	Position	Responsibility
Nat B. Dellavalle	Laboratory Director	Laboratory Operations
Scott Fridlund	Laboratory Supervisor	Laboratory Organization, QA/QC Records, Daily Operation

Dellavalle Laboratory, Inc., 1910 W. McKinley, Suite 110, Fresno, CA 93728 (559) 223-6129 is the contract laboratory for the testing for acrolein and copper sulfate residues. Dellavalle will conduct tests for acrolein and copper sulfate. Data will be kept by both Dellavalle and Woodbridge. Field samples will be collected by Woodbridge Irrigation District and data collection for temperature will be taken by WID at site. Dellavalle will test samples at the laboratory.

5.0 DATA QUALITY OBJECTIVES AND QUALITY ASSURANCE OBJECTIVES

Data Quality Objectives (DQOs) and Quality Assurance Objectives (QAOs) are related data quality planning and evaluation tools for all sampling and analysis activities. A consistent approach for developing and using these tools is necessary to ensure that enough data are produced and are of sufficient quality to make decisions for this program.

5.1 DQOs and Data Use Planning

DQOs specify the underlying reason for collection of data, data type, quality, quantity, and uses of data collection.

For this program, water sampling after each application or spray activity is needed to document the magnitude of acrolien and copper sulfate, in the Woodbridge Irrigation District Canal System after each application or spraying.

5.1.1 Data Quality Category

For this program, definitive data derived from standard U.S. EPA or other reference methods in an analytical laboratory will be used. Data are to be analyte-specific and both identification and quantitation are to be confirmed. Samples will be analyzed for acrolein and copper sulfate.

5.2 Quality Assurance Objectives (QAOs)

Quality assurance objectives are the detailed QC specifications for precision, accuracy, representativeness, and completeness (PARC). The QAOs presented in this QAPP represent the minimum acceptable specifications for field and analysis that should be considered for field and analytical procedures. The QAOs are then used as comparison criteria during the data quality review to determine if the minimum requirements have been met and if data may be used as planned.

- **Development of Precision and Accuracy Objectives**

  Laboratory control samples (LCSs) are used to determine the precision and accuracy objectives. LCSs are fortified with acrolein and copper sulfate to monitor the laboratory precision and accuracy. The LCS for this program will be developed by analyzing several reagent spikes at different concentration levels. These data will be compiled over a defined time period. Control charts will be developed for all target compounds. Until a sufficient number of samples are analyzed to compile at the minimum 20 LCSs or more for determining precision and accuracy limits, an 80-120 % recovery range will be used in the interim.

  Field duplicates measure sampling precision and variability for comparison of project data. Acceptable relative percent differences (RPDs) are less than 50 for field duplicate analyses. If field duplicate sample results vary beyond these objectives, the results are further evaluated to identify the cause of the variability.

- **PARC Definitions**

Precision measures the reproducibility of repetitive measurements. Precision is evaluated by calculating the RPD between duplicate spikes, duplicate sample analyses, or field duplicate samples and comparing it with appropriate precision objectives established in this QAPP. Analytical precision is developed using repeated analyses of identically prepared control samples. Field duplicate samples analyses results are used to measure the field QA and matrix precision. Interpretation of precision data must include all possible sources of variability.

Accuracy measures correctness, or how close a measurement is to the true or expected value. Accuracy is measured by determining the percent recovery of known concentrations of analytes spiked into field sample or reagent water before extraction. The stated accuracy objectives for laboratory control samples and matrix spikes must reflect the sample concentration and/or middle of the calibration range.

Representativeness is obtained by using standard sampling and analytical procedures in this QAPP to generate data that is representative of the sites.

Completeness is calculated for each method and matrix for an assigned group of samples. Completeness for a data set is defined as the percentage of unqualified and estimated results divided by the total number of the data points. This represents the useable data for data interpretation and decision-making. Results qualified as rejected or unusable or that were not reported because of sample loss or breakage or analytical error will be subtracted from the total number of results to calculate completeness. The overall objective for completeness is 95%.

Table 5-1 presents the quality control acceptance limits for this program.

Table 5-1 Quality Control Acceptance Criteria for Required Analyses in Surface Water:

Analyte:	Acrolein	Total Copper	Sulfate
Standard	*	2 ppm	1 ppm
Acceptance Criteria	80-120%	(+) or (-) 10%	(+) or (-) 10%

* A Confirming Calibration Verification (CCV) is performed before and after the analysis.
ppm=part per million

6.0 FIELD PROCEDURES

This section includes brief descriptions of field procedures used for this program. Detailed equipment and procedure descriptions are included in the surface water sampling SOP. A copy of this SOP is presented in Attachment A of this QAPP.

Field coordinators must ensure that field personnel have a copy of the QAPP and that all field activities are conducted following the health and safety procedures included in Attachment B of this QAPP.

6.1 Site Selection

Proper site selection is critical to producing representative data. Locations selected for sampling must represent site, zone and matrix under this program.

- **Sampling Locations**

  Sampling locations for surface water is selected using a judgmental sampling approach.

  The criteria used to select sampling locations are:

  - Choose area where treatment occurs representative of entire project/system.
  - Choose area where treated water is intentionally or has potential to discharge into a natural water body.

6.2 Sampling Frequency and Duration

Proper sampling frequency and duration is critical to producing representative data. Timing must represent that treated water has returned to its pre-treatment state or that active ingredient(s) is below critical levels and/or undetectable.

The criteria used to select sampling frequency and duration are:

- Obtain a pre-treatment sample (Optional)
- Post-treatment samples will be collected one week after the application and should reflect degradation of active ingredient(s) after each application event.

6.3 General Field Sampling Requirements

The standard elements for field and sampling activities are addressed in this section.

6.3.1 Decontamination Procedures

All field and sampling equipment that may contact samples must be decontaminated after each use in a designated area. A detailed description of cleaning of equipment for water sampling is included in surface water sampling SOP.

Sample Storage, Preservation and Holding Times

Sample containers are pre-cleaned according to specification for the appropriate methods. Table 6-1 lists the sample container, storage and preservation requirements for this.

Table 6-1 Sample Storage and Preservations Requirements

Analyte	Methods	Container	Holding Time	Preservation	Storage
Acrolein	EPA 8260	40 ml VOA	14 days	HCL to pH<2	Ref. at 4 Degrees C.
Total Copper	EPA 200.7	250 ml plastic	6 months	HNO_3 to ph<2	Ref. at 4 Degrees C.
Sulfate	SMH4500 SO_4 -2E	250 ml plastic	28 days	None	Ref. at 4 Degrees C.

gc/ms = gas chromatography/ mass spectrometry

6.3.3 Documentation

All field activities must be adequately and consistently documented to support data interpretation and ensure defensibility of any data used for decision-making. Example of field data sheets and other documentation's required for this field procedure are included in Attachment C by Woodbridge Irrigation District for this QAPP. Field personnel must record the following information:

- Name(s) of field personnel;
- Site/ sampling location identification;
- Date and time of sample collection;
- All field measurement of temperature.
- Observation of weather and conditions that can influence sample results; and
- Any problems encountered during sampling.

6.3.4 Sample Identification Scheme

All samples must be uniquely identified to ensure that results are properly reported and interpreted. Samples must be identified such that the site, sampling location, sample date and time, matrix, sampling equipment and sample type (normal field sample or QC sample) can be distinguished by a data reviewer or user.

6.3.5 Field and Laboratory Staff Training

All staff performing field or laboratory procedures shall receive training to ensure that the work is conducted correctly and safely. At a minimum all staff shall be familiar with the field guidelines and procedures and the laboratory SOP included in this QAPP. All work shall be performed at least once under the supervision of experienced staff, field managers, laboratory managers or other qualified individuals before field staff perform procedures on their own.

6.4 Sample Collection Methods

Proper sampling techniques must be used to ensure that a sample is representative of the flow in the cross section.

- **QC Sample Collection**

Field blanks and field duplicates are collected at a frequency of approximately 1 per application event. Matrix spikes are collected at frequency of approximately 1 pair per application event.

- **Field Measurements**

For all water bodies sampled, temperature is measured prior to collecting samples for laboratory analyses. Field instrument calibration and operation of the instruments are presented in SOP 2 of this QAPP.

- **Record Keeping and Sample Handling Procedure**

All data collected in the field are recorded on sample field sheets. Pertinent field information, including (as applicable), width, depth, flow rate of the stream, surface water conditions and location of tributaries are recorded on the field sheets. Sample control information is documented in a master sample log. Chain of custody record is completed subsequent to sample collection.

7.0 SAMPLE CUSTODY AND DOCUMENTATION

Sample possession during all sampling efforts must be traceable from the time of collection until results are reported and verified by the laboratory and samples are disposed of. Sample custody procedures provide a mechanism for documenting information related to sample collection and handling.

7.1 Documentation Procedures

The field activities coordinator is responsible for ensuring that the field sampling team adheres to proper custody and documentation procedures. A master sample logbook is maintained for all samples collected during each sampling activity.

Field personnel have the following responsibilities:

- Keep an accurate written record of sample collection activities on the field form and logbook
- Ensure that all entries are legible, written in waterproof ink and contain accurate and inclusive documentation of the field activities.
- Date and initial daily entries
- Note errors or changes using a single line to cross out the entry and date and initial the change
- Complete the chain of custody forms accurately and legibly

A sample label is affixed to each sample collected. Sample labels uniquely identify samples with an identification number, analytical method requested; and date and time of sample collection. Figure 7-1 shows an example sample label Woodbridge Irrigation District.

Figure 7-1 Sample label:

(Label)

Label No. _____ Sample Date_____Time_____
Sampled By_____
Sample Description_____
Client (Woodbridge Irrigation District)
Analysis Required: Acidified: HNO_3
H_2SO_4
HCL

Delavalle Laboratory, Inc.
1910 McKinley Ave., #110, Fresno 93728 - 800 228-9896 - 559 233-6129

7.2 Chain-of-Custody Form

A chain-of-custody form is completed after sample collection, and prior to sample shipment or release. The chain-of-custody form, sample labels, and field documentation are crossed checked to verify sample identification, number of containers, sample volume, and type of containers.

Information to be included in the chain of custody forms includes:

- Sample identification;

- Date and time of collection;
- Samplers' initials;
- Analytical method(s) requested;
- Sample volume;
- QC sample identification;
- Signature blocks for release and acceptance of samples; and
- Any comments to identify special conditions or requests.

Sample transfer between field staff, courier, and laboratory is documented by signing and dating "relinquished by" and "received by" blocks whenever sample possession changes. If samples are not shipped on the collection day, they are refrigerated in a sample control area. An example of chain-of-custody form is shown in Figure 7-2 Woodbridge Irrigation District.

FIGURE 7-2 Example of a chain-of-custody Form:

Delavalle Laboraratory , Inc.
1910 W. McKinley, Suite 110
Fresno, CA 93728

Chain of Custody Form

Woodbridge Irrigation District **P.O. #** _____
18777 N. Lwr Sacto Rd. **Requested By:** _____
Woodbridge, CA 95258 **Date/Time:** _____

SAMPLE IDENTIFICATION QC Number & Volume	Sample Type	Sample DATE/TIME:	Analysis

BY: _____ **(Sign)**

Relinquished By Sampler (Initial)	**Woodbridge ID**	**Date / Time**
Received By	**Affiliation**	**Date / Time**
Relinquished By	**Affiliation**	**Date / Time**
Received By	**Affiliation**	**Date / Time**
Relinquished By	**Affiliation**	**Date / Time**
Recieved By	**Affiliation**	**Date / Time**
Relinquished By	**Affiliation**	**Date / Time**
Received By	**Affiliation**	**Date / Time**

REMARKS: _____

7.3 Sample Shipments and Handling

All sample shipments are accompanied by the chain-of-custody form, which identifies the content. The original form accompanies the shipment and a copy is retained in the project file.

All shipping containers are secured with chain-of-custody seals for transportation to the laboratory. Samples are either shipped to the laboratory according to Department of Transportation standard or picked up by the laboratory from the field. A generous amount of ice is packed with the samples. The ice must contact each sample and be approximately 2 inches deep at the top and bottom of the cooler. The ice may be contained in recloseable bags, but must contact the samples to maintain temperature. The methods of shipment, courier name, and other pertinent information are entered in the "Received By" or "Remark" section of the chain of custody form.

The following procedures are used to prevent bottle breakage and cross-contamination:

- Bubble wrap or other cushioning material is used to keep bottles from contacting one another to prevent breakage.
- Sample bottles are individually sealed in plastic recloseable bags.
- All samples are transported inside hard plastic coolers.
- The coolers are taped shut and sealed with chain-of-custody seals to prevent accidental opening.
- Field staff must notify laboratory sample control prior to shipment of the samples.

7.4 Laboratory Custody Procedures

The following sample control activities must be conducted in the laboratory:

- Initial sample log-in and verification of samples received with the chain of custody form;
- Document discrepancies noted during log-in on the chain of custody;
- Initiate internal laboratory custody procedure;
- Verify sample preservation such as temperature;

- Notify the project coordinator if any problems or discrepancies are identified;
- Proper sample storage, including daily refrigerator temperature monitoring and sample security;
- Return shipment of coolers

8.0 Left Blank

8.1 Left Blank

9.0 ANALYTICAL PROCEDURES AND CALIBRATION

This section lists the analytical methods for surface water samples that will be collected for this program. The analytical methods included in this QAPP are published in the U.S. EPA Test Methods for Evaluating Solid Waste Physical/Chemical SW 846 or U.S. EPA Methods for Chemical Analysis of Water and Waste. The primary methods and MDL's for these analytes are included in the preceding table including:

Analyte	Active Ingredient	Methodology	MDL
Acrolein	Acrolein	EPA 8260	2.641 ug/L
Copper	Copper	EPA 200.7	.0017 mg/L
Sulfate (SO_4)	Sulfate	SM 4500 SO_4-E	.0516 mg/L

9.1 Detection and Quantitation Limits

The method detection limit (MDL) is the minimum analyte concentration that can be measured and reported with a 99% confidence that the concentration is greater than zero. The quantitation limit (QL) represents the concentration of an analyte that can be routinely measured in the sample matrix within stated limits and confidence in both identification and quantitation. Attachment D presented the method detection limit studies conducted for each methods used in this program. These detection limits will be used as project quantitation limits.

9.2 Sample Preparation Procedure

The sample is received by a receptionist, who places it in the sample reception area. A technician reviews the Laboratory Work Request , assigns a unique sample number, places the number on the form and sample container. The technician refers to the Procedures manual for proper disposition. The sample is

preserved accordingly by a Laboratory Technician. The sample is stored in a 4-6 degree C refrigerated storage area. Samples are held or preserved according to Table 1060:I in Standard Methods 18th Edition, pg 1-22. The Laboratory Work Request form is delivered to the scheduler. The scheduler prepares worksheets and work assignments and distributes them to laboratory technicians. Samples are disposed of after recommended/regulatory holding times have expired.

9.3 Analytical Procedures

Analytical procedures for water and waste water are derived from Standard Methods for the Examination of Water and Waste Water, 18th Edition.

10.0 DATA REDUCTION, VERIFICATION, AND REPORTING

The laboratory data reduction, verification, and reporting procedures ensures that complete documentation is maintained, transcription and reporting errors are minimized, and data received from laboratory are properly reviewed.

10.1 Laboratory Data Reduction and Verification

The laboratory analyst performing the analyses is responsible for the reduction of the raw data generated at the laboratory bench to calculate the concentrations. The analytical process includes verification or a quality assurance review of the data. This includes:

- Verifying the calibration samples for compliance with the laboratory and project criteria;
- Verifying that the batch QC were analyzed at a proper frequency and results were within specifications;
- Comparing raw data (e.g., chromatogram) with reported concentration for accuracy and consistency;
- Verifying that holding times were met and that reporting units and quantitation limits are correct;
- Determining whether corrective action was performed and control was re-established and documented prior to re-analysis of QC or project samples;
- Verifying all project and QC sample results were properly reported and flagged; and
- Preparing batch narratives that adequately identify and discuss any problems encountered.

The QC check is conducted at several levels by the laboratory analyst, supervisors, and laboratory quality assurance staff. The specific procedures are documented in the laboratory quality assurance manual. After the data have been reviewed and verified, the laboratory reports are signed for release and

distributions. Raw data and supporting documentation is stored in confidential files by laboratory document control.

11.0 INTERNAL QUALITY CONTROL (QC)

Internal quality control (QC) is achieved by collecting and/ or analyzing a series of duplicate, blank, spike and spike duplicate samples to ensure that analytical results are within the specified QC objectives. The QC sample results are used to quantify precision and accuracy and identify any problem or limitation in the associated sample results. The internal QC components of a sampling and analyses program will ensure that the data of known quality are produced and documented. The internal QC checks, frequency, acceptance criteria and corrective action required to meet project objectives are presented in the Dellavalle Laboratory, Inc. laboratory Quality Assurance Manual included in Attachment E of this QAPP.

11.1 Analytical Laboratory QC Samples

Laboratory QC is necessary to control the analytical process within method and project specifications, assess the accuracy and precision of analytical results.

The laboratory will perform the following QC checks:

- Calibration standards
- Laboratory control samples
- Method blanks
- Matrix spike and matrix spike duplicates
- Surrogate spikes
- Laboratory duplicate samples, and
- Control standards

The procedures for analysis and review of these QC checks samples are described in the Laboratory Quality Assurance Manual presented in Attachment E of this QAPP.

11.2 Field QC Samples

Field QC samples are used to assess the influence of sampling procedures and equipment used in sampling. They are also used to characterize matrix heterogeneity.

The following field QC samples will need to be collected for this program:

- Field duplicate samples

- Equipment blanks and
- Field Spikes

12.0 AUDIT AND DATA VALIDATION

The laboratory will be audited by the California Regional Water Quality Control Board (RWQCB) technical staff on a yearly basis. The RWQCB field audit team conducts the field audit on a yearly basis. These audits are independent of sample collection and analysis procedures.

12.1 Technical System Audit:

A technical system audit is a quantitative review of a sampling or analytical system. Qualified technical staff members who have the authority to act independently of the laboratory, field and project management perform audits.

The laboratory system audit results are used to review operations and ensure that the technical and documentation procedures provide valid and defensible data

Critical items for a laboratory system audit include:

- Sample storage procedures;
- Availability of and compliance with calibration procedures and documentation requirements;
- Standard operating procedures;
- Source and handling of standards;
- Completeness of data forms, notebooks and other records of analysis and QC activities;
- Data review and verification procedures;
- Data storage, filing and record keeping procedures;
- Sample custody procedures;
- Establishment and use of quality control procedures, control limits and corrective actions that comply with specification in this QAPP;
- Operating conditions of the facilities and the equipment;

- Documentation of the instruments maintenance activities; and

- Laboratory staff training and documentation.

Critical items for sampling system audits includes:

- Calibration procedures and documentation for field meters;
- Field activity documentation in logbooks and sampling data sheets;
- Minimization of potential sample contamination in the field by using proper equipment decontamination procedures;
- Availability of SOPs and compliance to ensure proper sample collection, storage and transportation procedures;
- Compliance with established chain of custody procedures for sample documentation and transfer to the laboratory; and
- Field staff training and implementation of project-specific-requirements.

The checklist for each audit contains detailed questions regarding the critical items, requesting yes/no answers and comments. The laboratory manager and field coordinator must prepare a corrective action plan to address any findings or negative observations noted in the project audit report. The corrective action plan must address the immediate corrective actions and procedures that will be implemented to prevent recurrence of problems noted. A copy of each audit report and the corresponding corrective action report are provided to RWQCB.

12.2 Performance Evaluation Audits

Performance evaluation audits quantitatively assesses the data produced by a measurement system. Performing evaluation audit involves submitting certified samples for each analytical method. The matrix standards are selected to reflect the concentration range expected for the sampling program. The performance evaluation audit evaluates whether the measurement system is operating within the project control limit specified in this QAPP and the data produced meet the project and analytical quality control specifications.

The performance evaluation (PE) samples are prepared and submitted to the laboratory by the Woodbridge Irrigation District. The PE samples are submitted as normal samples to the laboratory. A copy of the information including the content of the PE samples and the expected concentrations are submitted to RWQCB. Critical items for the performance evaluation audits are:

- Accurate identification of the analytes included in the PE samples
- Quantitation within acceptance limits
- Accurate reporting of results and any problems identified
- Acceptable analytical batch QC sample results

These items are used to identify when a system is outside acceptable control limits. Any problem associated with PE samples must be evaluated to determine the influence on field samples analyzed during the same time period. The laboratory must provide a written response to Woodbridge Irrigation District of any PE sample result deficiencies. A copy of the results will be submitted to the RWQCB.

12.3 Data Validation

Data validation (data quality audit) is conducted to verify whether an analytical method has been performed according to the method and project specifications, and the results have been correctly calculated and reported.

The RWQCB will perform the data validation on 1 % of the data generated during each quarter.

Specific items that are reviewed during data validation are:

- Chain of custody record
- Documentation of laboratory procedures (e.g., standard preparation records, run logs, data reduction and verification)
- Accuracy of data reduction, transcription, and reporting
- Adherence to method-specific calibration procedures and quality control parameters
- Precision and accuracy of recorded results

12.4 Field Technical Audits

The Woodbridge Irrigation District project managers routinely observe field operations to ensure consistency and compliance with sampling specifications presented in the QAPP. Audit checklists that will document field observations and activities will be completed. A copy of the field audit will be available in the project file. The RWQCB will conduct annual technical systems audits of the field procedures. Results of the audits including recommendations will be provided to the Woodbridge Irrigation District. A copy of the field audit checklist is included in Attachment F of this QAPP.

12.5 Split Samples (if applicable)

A second laboratory that meets the analytical requirements stated in this QAPP will be selected for performing the split samples. The Woodbridge Irrigation District will arrange for the field team to ship 1% of samples to the designated laboratory. Chain of custody procedures must be followed at all times. A copy of the results of split samples will be submitted to the Regional Board.

13.0 PREVENTATIVE MAINTENANCE

A preventive maintenance program's primary objective is to assure the timely and effective completion of a measurement effort by minimizing the downtime of crucial sampling and/or analytical equipment from unexpected component failure. The program efforts are focused in the three principal areas: maintenance responsibilities, maintenance schedule and inventory of critical spare parts and equipment.

The maintenance performed on the analytical instruments that are used for this project is described in the laboratory quality assurance manual.

14.0 DATA ASSESSMENT PROCEDURES

Measurement data must be consistently assessed and documented to determine whether project quality assurance objectives (QAOs) have been met, quantitatively assess data quality and identify potential limitations on data use.

The laboratory is responsible for following the procedures and operating the analytical systems within the statistical control limits. These procedures include proper instrument maintenance, instrument calibration, and the laboratory QC sample analyses at the required frequencies (i.e., method blanks, laboratory control samples, etc.). Associated QC sample results are reported with all sample results so project staff can evaluate the analytical process performance.

All project data must be reviewed by Woodbridge Irrigation District as part of the data assessment. Review is conducted on a preparation batch basis by assessing QC samples and all associated field sample results.

Project data review established for this project includes the following steps:

- Initial review of analytical and field data for complete and accurate documentation, chain of custody procedures, analytical holding times compliance, and required frequency of field and laboratory QC samples;
- Evaluation of analytical and field blank results to identify random and systematic contamination;
- Comparison of all spike and duplicate results with project objectives for precision and accuracy;
- Assigning data qualifier flags to the data as necessary to reflect limitations identified by the process; and
- Calculating completeness by matrix and analyte.

The Woodbridge Irrigation District staff conducting the data assessment is responsible for ensuring that data qualifier flags are assigned as needed, based on the established QC criteria. Staff is also responsible for communicating any limitations to data users. A data

review checklist will be completed upon completion of each laboratory package by the Woodbridge Irrigation District staff. A copy of the data review checklist is presented in Attachment G of this QAPP. One percent of the reviewed data will be validated by the RWQCB staff on a quarterly basis.

15.0 CORRECTIVE ACTION

During the course of sample collection and analysis in this study, the laboratory supervisors and analysts, field supervisors and team members will make sure that all measurements and procedures are followed as specified in this QAPP, and measurements meet the prescribed acceptance criteria.

Problems about analytical data quality that may require corrective action are documented on a corrective action form presented in the laboratory quality assurance manual. Problems about field data quality that may require corrective action are documented in the field data sheets.

16.0 ANALYTICAL DATA AND QUALITY ASSURANCE REPORT

The RWQCB will prepare a report after conducting a data validation on a quarterly basis.

Elements described below will be addressed and included in the report:

- Description of the project including number of samples, analyses, completeness and any significant problems or occurrences that influence data use.
- The QA/QC activities performed during the previous quarter.
- QC sample results, type and number of samples including results that did not meet the projective objectives, and impact on usability.
- Tables of analytical results for usable and unusable data.

17.0 SITE MANAGEMENT

The Woodbridge Irrigation District field manager observes field activities to ensure tasks are conducted according to the project specifications. The field coordinator is equipped with a cellular telephone for improved communication among team members.

Decontamination of field equipment occurs at a designated area assigned by the field manager. Access for sites is coordinated through the Woodbridge Irrigation District.

Attachment

"A"

Attachment A

ATTACHMENT A

The Woodbridge Irrigation District Surface Water Sampling SOP For Acrolein and Copper Sulfate in the Woodbridge Irrigation District Canal System (SOP 01)

Sampling:

Sampling shall be conducted in the following manner to insure that a representative sample in obtained:

1. Samplers shall read and follow the Health and Safety Plan as shown in the foregoing Attachment "B".
2. Use the sample bottles as provided by the testing laboratory that will examine the sample.
3. Be careful so that nothing except water to be analyzed comes in contact with the inside of the bottle or cap. Caps should be held continuously and with the inside of the cap pointing down. Care should be taken for sampler's fingers to touch only the outside of the cap. Do not rinse the bottle.
4. When filling the bottle, take a representative sample from the middle of the stream. Be sure that the bottle is held so that no water which contacts the hands runs into the bottle.
5. Deliver the sample immediately to the laboratory following the recommended procedures detailed in 7.3 of this plan.
6. In no case shall the time elapsing between collection and receipt by testing laboratory shall exceed 30 hours.

Attachment

"B"

Attachment B

ATTACHMENT B

The Woodbridge Irrigation District
Monitoring Acrolein and Copper Sulfate
in the Woodbridge Irrigation District Canal System
Health and Safety Plan

General Information: The testing of waters containing any hazardous chemicals shall follow the Woodbridge Irrigation District written hazardous chemicals communication program dated 7-24-00. The manual specifically spells out procedures to be followed. Employees are given regular training for implementation of the plan. A copy of the plan is included as a reference.

Additionally, employees taking water samples containing Acrolein and Copper Sulfate shall put on splash goggles and butyl rubber gloves, wear rubber boots, and have an air purifying respirator assembled and ready and eye and wash water available before proceeding with testing. A Coast Guard approved personal flotation device shall also be worn by the samplers.

Samplers should read and follow the most current MSDS Sheets for the above referenced chemicals.

Sample bottles should be clearly labeled.

Effects of the above referenced chemicals can be delayed. Medical attention should be sought immediately if any symptoms occur. Medical attention can of any injury can be obtained as listed below:

- Dr. Ben Watson, Occupational Health Services, 840 S. Fairmont Street #9, Lodi, CA (209)333-1751

- Lodi Memorial Hospital Emergency, 975 Fairmont Avenue, Lodi, CA (209)339-7575

Attachment C

ATTACHMENT C

The Woodbridge Irrigation District
Monitoring Acrolein and Copper Sulfate
in the Woodbridge Irrigation District Canal System
Example Field Data Sheets

Field Data Sheet Form

Sampler's Names(s):_____
_____
Constituent to be Sampled:____Acrolien ___Copper Sulfate
Type of Sample: _____Normal Field _____QC Sample or Recheck
Sample Site Location:_____
Date: Mo._____ Day_____ Year_____
Time of Sample: _____ AM/PM (Circle One)
Water Temperature: _____Degrees Celsius
Weather Conditions:
Air Temperature: _____Degrees Fahrenheit
Wind: _____Miles/Hr.
Sky Conditions: Circle One: Sunny, Partly Sunny, Overcast, Rainy
Comments: (Area to be used to note additional information or problems encountered during sampling)_____
_____
_____
_____
_____
_____

Signed: _____

ATTACHMENT D

Laboratory Method Detection Limits Studies

METHOD 547

DETERMINATION OF GLYPHOSATE IN DRINKING WATER BY DIRECT-AQUEOUS-INJECTION HPLC, POST-COLUMN DERIVATIZATION, AND FLUORESCENCE DETECTION

July 1990

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METHOD 547

DETERMINATION OF GLYPHOSATE IN DRINKING WATER BY DIRECT-AQUEOUS-INJECTION HPLC, POST-COLUMN DERIVATIZATION, AND FLUORESCENCE DETECTION

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for the identification and measurement of Glyphosate (N-phosphonomethyl glycine) in drinking water matrices. Single laboratory accuracy and precision data have been determined for this method.

1.2 Glyphosate was found to rapidly decompose in chlorinated waters[1]. It is therefore unlikely that the analyte will be evidenced in tap water except as separate glycine and N-phosphonomethyl moieties, neither of which is applicable to this method.

Analyte	Chemical Abstract Services Registry Number
Glyphosate	1071-83-6

1.3 The method detection limits (MDL, defined in Section 13.0) for glyphosate are listed in Table 1[2]. The MDLs for a specific sample may differ from those listed.

2.0 SUMMARY OF METHOD

2.1 A water sample is filtered and a 200 µL aliquot injected into a cation exchange HPLC column. Separation is achieved by using an isocratic elution. After elution from the analytical column at 65°C, the analyte is oxidized with calcium hypochlorite. The product (glycine) is then coupled with o-phthalaldehyde-2-mercaptoethanol complex at 38°C to give a fluorophor, which is detected by a fluorometer with excitation at 340 nm and detection of emission measured at >455 nm[1,3].

3.0 DEFINITIONS

3.1 Laboratory Duplicates (LD1 and LD2) -- Two sample aliquots taken in the analytical laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 give a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.2 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.3 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.4 Field Reagent Blank (FRB) -- Reagent water placed in a sample container in the laboratory and treated as a sample in all respects, including exposure to sampling site conditions, storage, preservation and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.5 Laboratory Performance Check Solution (LPC) -- A solution of method analytes, surrogate compounds, and internal standards used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the method is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

3.7 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 Stock Standard Solution -- A concentrated solution containing a single certified standard that is a method analyte, or a concentrated solution of a single analyte prepared in the laboratory with an assayed reference compound. Stock standard solutions are used to prepare primary dilution standards.

3.9 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution and stock standard solutions of the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.10 Quality Control Sample (QCS) -- A sample matrix containing method analytes or a solution of method analytes in a water miscible solvent which is used to fortify reagent water or environmental samples. The QCS is obtained from a

source external to the laboratory, and is used to check laboratory performance with externally prepared test materials.

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware that lead to discrete artifacts and/or elevated baselines in the chromatograms. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks as required by Section 10.2.

4.1.1 Glassware must be scrupulously cleaned[4]. Clean all glassware as soon as possible after use by rinsing with the last solvent used in it. This should be followed by detergent washing with hot water, and rinses with tap water and distilled water. Glassware should then be drained dry, and heated in a laboratory oven at 400°C for several hours before use. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required to achieve necessary purity.

4.2 Samples may become contaminated during shipment or storage. Field blanks must be analyzed to determine that sampling and storage procedures have prevented contamination.

4.3 The extent of matrix interferences may vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. No interferences have been observed in the matrices studied.

4.4 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a unique resolution of the compound covered in this method, other matrix components may interfere.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method[5]. A reference file of material data handling sheets should be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND EQUIPMENT

6.1 Sampling Equipment -- For discrete or composite sampling.

6.1.1 Grab sample bottle -- 60 mL screw cap bottles (Pierce No. 13075 or equivalent) and caps equipped with a teflon-faced silicone septa (Pierce No. 12722 or equivalent). Prior to use, wash vials and septa as described in Section 4.1.1.

6.2 Glassware

6.2.1 Autosampler vials -- Glass, 3.7 mL, with teflon-lined septa and screw caps. (Supelco, #2-3219, or equivalent)

6.2.2 Volumetric flask -- 1000 mL and 100 mL

6.3 Balance -- Analytical, capable of accurately weighing 0.0001 g.

6.4 pH Meter -- Capable of measuring pH to 0.01 units.

6.5 Filtration Apparatus

6.5.1 Macrofiltration -- To filter mobile phase and derivatization solutions used in HPLC system. Membrane filter, 0.2 µ mesh, 47 mm diameter, Nylon 66 (Alltech, #2034 or equivalent)

6.5.2 Microfiltration -- To filter samples prior to HPLC analysis. Use 0.45 µ filters (Gelman Acrodisc - CR or equivalent)

6.5.3 Helium -- For degassing solutions and solvents.

6.6 Syringes

6.6.1 One 250 µL glass syringe, with blunt tip needle for manual injection.

6.6.2 Three tofive mL disposable hypodermic syringes with Luer-Lok tip.

6.6.3 Micro syringes -- Various sizes.

6.7 Instrumentation -- A schematic diagram of the analytical system is shown in Figure 1.

6.7.1 A high performance liquid chromatograph (HPLC) capable of injecting 200 µL aliquots and utilizing an isocratic pumping system with constant flow rate of 0.5 mL/min.

6.7.2 Column -- 250 x 4 mm, Bio-Rad, Aminex A-9. Column specifications: K^+ form, packed at 65°C, pH = 1.9. This column was used to generate the method performance statements in Section 13.0. Different HPLC

columns may be used if requirements described in Section 10.3 are met. Use of guard columns is recommended.

6.7.3 Guard column -- C_{18} packing - (Dupont, Zorbax Guard Column or equivalent). An alternative guard column similar in composition to the analytical column may also be used provided the requirements of Section 10.3 are met.

6.7.4 Column oven -- Fiatron, Model CH-30 and controller, Model TC-50, or equivalent.

6.7.5 Post Column Reactor (PCR) -- Capable of mixing reagents into the mobile phase. Reactor to be equipped with pumps to deliver 0.5 mL/min of each reagent; mixing tees; two 1.0 mL delay coils, both thermostatted at 38°C; and constructed using teflon tubing (Kratos Model URS 051 and URA 200 or equivalent).

6.7.6 Fluorescence detector -- Capable of excitation at 340 nm and detecting of emission >455 nm. A Schoeffel Model 970 fluorescence detector was used to generate the validation data presented in this method.

6.7.7 Data system -- A strip chart recording of the detector response must be provided as a minimum requirement. The use of a data system to calculate retention times and peak areas is recommended but not required.

7.0 REAGENTS AND CONSUMABLE MATERIALS

7.1 HPLC Mobile Phase

7.1.1 Reagent water -- Reagent water is defined as water of very high purity, equivalent to distilled-in-glass solvents.

7.1.2 Mobile phase -- 0.005 M KH_2PO_4 (0.68 gm) in 960 mL reagent water, add 40 mL HPLC grade methanol, adjust pH of solution to 1.9 with concentrated phosphoric acid then filter with 0.22 µ filter and degas with helium before use.

7.2 Post-column Derivatization Solutions

7.2.1 Calcium hypochlorite solution -- Dissolve 1.36 g KH_2PO_4, 11.6 g NaCl and 0.4 g NaOH in 500 mL deionized water. Add 15 mg Ca $(C1O)_2$ dissolved in 50 mL deionized water and dilute solution to 1000 mL with deionized water. Filter solution through 0.22 µ membrane filter and degas with helium before use. It is recommended that this solution be made fresh daily.

7.2.2 O-phthalaldehyde (OPA) reaction solution

7.2.2.1 2-Mercaptoethanol (1+1) -- Mix 10.0 mL of 2-mercaptoethanol and 10.0 mL of acetonitrile. Cap and store in hood.

CAUTION: Stench.

7.2.2.2 Sodium borate (0.05 N) -- Dissolve 19.1 g of sodium borate ($Na_2B_4O_7 \cdot 10\ H_2O$) in 1.0 L of reagent water. The sodium borate will completely dissolve at room temperature if prepared a day before use.

7.2.2.3 OPA reaction solution -- Dissolve 100 ±10 mg of o-phthalaldehyde (mp 55-58°C) in 10 mL of methanol. Add to 1.0 L of 0.05 N sodium borate. Mix, filter through 0.45 µ membrane filter, and degas. Add 100 µL of 2-mercaptoethanol (1+1) and mix. Make up fresh solution daily unless the reagent solution is protected from atmospheric oxygen. The solution can be stored in glass bottles under atmospheric conditions at 4°C for up to two weeks without appreciable increases in background fluorescence or stored under nitrogen for indefinite periods.

NOTE: Fluoraldehyde (Pierce Chemical), a commercially formulated OPA reaction solution, may be substituted for Steps 7.2.2.1 through 7.2.2.3.

7.3 Sample Preservation Reagents

7.3.1 Sodium thiosulfate -- Granular, ACS grade or better (Fisher, S-446).

7.4 Stock Standard Solution (1.00 µg/mL)

7.4.1 Accurately weigh and dissolve 0.1000 g of pure glyphosate in 1000 mL of deionized water. Larger or smaller volumes may be used at the convenience of the analyst. If compound purity is certified at 96% of greater, the weight may be used without correction to calculate the concentration of the stock standard.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Collect samples in glass containers (Section 6.1.1). Conventional sampling practices[6] are to be followed.

8.2 Sample Preservation -- Treatment of samples to remove residual chlorine will eliminate the possibility of glyphosate losses due to chlorine during storage. Chlorine is destroyed by adding 100 mg/L of sodium thiosulfate to the sample.

8.3 Sample Storage -- Samples should be stored at 4°C away from light and analyzed within two weeks. A preservation study[7] has demonstrated the stability of glyphosate in frozen samples for up to 18 months. The analyst

should verify appropriate sample holding times applicable to the sample under study.

9.0 CALIBRATION

9.1 Establish liquid chromatographic operating conditions indicated in Table 1.

9.2 Prepare a minimum of three calibration standards of glyphosate by serial dilution of the stock standard solution in deionized water. One of the calibration standards should correspond to a glyphosate concentration near to, but above the MDL. The other concentrations should comprise the range of concentrations expected for the samples, or, otherwise, define the working range of the detector.

9.3 Analyze each calibration standard and tabulate peak area against concentration (in µg/L) injected. The results may be used to prepare a calibration curve for glyphosate.

Alternatively, if the ratio of response to concentration (response factor) is constant over the working range (<10% relative standard deviation), linearity through the origin can be assumed and the average ratio or response factor can be used in place of a calibration curve.

9.4 The working calibration curve must be verified on each working day by the measurement of a minimum of two calibration check standards, one at the beginning and one at the end of the analysis day. These check standards should be at two different concentration levels to verify the calibration curve. For extended periods of analysis (greater than eight hours), it is strongly recommended that check standards be interspersed with samples at regular intervals during the course of the analyses. If the response for the analyte varies from the predicted response by more than ±20%, the test must be repeated using a fresh calibration standard. If the results still do not agree, generate a new calibration curve.

10.0 QUALITY CONTROL

10.1 Minimum quality control (QC) requirements are initial demonstration of laboratory capability, analysis of laboratory reagent blanks, laboratory fortified matrix samples, laboratory fortified blanks and QC samples.

10.2 Laboratory Reagent Blanks (LRB) -- Before processing any samples, the analyst must demonstrate that all glassware and reagent interferences are under control. Each time a set of samples is extracted or reagents are changed, a LRB must be analyzed. If within the retention time window of the analyte of interest the LRB produces a peak that would prevent the determination of that analyte, determine the source of contamination and eliminate the interference before processing samples.

10.3 Initial Demonstration of Capability

10.3.1 Prepare laboratory fortified blanks (LFBs) at an analyte concentration of 250 µg/L. With a syringe, add .250 mL of the stock standard (Section 7.4) to at least four 100 mL aliquots of reagent water and analyze each aliquot according to procedures beginning in Section 11.0.

10.3.2 The glyphosate recovery (R) values determined in Section 10.3.1 should be within ±30% of the R values listed in Table 2 for at least three of four consecutive samples. The relative standard deviation (Sr) of the mean recovery (R) should be less than 30%. If the analyte of interest meets the acceptance criterion, performance is judged acceptable and sample analysis may begin. For analytes that fail this criterion, initial demonstration procedures should be repeated.

10.3.3 The initial demonstration of capability is used primarily to preclude a laboratory from analyzing unknown samples via a new, unfamiliar method prior to obtaining some experience with it. It is expected that as laboratory personnel gain experience with this method the quality of the data will improve beyond the requirements stated in Section 10.3.2.

10.4 The analyst is permitted to modify HPLC column, HPLC conditions, or detectors to improve separations or lower analytical costs. Each time such method modifications are made, the analyst must repeat the procedures in Section 10.3.

10.5 Laboratory Fortified Blanks (LFB)

10.5.1 The laboratory must analyze at least one LFB sample per sample set (all samples analyzed within a 24-hour period). The fortified concentration of glyphosate in the LFB should be 10 times the MDL. Calculate accuracy as percent recovery (R). If R falls outside the control limits (See Section 10.5.2.), the analysis is judged out of control, and the source of the problem must be identified and resolved before continuing analyses.

10.5.2 Until sufficient data become available from within their own laboratory, usually a minimum of results from 20-30 analyses, the laboratory should assess laboratory performance against the control limits in Section 10.3.2. When sufficient internal performance data become available, develop control limits from the mean percent recovery (R) and S_R of the percent recovery. These data are used to establish upper and lower control limits as follows:

UPPER CONTROL LIMIT = $R + 3S_R$
LOWER CONTROL LIMIT = $X - 3S_R$

After each 5-10 new recovery measurements, new control limits should be calculated using only the most recent 20-30 data points.

$$C\ (\mu g/L) = \frac{A}{RF}$$

where: A = Area of glyphosate peak in sample.
RF = Response factor derived from calibration data.

12.2 For samples processed as part of a set where laboratory fortified blank and/or laboratory fortified matrix recoveries fall outside control limits in Sections 10.5 and 10.6, data for the affected samples must be labeled as suspect.

13.0 METHOD PERFORMANCE

13.1 Method Detection Limits (MDL) -- The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above the background level[2]. The concentrations listed in Table 1 were obtained using reagent water, ground water and dechlorinated tap water.

13.2 Single-laboratory precision and accuracy results at several concentrations in drinking water matrices are presented in Table 2.

14.0 REFERENCES

1. Bashe, W.J., Baker, T.V. "Analysis of Glyphosate in Drinking Water by Direct Aqueous Injection HPLC with Post Column Derivatization," in preparation, Technology Applications, Inc., 1988.

2. Glaser, J.A., Foerst, D.L., McKee, G.M., Quave, S.A., and Budde, W.L. "Trace Analyses for Wastewaters", Environ. Sci. Technol., 15, 1426, 1981.

3. Cowell, J.E. "Analytical Residue Method for N-phosphonomethyl Glycine and Aminomethyl phosphonic Acid in Environmental Water," Monsanto Company, Method Number 86-63-1, 1987.

4. ASTM Annual Book of Standards, Part 31, D3694, "Standard Practice for Preparation of Sample Containers and for Preservation, "American Society for Testing and Materials, Philadelphia, PA, p. 679, 1980.

5. "OSHA Safety and Health Standards, General Industry," (29 CRF 1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

6. ASTM Annual Book of Standards, Part II, Volume 11.01, D3370-82, "Standard Practice for Sampling Water", American Society for Testing and Materials, Philadelphia, PA, 1986.

11.2.3 Filter samples using 0.45 µ Acrodisc filters (Section 6.5.2) and inject 200 µL of sample into the HPLC-PCR system for analysis.

11.2.4 Record resulting peak sizes in area units.

11.2.5 If the response for a glyphosate peak in a sample chromatogram exceeds the working calibration range, dilute the sample with reagent water and reanalyze.

11.2.6 Some changes in analyte retention time may be observed following the analysis of matrices with moderate to high ionic strength. The equilibration of the analytical column with the mobile phase will minimize this problem.

NOTE: The use of alternative analytical columns is mentioned in Section 6.7.2.

11.3 Identification of Analytes

11.3.1 Identify a sample component by comparison of its retention time to the retention time of a reference chromatogram. If the retention time of an unknown compound corresponds, within limits (Section 11.3.2), to the retention time of the standard, then identification is considered positive.

11.3.2 The width of the retention time window used to make identification should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation in retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.3.3 Identification requires expert judgement when sample components are not resolved chromatographically. When peaks obviously represent more then one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), or any time doubt exists over the identification of a peak in a chromatogram, appropriate confirmatory techniques such as use of an alternative detector which operates on a physical/chemical principle different from that originally used, e.g., mass spectrometry, or the use of an alternative separation technology, e.g., anion exchange chromatography, must be employed.

12.0 CALCULATIONS

12.1 Determine the concentration (C) of glyphosate in the sample by direct comparison with the calibration curve described in Section 9.0, or alternatively, by means of the equation below derived from the calibration data.

10.6 Laboratory Fortified Sample Matrix

10.6.1 The laboratory must add a known fortified concentration to a minimum of 10% of the routine samples or one fortified sample per set, whichever is greater. The fortified concentration should not be less then the background concentration of the original sample. Ideally, the fortified concentration should be the same as that used for the laboratory fortified blank (Section 10.5). Over time, samples from all routine samples sources should be fortified.

10.6.2 Calculate the accuracy as R for the analyte, corrected for background concentrations measured in the original sample, and compare these values to the control limits established in Section 10.5.2 from the analyses of LFBs.

10.6.3 If the recovery of any sample falls outside the designated range, and the laboratory performance for the analyte is shown to be in control (Section 10.5), the recovery problem encountered with the dosed sample is judged to be matrix related, not system related. The result for the analyte in the original sample is labeled suspect/matrix to inform the data user that the results are suspect due to matrix effects.

10.7 Quality Control Samples (QCS) -- Each quarter the laboratory should analyze at least one QCS (if available). If criteria provided with the QCS are not met, corrective action should be taken and documented.

10.8 The laboratory may adopt additional quality control practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. For example, field or laboratory duplicates may be analyzed to assess the precision of the environmental measurements or field reagent blanks may be used to assess contamination of samples under site conditions, transportation and storage.

11.0 PROCEDURE

11.1 Sample Cleanup -- The cleanup procedure for this direct aqueous injection HPLC method is limited to the filtration procedure described in Section 11.2.3. Applying only filtration, no interferences were evidenced in the analysis of tap water, ground water and municipal effluent. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must demonstrate that the recovery of the analyte is within limits specified by the method.

11.2 Analysis

11.2.1 Table 1 details the recommended HPLC-PCR operating conditions. An example of the chromatography achieved under these conditions is shown in Figure 2.

11.2.2 Calibrate the system daily as described in Section 9.0.

7. Cowell, J.E. "Storage Stability of Glyphosate in Environmental Water," Monsanto Company, 1988.

TABLE 1. ANALYTICAL CONDITIONS AND METHOD DETECTION LIMITS FOR GLYPHOSATE

Matrix[1]	Retention Time (min)	MDL[2] (µg/L)
RW	13.5	6.00
GW	13.7	8.99
TW-T	11.8	5.99

Conditions:

Column:	250 x 4 mm, Bio-Rad, Aminex A-9 (Specifications as per Subsection 6.7) thermostatted at 65°C.
Mobile Phase:	0.005 M KH_2PO_4 - water:methanol (24:1) buffered at pH = 1.9 (Section 7.0).
Elution Mode:	Isocratic
Flow Rate:	0.5 mL/min
Injection Volume:	200 µL
PCR:	Calcium Hypochlorite flow rate = 0.5 mL/min., OPA solution flow rate = 0.5 mL/min, reactor temperature = 38°C.
Detector:	Excitation wavelength at 340 nm and detection emission at 455 nm.

[1]RW = reagent water,
GW = ground water,
TW-T = tap water spiked after dechlorination treatment.
[2]All MDL data were generated from spiked samples at 25 µg/L.

TABLE 2. RECOVERY OF GLYPHOSATE IN REPRESENTATIVE DRINKING WATER MATRICES

Fortified Concentration (µg/L)	Matrix[1]	Number of Replicates	Mean Recovery %	Relative Standard Deviation %
2500	RW	8	102	1.96
	GW	8	103	1.25
	TW-T	8	99.2	1.74
700	RW	8	101	2.65
	GW	8	98.7	2.01
	TW-T	8	96.4	1.80
250	RW	8	95.6	3.91
	GW	8	101	1.77
	TW-T	8	98.0	1.75
25	RW	8	96.0	9.07
	GW	8	96.0	12.3
	TW-T	8	108	6.57

[1]RW = Reagent water.
GW = Ground water.
TW-T = Tap water spiked after dechlorination treatment.

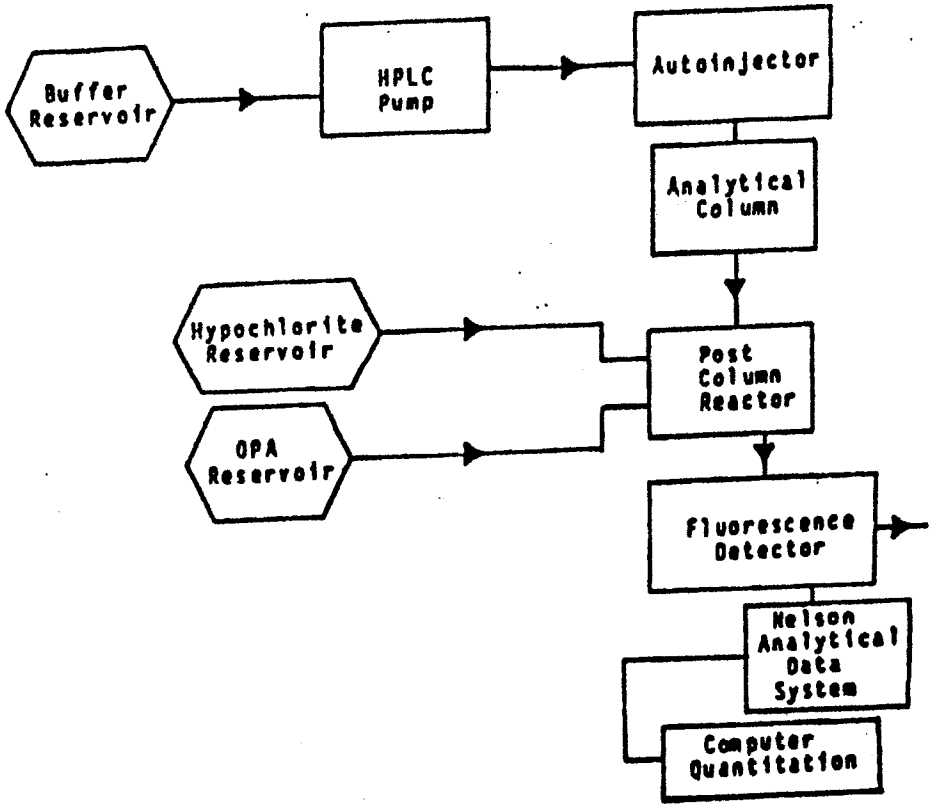

Figure 1. HPLC, Post-Column Reactor System

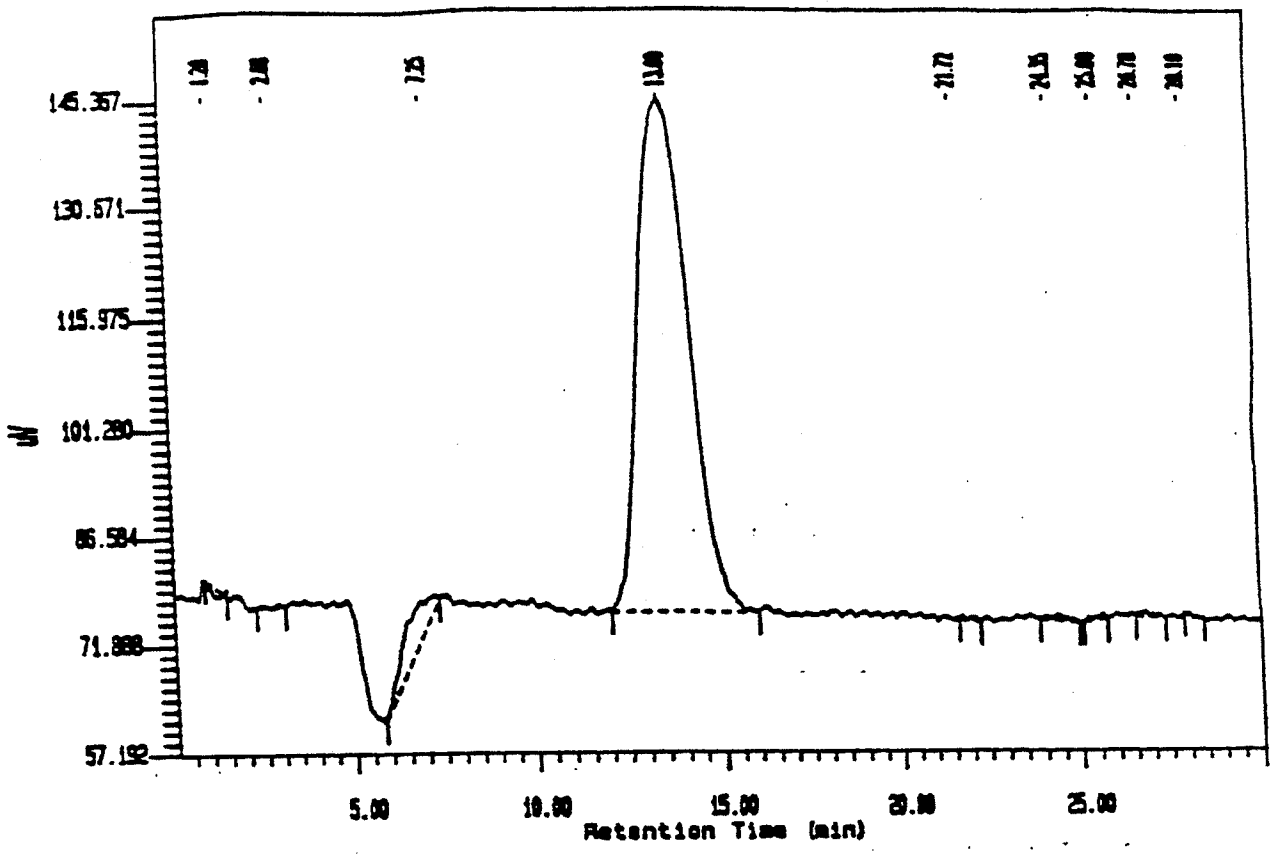

Figure 2. Liquid Chromatogram of glyphosate at 250 ug/L. Conditions are as stated in Table 1.

4500-SO_4^{2-} E. Turbidimetric Method

General Discussion

a. Principle: Sulfate ion (SO_4^{2-}) is precipitated in an acetic acid medium with barium chloride ($BaCl_2$) so as to form barium sulfate ($BaSO_4$) crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the SO_4^{2-} concentration is determined by comparison of the reading with a standard curve.

b. Interference: Color or suspended matter in large amounts will interfere. Some suspended matter may be removed by filtration. If both are small in comparison with the SO_4^{2-} concentration, correct for interference as indicated in ¶ 4*d* below. Silica in excess of 500 mg/L will interfere, and in waters containing large quantities of organic material it may not be possible to precipitate $BaSO_4$ satisfactorily.

In potable waters there are no ions other than SO_4^{2-} that will form insoluble compounds with barium under strongly acid conditions. Make determination at room temperature; variation over a range of 10°C will not cause appreciable error.

c. Minimum detectable concentration: Approximately 1 mg SO_4^{2-}/L.

2. Apparatus

a. Magnetic stirrer: Use a constant stirring speed. It is convenient to incorporate a fixed resistance in series with the motor erating the magnetic stirrer to regulate stirring speed. Use gnets of identical shape and size. The exact speed of stirring ot critical, but keep it constant for each run of samples and standards and adjust it to prevent splashing.

b. Photometer: One of the following is required, with preference in the order given:

1) *Nephelometer.*

2) *Spectrophotometer,* for use at 420 nm, providing a light path of 2.5 to 10 cm.

3) *Filter photometer,* equipped with a violet filter having maximum transmittance near 420 nm and providing a light path of 2.5 to 10 cm.

c. Stopwatch or electric timer.

d. Measuring spoon, capacity 0.2 to 0.3 mL.

3. Reagents

a. Buffer solution A: Dissolve 30 g magnesium chloride, $MgCl_2 \cdot 6H_2O$, 5 g sodium acetate, $CH_3COONa \cdot 3H_2O$, 1.0 g potassium nitrate, KNO_3, and 20 mL acetic acid, CH_3COOH (99%), in 500 mL distilled water and make up to 1000 mL.

b. Buffer solution B (required when the sample SO_4^{2-} concentration is less than 10 mg/L): Dissolve 30 g $MgCl_2 \cdot 6H_2O$, 5 g $CH_3COONa \cdot 3H_2O$, 1.0 g KNO_3, 0.111 g sodium sulfate, Na_2SO_4, and 20 mL acetic acid (99%) in 500 mL distilled water and make up to 1000 mL.

c. Barium chloride, $BaCl_2$, crystals, 20 to 30 mesh. In standardization, uniform turbidity is produced with this mesh range d the appropriate buffer.

l. Standard sulfate solution: Prepare a standard sulfate solution as described in 1) or 2) below; 1.00 mL = 100 µg SO_4^{2-}.

1) Dilute 10.4 mL standard 0.0200*N* H_2SO_4 titrant specified in Alkalinity, Section 2320B.3*c*, to 100 mL with distilled water.

2) Dissolve 0.1479 g anhydrous Na_2SO_4 in distilled water and dilute to 1000 mL.

4. Procedure

a. Formation of barium sulfate turbidity: Measure 100 mL sample, or a suitable portion made up to 100 mL, into a 250-mL erlenmeyer flask. Add 20 mL buffer solution and mix in stirring apparatus. While stirring, add a spoonful of $BaCl_2$ crystals and begin timing immediately. Stir for 60 ± 2 s at constant speed.

b. Measurement of barium sulfate turbidity: After stirring period has ended, pour solution into absorption cell of photometer and measure turbidity at 5 ± 0.5 min.

c. Preparation of calibration curve: Estimate SO_4^{2-} concentration in sample by comparing turbidity reading with a calibration curve prepared by carrying SO_4^{2-} standards through the entire procedure. Space standards at 5-mg/L increments in the 0- to 40-mg/L SO_4^{2-} range. Above 40 mg/L accuracy decreases and $BaSO_4$ suspensions lose stability. Check reliability of calibration curve by running a standard with every three or four samples.

d. Correction for sample color and turbidity: Correct for sample color and turbidity by running blanks to which $BaCl_2$ is not added.

5. Calculation

$$\text{mg } SO_4^{2-}/\text{L} = \frac{\text{mg } SO_4^{2-} \times 1000}{\text{mL sample}}$$

If buffer solution A was used, determine SO_4^{2-} concentration directly from the calibration curve after subtracting sample absorbance before adding $BaCl_2$. If buffer solution B was used subtract SO_4^{2-} concentration of blank from apparent SO_4^{2-} concentration as determined above; because the calibration curve is not a straight line, this is not equivalent to subtracting blank absorbance from sample absorbance.

6. Precision and Bias

With a turbidimeter,* in a single laboratory with a sample having a mean of 7.45 mg SO_4^{2-}/L, a standard deviation of 0.13 mg/L and a coefficient of variation of 1.7% were obtained. Two samples dosed with sulfate gave recoveries of 85 and 91%.

7. Bibliography

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* Hach 2100 A.

METHOD 8260B

VOLATILE ORGANIC COMPOUNDS BY GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS)

1.0 SCOPE AND APPLICATION

1.1 Method 8260 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Preparation Technique[a]					
Compound	CAS No.[b]	5030/ 5035	5031	5032	5021	5041	Direct Inject.
Acetone	67-64-1	pp	c	c	nd	c	c
Acetonitrile	75-05-8	pp	c	nd	nd	nd	c
Acrolein (Propenal)	107-02-8	pp	c	c	nd	nd	c
Acrylonitrile	107-13-1	pp	c	c	nd	c	c
Allyl alcohol	107-18-6	ht	c	nd	nd	nd	c
Allyl chloride	107-05-1	c	nd	nd	nd	nd	c
Benzene	71-43-2	c	nd	c	c	c	c
Benzyl chloride	100-44-7	c	nd	nd	nd	nd	c
Bis(2-chloroethyl)sulfide	505-60-2	pp	nd	nd	nd	nd	c
Bromoacetone	598-31-2	pp	nd	nd	nd	nd	c
Bromochloromethane	74-97-5	c	nd	c	c	c	c
Bromodichloromethane	75-27-4	c	nd	c	c	c	c
4-Bromofluorobenzene (surr)	460-00-4	c	nd	c	c	c	c
Bromoform	75-25-2	c	nd	c	c	c	c
Bromomethane	74-83-9	c	nd	c	c	c	c
n-Butanol	71-36-3	ht	c	nd	nd	nd	c
2-Butanone (MEK)	78-93-3	pp	c	c	nd	nd	c
t-Butyl alcohol	75-65-0	pp	c	nd	nd	nd	c
Carbon disulfide	75-15-0	pp	nd	c	nd	c	c
Carbon tetrachloride	56-23-5	c	nd	c	c	c	c
Chloral hydrate	302-17-0	pp	nd	nd	nd	nd	c
Chlorobenzene	108-90-7	c	nd	c	c	c	c
Chlorobenzene-d_5 (IS)		c	nd	c	c	c	c
Chlorodibromomethane	124-48-1	c	nd	c	nd	c	c
Chloroethane	75-00-3	c	nd	c	c	c	c
2-Chloroethanol	107-07-3	pp	nd	nd	nd	nd	c
2-Chloroethyl vinyl ether	110-75-8	c	nd	c	nd	nd	c
Chloroform	67-66-3	c	nd	c	c	c	c
Chloromethane	74-87-3	c	nd	c	c	c	c
Chloroprene	126-99-8	c	nd	nd	nd	nd	c
3-Chloropropionitrile	542-76-7	l	nd	nd	nd	nd	pc

(continued)

Acrolein

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Crotonaldehyde	4170-30-3	pp	c	nd	nd	nd	c
1,2-Dibromo-3-chloropropane	96-12-8	pp	nd	nd	c	nd	c
1,2-Dibromoethane	106-93-4	c	nd	nd	c	nd	c
Dibromomethane	74-95-3	c	nd	c	c	c	c
1,2-Dichlorobenzene	95-50-1	c	nd	nd	c	nd	c
1,3-Dichlorobenzene	541-73-1	c	nd	nd	c	nd	c
1,4-Dichlorobenzene	106-46-7	c	nd	nd	c	nd	c
1,4-Dichlorobenzene-d_4 (IS)		c	nd	nd	c	nd	c
cis-1,4-Dichloro-2-butene	1476-11-5	c	nd	c	nd	nd	c
trans-1,4-Dichloro-2-butene	110-57-6	pp	nd	c	nd	nd	c
Dichlorodifluoromethane	75-71-8	c	nd	c	c	nd	c
1,1-Dichloroethane	75-34-3	c	nd	c	c	c	c
1,2-Dichloroethane	107-06-2	c	nd	c	c	c	c
1,2-Dichloroethane-d_4 (surr)		c	nd	c	c	c	c
1,1-Dichloroethene	75-35-4	c	nd	c	c	c	c
trans-1,2-Dichloroethene	156-60-5	c	nd	c	c	c	c
1,2-Dichloropropane	78-87-5	c	nd	c	c	c	c
1,3-Dichloro-2-propanol	96-23-1	pp	nd	nd	nd	nd	c
cis-1,3-Dichloropropene	10061-01-5	c	nd	c	nd	c	c
trans-1,3-Dichloropropene	10061-02-6	c	nd	c	nd	c	c
1,2,3,4-Diepoxybutane	1464-53-5	c	nd	nd	nd	nd	c
Diethyl ether	60-29-7	c	nd	nd	nd	nd	c
1,4-Difluorobenzene (IS)	540-36-3	nd	nd	nd	nd	c	nd
1,4-Dioxane	123-91-1	pp	c	c	nd	nd	c
Epichlorohydrin	106-89-8	l	nd	nd	nd	nd	c
Ethanol	64-17-5	l	c	c	nd	nd	c
Ethyl acetate	141-78-6	l	c	nd	nd	nd	c
Ethylbenzene	100-41-4	c	nd	c	c	c	c
Ethylene oxide	75-21-8	pp	c	nd	nd	nd	c
Ethyl methacrylate	97-63-2	c	nd	c	nd	nd	c
Fluorobenzene (IS)	462-06-6	c	nd	nd	nd	nd	nd
Hexachlorobutadiene	87-68-3	c	nd	nd	c	nd	c
Hexachloroethane	67-72-1	l	nd	nd	nd	nd	c
2-Hexanone	591-78-6	pp	nd	c	nd	nd	c
2-Hydroxypropionitrile	78-97-7	l	nd	nd	nd	nd	pc
Iodomethane	74-88-4	c	nd	c	nd	c	c
Isobutyl alcohol	78-83-1	pp	c	nd	nd	nd	c
Isopropylbenzene	98-82-8	c	nd	nd	c	nd	c
Malononitrile	109-77-3	pp	nd	nd	nd	nd	c
Methacrylonitrile	126-98-7	pp	l	nd	nd	nd	c
Methanol	67-56-1	l	c	nd	nd	nd	c
Methylene chloride	75-09-2	c	nd	c	c	c	c
Methyl methacrylate	80-62-6	c	nd	nd	nd	nd	c
4-Methyl-2-pentanone (MIBK)	108-10-1	pp	c	c	nd	nd	c
Naphthalene	91-20-3	c	nd	nd	c	nd	c

(continued)

Compound	CAS No.[b]	Appropriate Preparation Technique[a] 5030/ 5035	5031	5032	5021	5041	Direct Inject.
Nitrobenzene	98-95-3	c	nd	nd	nd	nd	c
2-Nitropropane	79-46-9	c	nd	nd	nd	nd	c
N-Nitroso-di-n-butylamine	924-16-3	pp	c	nd	nd	nd	c
Paraldehyde	123-63-7	pp	c	nd	nd	nd	c
Pentachloroethane	76-01-7	l	nd	nd	nd	nd	c
2-Pentanone	107-87-9	pp	c	nd	nd	nd	c
2-Picoline	109-06-8	pp	c	nd	nd	nd	c
1-Propanol	71-23-8	pp	c	nd	nd	nd	c
2-Propanol	67-63-0	pp	c	nd	nd	nd	c
Propargyl alcohol	107-19-7	pp	l	nd	nd	nd	c
β-Propiolactone	57-57-8	pp	nd	nd	nd	nd	c
Propionitrile (ethyl cyanide)	107-12-0	ht	c	nd	nd	nd	pc
n-Propylamine	107-10-8	c	nd	nd	nd	nd	c
Pyridine	110-86-1	l	c	nd	nd	nd	c
Styrene	100-42-5	c	nd	c	c	c	c
1,1,1,2-Tetrachloroethane	630-20-6	c	nd	nd	c	c	c
1,1,2,2-Tetrachloroethane	79-34-5	c	nd	c	c	c	c
Tetrachloroethene	127-18-4	c	nd	c	c	c	c
Toluene	108-88-3	c	nd	c	c	c	c
Toluene-d_8 (surr)	2037-26-5	c	nd	c	c	c	c
o-Toluidine	95-53-4	pp	c	nd	nd	nd	c
1,2,4-Trichlorobenzene	120-82-1	c	nd	nd	c	nd	c
1,1,1-Trichloroethane	71-55-6	c	nd	c	c	c	c
1,1,2-Trichloroethane	79-00-5	c	nd	c	c	c	c
Trichloroethene	79-01-6	c	nd	c	c	c	c
Trichlorofluoromethane	75-69-4	c	nd	c	c	c	c
1,2,3-Trichloropropane	96-18-4	c	nd	c	c	c	c
Vinyl acetate	108-05-4	c	nd	c	nd	nd	c
Vinyl chloride	75-01-4	c	nd	c	c	c	c
o-Xylene	95-47-6	c	nd	c	c	c	c
m-Xylene	108-38-3	c	nd	c	c	c	c
p-Xylene	106-42-3	c	nd	c	c	c	c

[a] See Sec. 1.2 for other appropriate sample preparation techniques
[b] Chemical Abstract Service Registry Number

c = Adequate response by this technique
ht = Method analyte only when purged at 80°C
nd = Not determined
l = Inappropriate technique for this analyte
pc = Poor chromatographic behavior
pp = Poor purging efficiency resulting in high Estimated Quantitation Limits
surr = Surrogate
IS = Internal Standard

1.2 There are various techniques by which these compounds may be introduced into the GC/MS system. The more common techniques are listed in the table above. Purge-and-trap, by Methods 5030 (aqueous samples) and 5035 (solid and waste oil samples), is the most commonly used technique for volatile organic analytes. However, other techniques are also appropriate and necessary for some analytes. These include direct injection following dilution with hexadecane (Method 3585) for waste oil samples; automated static headspace by Method 5021 for solid samples; direct injection of an aqueous sample (concentration permitting) or injection of a sample concentrated by azeotropic distillation (Method 5031); and closed system vacuum distillation (Method 5032) for aqueous, solid, oil and tissue samples. For air samples, Method 5041 provides methodology for desorbing volatile organics from trapping media (Methods 0010, 0030, and 0031). In addition, direct analysis utilizing a sample loop is used for sub-sampling from Tedlar® bags (Method 0040). Method 5000 provides more general information on the selection of the appropriate introduction method.

1.3 Method 8260 can be used to quantitate most volatile organic compounds that have boiling points below 200°C. Volatile, water soluble compounds can be included in this analytical technique by the use of azeotropic distillation or closed-system vacuum distillation. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides. See Tables 1 and 2 for analytes and retention times that have been evaluated on a purge-and-trap GC/MS system. Also, the method detection limits for 25-mL sample volumes are presented. The following compounds are also amenable to analysis by Method 8260:

Bromobenzene
n-Butylbenzene
sec-Butylbenzene
tert-Butylbenzene
Chloroacetonitrile
1-Chlorobutane
1-Chlorohexane
2-Chlorotoluene
4-Chlorotoluene
Dibromofluoromethane
cis-1,2-Dichloroethene
1,3-Dichloropropane
2,2-Dichloropropane
1,1-Dichloropropene
p-Isopropyltoluene
Methyl acrylate
Methyl-t-butyl ether
Pentafluorobenzene
n-Propylbenzene
1,2,3-Trichlorobenzene
1,2,4-Trimethylbenzene
1,3,5-Trimethylbenzene

1.4 The estimated quantitation limit (EQL) of Method 8260 for an individual compound is somewhat instrument dependent and also dependent on the choice of sample preparation/introduction method. Using standard quadrapole instrumentation and the purge-and-trap technique, limits should be approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for ground water (see Table 3). Somewhat lower limits may be achieved using an ion trap mass spectrometer or other instrumentation of improved design. No matter which instrument is used, EQLs will be proportionately higher for sample extracts and samples that require dilution or when a reduced sample size is used to avoid saturation of the detector.

1.5 This method is restricted to use by, or under the supervision of, analysts experienced in the use of gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

2.0 SUMMARY OF METHOD

2.1 The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by other methods (see Sec. 1.2). The analytes are introduced directly to a wide-bore capillary column or cryofocussed on a capillary pre-column before being flash evaporated to a narrow-bore capillary for analysis. The column is temperature-programmed to separate the analytes, which are then detected with a mass spectrometer (MS) interfaced to the gas chromatograph (GC).

2.2 Analytes eluted from the capillary column are introduced into the mass spectrometer via a jet separator or a direct connection. (Wide-bore capillary columns normally require a jet separator, whereas narrow-bore capillary columns may be directly interfaced to the ion source). Identification of target analytes is accomplished by comparing their mass spectra with the electron impact (or electron impact-like) spectra of authentic standards. Quantitation is accomplished by comparing the response of a major (quantitation) ion relative to an internal standard using a five-point calibration curve.

2.3 The method includes specific calibration and quality control steps that supersede the general requirements provided in Method 8000.

3.0 INTERFERENCES

3.1 Major contaminant sources are volatile materials in the laboratory and impurities in the inert purging gas and in the sorbent trap. The use of non-polytetrafluoroethylene (PTFE) thread sealants, plastic tubing, or flow controllers with rubber components should be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. Analyses of calibration and reagent blanks provide information about the presence of contaminants. When potential interfering peaks are noted in blanks, the analyst should change the purge gas source and regenerate the molecular sieve purge gas filter. Subtracting blank values from sample results is not permitted. If reporting values without correcting for the blank results in what the laboratory feels is a false positive result for a sample, the laboratory should fully explained this in text accompanying the uncorrected data.

3.2 Contamination may occur when a sample containing low concentrations of volatile organic compounds is analyzed immediately after a sample containing high concentrations of volatile organic compounds. A technique to prevent this problem is to rinse the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After the analysis of a sample containing high concentrations of volatile organic compounds, one or more blanks should be analyzed to check for cross-contamination. Alternatively, if the sample immediately following the high concentration sample does not contain the volatile organic compounds present in the high level sample, freedom from contamination has been established.

3.3 For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high concentrations of compounds being determined, it may be necessary to wash the purging device with a soap solution, rinse it with organic-free reagent water, and then dry the purging device in an oven at 105°C. In extreme situations, the entire purge-and-trap device may require dismantling and cleaning. Screening of the samples prior to purge-and-trap GC/MS analysis is highly recommended to prevent contamination of the system. This is especially true for soil and waste samples. Screening may be accomplished with an automated headspace technique (Method 5021) or by Method 3820 (Hexadecane Extraction and Screening of Purgeable Organics).

3.4 Many analytes exhibit low purging efficiencies from a 25-mL sample. This often results in significant amounts of these analytes remaining in the sample purge vessel after analysis. After removal of the sample aliquot that was purged, and rinsing the purge vessel three times with organic-free water, the empty vessel should be subjected to a heated purge cycle prior to the analysis of another sample in the same purge vessel. This will reduce sample-to-sample carryover.

3.5 Special precautions must be taken to analyze for methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride. Otherwise, random background levels will result. Since methylene chloride will permeate through PTFE tubing, all gas chromatography carrier gas lines and purge gas plumbing should be constructed from stainless steel or copper tubing. Laboratory clothing worn by the analyst should be clean, since clothing previously exposed to methylene chloride fumes during liquid/liquid extraction procedures can contribute to sample contamination.

3.6 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample container into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling, handling, and storage protocols can serve as a check on such contamination.

3.7 Use of sensitive mass spectrometers to achieve lower detection level will increase the potential to detect laboratory contaminants as interferences.

3.8 Direct injection - Some contamination may be eliminated by baking out the column between analyses. Changing the injector liner will reduce the potential for cross-contamination. A portion of the analytical column may need to be removed in the case of extreme contamination. The use of direct injection will result in the need for more frequent instrument maintenance.

3.9 If hexadecane is added to waste samples or petroleum samples that are analyzed, some chromatographic peaks will elute after the target analytes. The oven temperature program must include a post-analysis bake out period to ensure that semivolatile hydrocarbons are volatilized.

4.0 APPARATUS AND MATERIALS

4.1 Purge-and-trap device for aqueous samples - Described in Method 5030.

4.2 Purge-and-trap device for solid samples - Described in Method 5035.

4.3 Automated static headspace device for solid samples - Described in Method 5021.

4.4 Azeotropic distillation apparatus for aqueous and solid samples - Described in Method 5031.

4.5 Vacuum distillation apparatus for aqueous, solid and tissue samples - Described in Method 5032.

4.6 Desorption device for air trapping media for air samples - Described in Method 5041.

4.7 Air sampling loop for sampling from Tedlar® bags for air samples - Described in Method 0040.

4.8 Injection port liners (HP Catalog #18740-80200, or equivalent) - modified for direct injection analysis by placing a 1-cm plug of glass wool approximately 50-60 mm down the length of the injection port towards the oven (see illustration below). A 0.53-mm ID column is mounted 1 cm into the liner from the oven side of the injection port, according to manufacturer's specifications.

4.9 Gas chromatography/mass spectrometer/data system

4.9.1 Gas chromatograph - An analytical system complete with a temperature-programmable gas chromatograph suitable for splitless injection with appropriate interface for sample introduction device. The system includes all required accessories, including syringes, analytical columns, and gases.

4.9.1.1 The GC should be equipped with variable constant differential flow controllers so that the column flow rate will remain constant throughout desorption and temperature program operation.

4.9.1.2 For some column configurations, the column oven must be cooled to less than 30°C, therefore, a subambient oven controller may be necessary.

4.9.1.3 The capillary column is either directly coupled to the source or interfaced through a jet separator, depending on the size of the capillary and the requirements of the GC/MS system.

4.9.1.4 Capillary pre-column interface - This device is the interface between the sample introduction device and the capillary gas chromatograph, and is necessary when using cryogenic cooling. The interface condenses the desorbed sample components and focuses them into a narrow band on an uncoated fused-silica capillary pre-column. When the interface is flash heated, the sample is transferred to the analytical capillary column.

4.9.1.5 During the cryofocussing step, the temperature of the fused-silica in the interface is maintained at -150°C under a stream of liquid nitrogen. After the desorption period, the interface must be capable of rapid heating to 250°C in 15 seconds or less to complete the transfer of analytes.

4.9.2 Gas chromatographic columns

4.9.2.1 Column 1 - 60 m x 0.75 mm ID capillary column coated with VOCOL (Supelco), 1.5-µm film thickness, or equivalent.

4.9.2.2 Column 2 - 30 - 75 m x 0.53 mm ID capillary column coated with DB-624 (J&W Scientific), Rt_x-502.2 (RESTEK), or VOCOL (Supelco), 3-µm film thickness, or equivalent.

4.9.2.3 Column 3 - 30 m x 0.25 - 0.32 mm ID capillary column coated with 95% dimethyl - 5% diphenyl polysiloxane (DB-5, Rt_x-5, SPB-5, or equivalent), 1-µm film thickness.

4.9.2.4 Column 4 - 60 m x 0.32 mm ID capillary column coated with DB-624 (J&W Scientific), 1.8-µm film thickness, or equivalent.

4.9.3 Mass spectrometer - Capable of scanning from 35 to 300 amu every 2 sec or less, using 70 volts (nominal) electron energy in the electron impact ionization mode. The mass spectrometer must be capable of producing a mass spectrum for 4-Bromofluorobenzene (BFB) which meets all of the criteria in Table 4 when 5-50 ng of the GC/MS tuning standard (BFB) are injected through the GC. To ensure sufficient precision of mass spectral data, the desirable MS scan rate allows acquisition of at least five spectra while a sample component elutes from the GC.

An ion trap mass spectrometer may be used if it is capable of axial modulation to reduce ion-molecule reactions and can produce electron impact-like spectra that match those in the EPA/NIST Library. Because ion-molecule reactions with water and methanol in an ion trap mass spectrometer may produce interferences that coelute with chloromethane and chloroethane, the base peak for both of these analytes will be at m/z 49. This ion should be used as the quantitation ion in this case. The mass spectrometer must be capable of producing a mass spectrum for BFB which meets all of the criteria in Table 3 when 5 or 50 ng are introduced.

4.9.4 GC/MS interface - Two alternatives may be used to interface the GC to the mass spectrometer.

4.9.4.1 Direct coupling, by inserting the column into the mass spectrometer, is generally used for 0.25 - 0.32 mm ID columns.

4.9.4.2 A jet separator, including an all-glass transfer line and glass enrichment device or split interface, is used with a 0.53 mm column.

4.9.4.3 Any enrichment device or transfer line may be used, if all of the performance specifications described in Sec. 8.0 (including acceptable calibration at 50 ng or less) can be achieved. GC/MS interfaces constructed entirely of glass or of glass-lined materials are recommended. Glass may be deactivated by silanizing with dichlorodimethylsilane.

4.9.5 Data system - A computer system that allows the continuous acquisition and storage on machine-readable media of all mass spectra obtained throughout the duration of the chromatographic program must be interfaced to the mass spectrometer. The computer must have software that allows searching any GC/MS data file for ions of a specified mass and plotting such ion abundances versus time or scan number. This type of plot is defined as an Extracted Ion Current Profile (EICP). Software must also be available that allows integrating the abundances in any EICP between specified time or scan-number limits. The most recent version of the EPA/NIST Mass Spectral Library should also be available.

4.10 Microsyringes - 10-, 25-, 100-, 250-, 500-, and 1,000-µL.

4.11 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.12 Syringes - 5-, 10-, or 25-mL, gas-tight with shutoff valve.

4.13 Balance - Analytical, capable of weighing 0.0001 g, and top-loading, capable of weighing 0.1 g.

4.14 Glass scintillation vials - 20-mL, with PTFE-lined screw-caps or glass culture tubes with PTFE-lined screw-caps.

4.15 Vials - 2-mL, for GC autosampler.

4.16 Disposable pipets - Pasteur.

4.17 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.18 Spatula - Stainless steel.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store apart from other solvents.

5.4 Reagent Hexadecane - Reagent hexadecane is defined as hexadecane in which interference is not observed at the method detection limit of compounds of interest. Hexadecane quality is demonstrated through the analysis of a solvent blank injected directly into the GC/MS. The results of such a blank analysis must demonstrate that all interfering volatiles have been removed from the hexadecane.

5.5 Polyethylene glycol, $H(OCH_2CH_2)_nOH$ - Free of interferences at the detection limit of the target analytes.

5.6 Hydrochloric acid (1:1 v/v), HCl - Carefully add a measured volume of concentrated HCl to an equal volume of organic-free reagent water.

5.7 Stock solutions - Stock solutions may be prepared from pure standard materials or purchased as certified solutions. Prepare stock standard solutions in methanol, using assayed liquids or gases, as appropriate.

5.7.1 Place about 9.8 mL of methanol in a 10-mL tared ground-glass-stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.0001 g.

5.7.2 Add the assayed reference material, as described below.

5.7.2.1 Liquids - Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.7.2.2 Gases - To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, or vinyl chloride), fill a 5-mL valved gas-tight syringe with the reference standard to the 5.0 mL mark. Lower the needle to

5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas will rapidly dissolve in the methanol. Standards may also be prepared by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.7.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially-prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.7.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap. Store, with minimal headspace and protected from light, at -10°C or less or as recommended by the standard manufacturer. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.7.5 Frequency of Standard Preparation

5.7.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.7.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.7.6 Preparation of Calibration Standards From a Gas Mixture

An optional calibration procedure involves using a certified gaseous mixture daily, utilizing a commercially-available gaseous analyte mixture of bromomethane, chloromethane, chloroethane, vinyl chloride, dichloro-difluoromethane and trichlorofluoromethane in nitrogen. Mixtures of documented quality are stable for as long as six months without refrigeration. (VOA-CYL III, RESTEK Corporation, Cat. #20194 or equivalent).

5.7.6.1 Before removing the cylinder shipping cap, be sure the valve is completely closed (turn clockwise). The contents are under pressure and should be used in a well-ventilated area.

5.7.6.2 Wrap the pipe thread end of the Luer fitting with PTFE tape. Remove the shipping cap from the cylinder and replace it with the Luer fitting.

5.7.6.3 Transfer half the working standard containing other analytes, internal standards, and surrogates to the purge apparatus.

5.7.6.4 Purge the Luer fitting and stem on the gas cylinder prior to sample removal using the following sequence:

a) Connect either the 100-µL or 500-µL Luer syringe to the inlet fitting of the cylinder.

b) Make sure the on/off valve on the syringe is in the open position.

c) Slowly open the valve on the cylinder and withdraw a full syringe volume.

d) Be sure to close the valve on the cylinder before you withdraw the syringe from the Luer fitting.

e) Expel the gas from the syringe into a well-ventilated area.

f) Repeat steps a through e one more time to fully purge the fitting.

5.7.6.5 Once the fitting and stem have been purged, quickly withdraw the volume of gas you require using steps 5.6.6.1.4(a) through (d). Be sure to close the valve on the cylinder and syringe before you withdraw the syringe from the Luer fitting.

5.7.6.6 Open the syringe on/off valve for 5 seconds to reduce the syringe pressure to atmospheric pressure. The pressure in the cylinder is ~30 psi.

5.7.6.7 The gas mixture should be quickly transferred into the reagent water through the female Luer fitting located above the purging vessel.

NOTE: Make sure the arrow on the 4-way valve is pointing toward the female Luer fitting when transferring the sample from the syringe. Be sure to switch the 4-way valve back to the closed position before removing the syringe from the Luer fitting.

5.7.6.8 Transfer the remaining half of the working standard into the purging vessel. This procedure insures that the total volume of gas mix is flushed into the purging vessel, with none remaining in the valve or lines.

5.7.6.9 The concentration of each compound in the cylinder is typically 0.0025 µg/µL.

5.7.6.10 The following are the recommended gas volumes spiked into 5 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
40 µL	20 µg/L
100 µL	50 µg/L
200 µL	100 µg/L
300 µL	150 µg/L
400 µL	200 µg/L

5.7.6.11 The following are the recommended gas volumes spiked into 25 mL of water to produce a typical 5-point calibration:

Gas Volume	Calibration Concentration
10 µL	1 µg/L
20 µL	2 µg/L
50 µL	5 µg/L
100 µL	10 µg/L
250 µL	25 µg/L

5.8 Secondary dilution standards - Using stock standard solutions, prepare secondary dilution standards in methanol containing the compounds of interest, either singly or mixed together. Secondary dilution standards must be stored with minimal headspace and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Store in a vial with no headspace. Replace after one week. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.7.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.9 Surrogate standards - The recommended surrogates are toluene-d_8, 4-bromofluorobenzene, 1,2-dichloroethane-d_4, and dibromofluoromethane. Other compounds may be used as surrogates, depending upon the analysis requirements. A stock surrogate solution in methanol should be prepared as described above, and a surrogate standard spiking solution should be prepared from the stock at a concentration of 50-250 µg/10 mL, in methanol. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute surrogate solutions may be required.

5.10 Internal standards - The recommended internal standards are fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4. Other compounds may be used as internal standards as long as they have retention times similar to the compounds being detected by GC/MS. Prepare internal standard stock and secondary dilution standards in methanol using the procedures described in Secs. 5.7 and 5.8. It is recommended that the secondary dilution standard be prepared at a concentration of 25 mg/L of each internal standard compound. Addition of 10 µL of this standard to 5.0 mL of sample or calibration standard would be the equivalent of 50 µg/L. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then more dilute internal standard solutions may be required. Area counts of the internal standard peaks should be between 50-200% of the areas of the target analytes in the mid-point calibration analysis.

5.11 4-Bromofluorobenzene (BFB) standard - A standard solution containing 25 ng/µL of BFB in methanol should be prepared. If a more sensitive mass spectrometer is employed to achieve lower detection levels, then a more dilute BFB standard solution may be required.

5.12 Calibration standards -There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.12.1 Initial calibration standards should be prepared at a minimum of five different concentrations from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC/MS system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve.

5.12.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.7 and 5.8) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.4 for guidance on calibration verification.

5.12.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.12.4 The calibration standards must also contain the internal standards chosen for the analysis.

5.13 Matrix spiking and laboratory control sample (LCS) standards - Matrix spiking standards should be prepared from volatile organic compounds which are representative of the compounds being investigated. At a minimum, the matrix spike should include 1,1-dichloroethene, trichloroethene, chlorobenzene, toluene, and benzene. The matrix spiking solution should contain compounds that are expected to be found in the types of samples to be analyzed.

5.13.1 Some permits may require the spiking of specific compounds of interest, especially if polar compounds are a concern, since the spiking compounds listed above would not be representative of such compounds. The standard should be prepared in methanol, with each compound present at a concentration of 250 µg/10.0 mL.

5.13.2 The spiking solutions should not be prepared from the same standards as the calibration standards. However, the same spiking standard prepared for the matrix spike may be used for the LCS.

5.13.3 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking solutions may be required.

5.14 Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10°C or less, in amber bottles with PTFE-lined screw-caps.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Various alternative methods are provided for sample introduction. All internal standards, surrogates, and matrix spiking compounds (when applicable) must be added to the samples before introduction into the GC/MS system. Consult the sample introduction method for the procedures by which to add such standards.

7.1.1 Direct injection - This includes: injection of an aqueous sample containing a very high concentration of analytes; injection of aqueous concentrates from Method 5031 (azeotropic distillation); and injection of a waste oil diluted 1:1 with hexadecane (Method 3585). Direct injection of aqueous samples (non-concentrated) has very limited applications. It is only used for the determination of volatiles at the toxicity characteristic (TC) regulatory limits or at concentrations in excess of 10,000 µg/L. It may also be used in conjunction with the test for ignitability in aqueous samples (along with Methods 1010 and 1020), to determine if alcohol is present at greater than 24%.

7.1.2 Purge-and-trap - This includes purge-and-trap for aqueous samples (Method 5030) and purge-and-trap for solid samples (Method 5035). Method 5035 also provides techniques for extraction of high concentration solid and oily waste samples by methanol (and other water-miscible solvents) with subsequent purge-and-trap from an aqueous matrix using Method 5030.

7.1.2.1 Traditionally, the purge-and-trap of aqueous samples is performed at ambient temperature, while purging of soil/solid samples is performed at 40°C, to improve purging efficiency.

7.1.2.2 Aqueous and soil/solid samples may also be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature, appropriate trapping material is used to handle the excess water, and the laboratory demonstrates acceptable method performance for the project. Purging of aqueous samples at elevated temperatures (e.g., 40°C) may improve the purging performance of many of the water soluble compounds which have poor purging efficiencies at ambient temperatures.

7.1.3 Vacuum distillation - this technique may be used for the introduction of volatile organics from aqueous, solid, or tissue samples (Method 5032) into the GC/MS system.

7.1.4 Automated static headspace - this technique may be used for the introduction of volatile organics from solid samples (Method 5021) into the GC/MS system.

7.1.5 Cartridge desorption - this technique may be for the introduction of volatile organics from sorbent cartridges (Method 5041) used in the sampling of air. The sorbent cartridges are from the volatile organics sampling train (VOST) or SMVOC (Method 0031).

7.2 Recommended chromatographic conditions

7.2.1 General conditions

Injector temperature:	200 - 225°C
Transfer line temperature:	250 - 300°C

7.2.2 Column 1 and Column 2 with cryogenic cooling (example chromatograms are presented in Figures 1 and 2)

Carrier gas (He) flow rate:	15 mL/min
Initial temperature:	10°C, hold for 5 minutes
Temperature program:	6°C/min to 70°C, then 15°C/min to 145°C
Final temperature:	145°C, hold until all expected compounds have eluted.

7.2.5 Direct injection - Column 2

Carrier gas (He) flow rate:	4 mL/min
Column:	J&W DB-624, 70m x 0.53 mm
Initial temperature:	40°C, hold for 3 minutes
Temperature program:	8°C/min
Final temperature:	260°C, hold until all expected compounds have eluted.
Column Bake out:	75 minutes
Injector temperature:	200-225°C
Transfer line temperature:	250-300°C

7.2.6 Direct split interface - Column 4

Carrier gas (He) flow rate:	1.5 mL/min
Initial temperature:	35°C, hold for 2 minutes
Temperature program:	4°C/min to 50°C 10°C/min to 220°C
Final temperature:	220°C, hold until all expected compounds have eluted
Split ratio:	100:1
Injector temperature:	125°C

7.3 Initial calibration

Establish the GC/MS operating conditions, using the following as guidance:

Mass range:	35 - 260 amu
Scan time:	0.6 - 2 sec/scan
Source temperature:	According to manufacturer's specifications
Ion trap only:	Set axial modulation, manifold temperature, and emission current to manufacturer's recommendations

7.3.1 Each GC/MS system must be hardware-tuned to meet the criteria in Table 4 for a 5-50 ng injection or purging of 4-bromofluorobenzene (2-µL injection of the BFB standard). Analyses must not begin until these criteria are met.

7.3.1.1 In the absence of specific recommendations on how to acquire the mass spectrum of BFB from the instrument manufacturer, the following approach has been shown to be useful: The mass spectrum of BFB may be acquired in the following manner. Three scans (the peak apex scan and the scans immediately preceding and following the apex) are acquired and averaged. Background subtraction is required, and must be accomplished using a single scan no more than 20 scans prior to the elution of

BFB. Do not background subtract part of the BFB peak. Alternatively, the analyst may use other documented approaches suggested by the instrument manufacturer.

7.3.1.2 Use the BFB mass intensity criteria in Table 4 as tuning acceptance criteria. Alternatively, other documented tuning criteria may be used (e.g., CLP, Method 524.2, or manufacturer's instructions), provided that method performance is not adversely affected.

NOTE: All subsequent standards, samples, MS/MSDs, LCSs, and blanks associated with a BFB analysis must use identical mass spectrometer instrument conditions.

7.3.2 Set up the sample introduction system as outlined in the method of choice (see Sec. 7.1). A different calibration curve is necessary for each method because of the differences in conditions and equipment. A set of at least five different calibration standards is necessary (see Sec. 5.12 and Method 8000). Calibration must be performed using the sample introduction technique that will be used for samples. For Method 5030, the purging efficiency for 5 mL of water is greater than for 25 mL. Therefore, develop the standard curve with whichever volume of sample that will be analyzed.

7.3.2.1 To prepare a calibration standard, add an appropriate volume of a secondary dilution standard solution to an aliquot of organic-free reagent water in a volumetric flask. Use a microsyringe and rapidly inject the alcoholic standard into the expanded area of the filled volumetric flask. Remove the needle as quickly as possible after injection. Mix by inverting the flask three times only. Discard the contents contained in the neck of the flask. Aqueous standards are not stable and should be prepared daily. Transfer 5.0 mL (or 25 mL if lower detection limits are required) of each standard to a gas tight syringe along with 10 µL of internal standard. Then transfer the contents to the appropriate device or syringe. Some of the introduction methods may have specific guidance on the volume of calibration standard and the way the standards are transferred to the device.

7.3.2.2 The internal standards selected in Sec. 5.10 should permit most of the components of interest in a chromatogram to have retention times of 0.80 - 1.20, relative to one of the internal standards. Use the base peak ion from the specific internal standard as the primary ion for quantitation (see Table 1). If interferences are noted, use the next most intense ion as the quantitation ion.

7.3.2.3 To prepare a calibration standard for direct injection analysis of waste oil, dilute standards in hexadecane.

7.3.3 Proceed with the analysis of the calibration standards following the procedure in the introduction method of choice. For direct injection, inject 1 - 2 µL into the GC/MS system. The injection volume will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water.

7.3.4 Tabulate the area response of the characteristic ions (see Table 5) against the concentration for each target analyte and each internal standard. Calculate response factors (RF) for each target analyte relative to one of the internal standards. The internal standard selected for the calculation of the RF for a target analyte should be the internal standard that has a retention time closest to the analyte being measured (Sec. 7.6.2).

The RF is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s}$$

where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.
C_s = Concentration of the analyte or surrogate.
C_{is} = Concentration of the internal standard.

7.3.5 System performance check compounds (SPCCs) - Calculate the mean RF for each target analyte using the five RF values calculated from the initial (5-point) calibration curve. A system performance check should be made before this calibration curve is used. Five compounds (the System Performance Check Compounds, or SPCCs) are checked for a minimum average response factor. These compounds are chloromethane; 1,1-dichloroethane; bromoform; chlorobenzene; and 1,1,2,2-tetrachloroethane. These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system. Example problems include:

7.3.5.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.3.5.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response. Response of the quantitation ion (m/z 173) is directly affected by the tuning of BFB at ions m/z 174/176. Increasing the m/z 174/176 ratio relative to m/z 95 may improve bromoform response.

7.3.5.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.3.5.4 The minimum mean response factors for the volatile SPCCs are as follows:

Chloromethane	0.10
1,1-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2-Tetrachloroethane	0.30

7.3.6 Calibration check compounds (CCCs)

7.3.6.1 The purpose of the CCCs are to evaluate the calibration from the standpoint of the integrity of the system. High variability for these compounds may be indicative of system leaks or reactive sites on the column. Meeting the CCC criteria is not a substitute for successful calibration of the target analytes using one of the approaches described in Sec. 7.0 of Method 8000.

7.3.6.2 Calculate the standard deviation (SD) and relative standard deviation (RSD) of the response factors for all target analytes from the initial calibration, as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RF_i - \overline{RF})^2}{n-1}} \qquad RSD = \frac{SD}{\overline{RF}} \times 100$$

where:

RF_i = RF for each of the calibration standards
$\overline{RF}$ = mean RF for each compound from the initial calibration
n = Number of calibration standards, e.g., 5

7.3.6.3 The RSD should be less than or equal to 15% for each target analyte. However, the RSD for each individual Calibration Check Compound (CCC) must be equal or less than 30%. If the CCCs are not included in the list of analytes for a project, and therefore not included in the calibration standards, refer to Sec. 7.0 of Method 8000. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

7.3.6.4 If an RSD of greater than 30% is measured for any CCC, then corrective action to eliminate a system leak and/or column reactive sites is necessary before reattempting calibration.

7.3.7 Evaluation of retention times - The relative retention times of each target analyte in each calibration standard should agree within 0.06 relative retention time units. Late-eluting compounds usually have much better agreement.

7.3.8 Linearity of target analytes

7.3.8.1 If the RSD of any target analyte is 15% or less, then the response factor is assumed to be constant over the calibration range, and the average response factor may be used for quantitation (Sec. 7.7.2).

7.3.8.2 If the RSD of any target analyte is greater than 15%, refer to Sec. 7.0 of Method 8000 for additional calibration options. One of the options must be applied to GC/MS calibration in this situation, or a new initial calibration must be performed.

NOTE: Method 8000 specifies a linearity criterion of 20% RSD. That criterion pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD as evidence of sufficient linearity to employ an average response factor.

7.3.8.3 When the RSD exceeds 15%, the plotting and visual inspection of a calibration curve can be a useful diagnostic tool. The inspection may indicate analytical problems, including errors in standard preparation, the presence of active sites in the chromatographic system, analytes that exhibit poor chromatographic behavior, etc.

NOTE: The 20% RSD criteria in Method 8000 pertains to GC and HPLC methods other than GC/MS. Method 8260 requires 15% RSD.

7.4 GC/MS calibration verification - Calibration verification consists of three steps that are performed at the beginning of each 12-hour analytical shift.

7.4.1 Prior to the analysis of samples or calibration standards, inject or introduce 5-50 ng of the 4-bromofluorobenzene standard into the GC/MS system. The resultant mass spectra for the BFB must meet the criteria given in Table 4 before sample analysis begins. These criteria must be demonstrated each 12-hour shift during which samples are analyzed.

7.4.2 The initial calibration curve (Sec. 7.3) for each compound of interest should be verified once every 12 hours prior to sample analysis, using the introduction technique used for samples. This is accomplished by analyzing a calibration standard at a concentration near the midpoint concentration for the calibrating range of the GC/MS. The results from the calibration standard analysis should meet the verification acceptance criteria provided in Secs. 7.4.4 through 7.4.7.

NOTE: The BFB and calibration verification standard may be combined into a single standard as long as both tuning and calibration verification acceptance criteria for the project can be met without interferences.

7.4.3 A method blank should be analyzed after the calibration standard, or at any other time during the analytical shift, to ensure that the total system (introduction device, transfer lines and GC/MS system) is free of contaminants. If the method blank indicates contamination, then it may be appropriate to analyze a solvent blank to demonstrate that the contamination is not a result of carryover from standards or samples. See Sec. 8.0 of Method 8000 for method blank performance criteria.

7.4.4 System Performance Check Compounds (SPCCs)

7.4.4.1 A system performance check must be made during every 12-hour analytical shift. Each SPCC compound in the calibration verification standard must meet its minimum response factor (see Sec. 7.3.5.4). This is the same check that is applied during the initial calibration.

7.4.4.2 If the minimum response factors are not met, the system must be evaluated, and corrective action must be taken before sample analysis begins. Possible problems include standard mixture degradation, injection port inlet contamination, contamination at the front end of the analytical column, and active sites in the column or chromatographic system. This check must be met before sample analysis begins.

7.4.5 Calibration Check Compounds (CCCs)

7.4.5.1 After the system performance check is met, the CCCs listed in Sec. 7.3.6 are used to check the validity of the initial calibration. Use percent difference when performing the average response factor model calibration. Use percent drift when calibrating using a regression fit model. Refer to Sec. 7.0 of Method 8000 for guidance on calculating percent difference and drift.

7.4.5.2 If the percent difference or drift for each CCC is less than or equal to 20%, the initial calibration is assumed to be valid. If the criterion is not met (i.e., greater

than 20% difference or drift), for any one CCC, then corrective action must be taken prior to the analysis of samples. If the CCC's are not included in the list of analytes for a project, and therefore not included in the calibration standards, then all analytes must meet the 20% difference or drift criterion.

7.4.5.3 Problems similar to those listed under SPCCs could affect the CCCs. If the problem cannot be corrected by other measures, a new five-point initial calibration must be generated. The CCC criteria must be met before sample analysis begins.

7.4.6 Internal standard retention time - The retention times of the internal standards in the calibration verification standard must be evaluated immediately after or during data acquisition. If the retention time for any internal standard changes by more than 30 seconds from the that in the mid-point standard level of the most recent initial calibration sequence, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.4.7 Internal standard response - If the EICP area for any of the internal standards in the calibration verification standard changes by a factor of two (-50% to + 100%) from that in the mid-point standard level of the most recent initial calibration sequence, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. When corrections are made, reanalysis of samples analyzed while the system was malfunctioning is required.

7.5 GC/MS analysis of samples

7.5.1 It is highly recommended that the sample be screened to minimize contamination of the GC/MS system from unexpectedly high concentrations of organic compounds. Some of the screening options available utilizing SW-846 methods are automated headspace-GC/FID (Methods 5021/8015), automated headspace-GC/PID/ELCD (Methods 5021/8021), or waste dilution-GC/PID/ELCD (Methods 3585/8021) using the same type of capillary column. When used only for screening purposes, the quality control requirements in the methods above may be reduced as appropriate. Sample screening is particularly important when Method 8260 is used to achieve low detection levels.

7.5.2 BFB tuning criteria and GC/MS calibration verification criteria must be met before analyzing samples.

7.5.3 All samples and standard solutions must be allowed to warm to ambient temperature before analysis. Set up the introduction device as outlined in the method of choice.

7.5.4 The process of taking an aliquot destroys the validity of remaining volume of an aqueous sample for future analysis. Therefore, if only one VOA vial is provided to the laboratory, the analyst should prepare two aliquots for analysis at this time, to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. For aqueous samples, one 20-mL syringe could be used to hold two 5-mL aliquots. If the second aliquot is to be taken from the syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

7.5.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. If lower detection limits are required, use a 25-mL syringe, and adjust the final volume to 25.0 mL.

7.5.6 The following procedure may be used to dilute aqueous samples for analysis of volatiles. All steps must be performed without delays, until the diluted sample is in a gas-tight syringe.

7.5.6.1 Dilutions may be made in volumetric flasks (10- to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilution steps may be necessary for extremely large dilutions.

7.5.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask, and add slightly less than this quantity of organic-free reagent water to the flask.

7.5.6.3 Inject the appropriate volume of the original sample from the syringe into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat above procedure for additional dilutions.

7.5.6.4 Fill a 5-mL syringe with the diluted sample, as described in Sec. 7.5.5.

7.5.7 Compositing aqueous samples prior to GC/MS analysis

7.5.7.1 Add 5 mL of each sample (up to 5 samples are allowed) to a 25-mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe. Larger volumes of a smaller number of samples may be used, provided that equal volumes of each sample are composited.

7.5.7.2 The samples must be cooled to 4°C or less during this step to minimize volatilization losses. Sample vials may be placed in a tray of ice during the processing.

7.5.7.3 Mix each vial well and draw out a 5-mL aliquot with the 25-mL syringe.

7.5.7.4 Once all the aliquots have been combined on the syringe, invert the syringe several times to mix the aliquots. Introduce the composited sample into the instrument, using the method of choice (see Sec. 7.1).

7.5.7.5 If less than five samples are used for compositing, a proportionately smaller syringe may be used, unless a 25-mL sample is to be purged.

7.5.8 Add 10 µL of the surrogate spiking solution and 10 µL of the internal standard spiking solution to each sample either manually or by autosampler. The surrogate and internal standards may be mixed and added as a single spiking solution. The addition of 10 µL of the surrogate spiking solution to 5 mL of aqueous sample will yield a concentration of 50 µg/L of each surrogate standard. The addition of 10 µL of the surrogate spiking solution to 5 g of a non-aqueous sample will yield a concentration of 50 µg/kg of each standard.

If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute surrogate and internal standard solutions may be required.

7.5.9 Add 10 µL of the matrix spike solution (Sec. 5.13) to a 5-mL aliquot of the sample chosen for spiking. Disregarding any dilutions, this is equivalent to a concentration of 50 µg/L of each matrix spike standard.

7.5.9.1 Follow the same procedure in preparing the laboratory control sample (LCS), except the spike is added to a clean matrix. See Sec. 8.4 and Method 5000 for more guidance on the selection and preparation of the matrix spike and the LCS.

7.5.9.2 If a more sensitive mass spectrometer is employed to achieve lower detection levels, more dilute matrix spiking and LCS solutions may be required.

7.5.10 Analyze the sample following the procedure in the introduction method of choice.

7.5.10.1 For direct injection, inject 1 to 2 µL into the GC/MS system. The volume limitation will depend upon the chromatographic column chosen and the tolerance of the specific GC/MS system to water (if an aqueous sample is being analyzed).

7.5.10.2 The concentration of the internal standards, surrogates, and matrix spiking standards (if any) added to the injection aliquot must be adjusted to provide the same concentration in the 1-2 µL injection as would be introduced into the GC/MS by purging a 5-mL aliquot.

NOTE: It may be a useful diagnostic tool to monitor internal standard retention times and responses (area counts) in all samples, spikes, blanks, and standards to effectively check drifting method performance, poor injection execution, and anticipate the need for system inspection and/or maintenance.

7.5.11 If the initial analysis of the sample or a dilution of the sample has a concentration of any analyte that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. Secondary ion quantitation is allowed only when there are sample interferences with the primary ion.

7.5.11.1 When ions from a compound in the sample saturate the detector, this analysis must be followed by the analysis of an organic-free reagent water blank. If the blank analysis is not free of interferences, then the system must be decontaminated. Sample analysis may not resume until the blank analysis is demonstrated to be free of interferences.

7.5.11.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.5.12 The use of selected ion monitoring (SIM) is acceptable in situations requiring detection limits below the normal range of full EI spectra. However, SIM may provide a lesser degree of confidence in the compound identification unless multiple ions are monitored for each compound.

7.6 Qualitative analysis

7.6.1 The qualitative identification of each compound determined by this method is based on retention time, and on comparison of the sample mass spectrum, after background correction, with characteristic ions in a reference mass spectrum. The reference mass spectrum must be generated by the laboratory using the conditions of this method. The characteristic ions from the reference mass spectrum are defined to be the three ions of greatest relative intensity, or any ions over 30% relative intensity if less than three such ions occur in the reference spectrum. Compounds are identified as present when the following criteria are met.

7.6.1.1 The intensities of the characteristic ions of a compound maximize in the same scan or within one scan of each other. Selection of a peak by a data system target compound search routine where the search is based on the presence of a target chromatographic peak containing ions specific for the target compound at a compound-specific retention time will be accepted as meeting this criterion.

7.6.1.2 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

7.6.1.3 The relative intensities of the characteristic ions agree within 30% of the relative intensities of these ions in the reference spectrum. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding abundance in a sample spectrum can range between 20% and 80%.)

7.6.1.4 Structural isomers that produce very similar mass spectra should be identified as individual isomers if they have sufficiently different GC retention times. Sufficient GC resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the sum of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs.

7.6.1.5 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When gas chromatographic peaks obviously represent more than one sample component (i.e., a broadened peak with shoulder(s) or a valley between two or more maxima), appropriate selection of analyte spectra and background spectra is important.

7.6.1.6 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes coelute (i.e., only one chromatographic peak is apparent), the identification criteria may be met, but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

7.6.2 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The necessity to perform this type of identification will be determined by the purpose of the analyses being conducted. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.

For example, the RCRA permit or waste delisting requirements may require the reporting of non-target analytes. Only after visual comparison of sample spectra with the nearest library

searches may the analyst assign a tentative identification. Use the following guidelines for making tentative identifications:

(1) Relative intensities of major ions in the reference spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.

(2) The relative intensities of the major ions should agree within ± 20%. (Example: For an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%).

(3) Molecular ions present in the reference spectrum should be present in the sample spectrum.

(4) Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of coeluting compounds.

(5) Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of background contamination or coeluting peaks. Data system library reduction programs can sometimes create these discrepancies.

7.7 Quantitative analysis

7.7.1 Once a compound has been identified, the quantitation of that compound will be based on the integrated abundance from the EICP of the primary characteristic ion. The internal standard used shall be the one nearest the retention time of that of a given analyte.

7.7.2 If the RSD of a compound's response factors is 15% or less, then the concentration in the extract may be determined using the average response factor (RF) from initial calibration data (7.3.6). See Method 8000, Sec. 7.0, for the equations describing internal standard calibration and either linear or non-linear calibrations.

7.7.3 Where applicable, the concentration of any non-target analytes identified in the sample (Sec. 7.6.2) should be estimated. The same formulae should be used with the following modifications: The areas A_x and A_{is} should be from the total ion chromatograms, and the RF for the compound should be assumed to be 1.

7.7.4 The resulting concentration should be reported indicating: (1) that the value is an estimate, and (2) which internal standard was used to determine concentration. Use the nearest internal standard free of interferences.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and include evaluation of retention time windows, calibration verification and chromatographic analysis of samples. In addition, instrument QC requirements may be found in the following sections of Method 8260:

8.2.1 The GC/MS system must be tuned to meet the BFB specifications in Secs. 7.3.1 and 7.4.1.

8.2.2 There must be an initial calibration of the GC/MS system as described in Sec. 7.3.

8.2.3 The GC/MS system must meet the SPCC criteria described in Sec. 7.4.4 and the CCC criteria in Sec. 7.4.5, each 12 hours.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy, and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Before processing any samples, the analyst should demonstrate, through the analysis of a method blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is analyzed or there is a change in reagents, a method blank should be analyzed as a safeguard against chronic laboratory contamination. The blanks should be carried through all stages of sample preparation and measurement.

8.4.2 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.3 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.4 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 The experience of the analyst performing GC/MS analyses is invaluable to the success of the methods. Each day that analysis is performed, the calibration verification standard should be evaluated to determine if the chromatographic system is operating properly. Questions that should be asked are: Do the peaks look normal? Is the response obtained comparable to the response from previous calibrations? Careful examination of the standard chromatogram can indicate whether the column is still performing acceptably, the injector is leaking, the injector septum needs replacing, etc. If any changes are made to the system (e.g., the column changed), recalibration of the system must take place.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL actually achieved in a given analysis will vary depending on instrument sensitivity and matrix effects.

9.2 This method has been tested using purge-and-trap (Method 5030) in a single laboratory using spiked water. Using a wide-bore capillary column, water was spiked at concentrations between 0.5 and 10 µg/L. Single laboratory accuracy and precision data are presented for the method analytes in Table 6. Calculated MDLs are presented in Table 1.

9.3 The method was tested using purge-and-trap (Method 5030) with water spiked at 0.1 to 0.5 µg/L and analyzed on a cryofocussed narrow-bore column. The accuracy and precision data for these compounds are presented in Table 7. MDL values were also calculated from these data and are presented in Table 2.

9.4 Direct injection (Method 3585) has been used for the analysis of waste motor oil samples using a wide-bore column. Single laboratory precision and accuracy data are presented in Tables 10 and 11 for TCLP volatiles in oil. The performance data were developed by spiking and analyzing seven replicates each of new and used oil. The oils were spiked at the TCLP regulatory concentrations for most analytes, except for the alcohols, ketones, ethyl acetate and chlorobenzene which are spiked at 5 ppm, well below the regulatory concentrations. Prior to spiking, the new oil (an SAE 30-weight motor oil) was heated at 80°C overnight to remove volatiles. The used oil (a mixture of used oil drained from passenger automobiles) was not heated and was contaminated with 20 - 300 ppm of BTEX compounds and isobutanol. These contaminants contributed to the extremely high recoveries of the BTEX compounds in the used oil. Therefore, the data from the deuterated analogs of these analytes represent more typical recovery values.

9.5 Single laboratory accuracy and precision data were obtained for the Method 5035 analytes in three soil matrices: sand; a soil collected 10 feet below the surface of a hazardous landfill, called C-Horizon; and a surface garden soil. Sample preparation was by Method 5035. Each

sample was fortified with the analytes at a concentration of 4 µg/kg. These data are listed in Tables 17, 18, and 19. All data were calculated using fluorobenzene as the internal standard added to the soil sample prior to extraction. This causes some of the results to be greater than 100% recovery because the precision of results is sometimes as great as 28%.

9.5.1 In general, the recoveries of the analytes from the sand matrix are the highest, the C-Horizon soil results are somewhat less, and the surface garden soil recoveries are the lowest. This is due to the greater adsorptive capacity of the garden soil. This illustrates the necessity of analyzing matrix spike samples to assess the degree of matrix effects.

9.5.2 The recoveries of some of the gases, or very volatile compounds, such as vinyl chloride, trichlorofluoromethane, and 1,1-dichloroethene, are somewhat greater than 100%. This is due to the difficulty encountered in fortifying the soil with these compounds, allowing an equilibration period, then extracting them with a high degree of precision. Also, the garden soil results in Table 19 include some extraordinarily high recoveries for some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection, and to the fact that no background was subtracted.

9.6 Performance data for nonpurgeable volatiles using azeotropic distillation (Method 5031) are included in Tables 12 to 16.

9.7 Performance data for volatiles prepared using vacuum distillation (Method 5032) in soil, water, oil and fish tissue matrices are included in Tables 20 to 27.

9.8 Single laboratory accuracy and precision data were obtained for the Method 5021 analytes in two soil matrices: sand and a surface garden soil. Replicate samples were fortified with the analytes at concentrations of 10 µg/kg. These data are listed in Table 30. All data were calculated using the internal standards listed for each analyte in Table 28. The recommended internal standards were selected because they generated the best accuracy and precision data for the analyte in both types of soil.

9.8.1 If a detector other than an MS is used for analysis, consideration must be given to the choice of internal standards and surrogates. They must not coelute with any other analyte and must have similar properties to the analytes. The recoveries of the analytes are 50% or higher for each matrix studied. The recoveries of the gases or very volatile compounds are greater than 100% in some cases. Also, results include high recoveries of some aromatic compounds, such as toluene, xylenes, and trimethylbenzenes. This is due to contamination of the soil prior to sample collection.

9.8.2 The method detection limits using Method 5021 listed in Table 29 were calculated from results of seven replicate analyses of the sand matrix. Sand was chosen because it demonstrated the least degree of matrix effect of the soils studied. These MDLs were calculated utilizing the procedure described in Chapter One and are intended to be a general indication of the capabilities of the method.

9.9 The MDL concentrations listed in Table 31 were determined using Method 5041 in conjunction with Method 8260. They were obtained using cleaned blank VOST tubes and reagent water. Similar results have been achieved with field samples. The MDL actually achieved in a given analysis will vary depending upon instrument sensitivity and the effects of the matrix. Preliminary spiking studies indicate that under the test conditions, the MDLs for spiked compounds in extremely complex matrices may be larger by a factor of 500 - 1000.

9.10 The EQL of sample taken by Method 0040 and analyzed by Method 8260 is estimated to be in the range of 0.03 to 0.9 ppm (See Table 33). Matrix effects may cause the individual compound detection limits to be higher.

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TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON WIDE-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2'[c]	MDL[d] (µg/L)
Dichlorodifluoromethane	1.35	0.70	3.13	0.10
Chloromethane	1.49	0.73	3.40	0.13
Vinyl Chloride	1.56	0.79	3.93	0.17
Bromomethane	2.19	0.96	4.80	0.11
Chloroethane	2.21	1.02	--	0.10
Trichlorofluoromethane	2.42	1.19	6.20	0.08
Acrolein	3.19			
Iodomethane	3.56			
Acetonitrile	4.11			
Carbon disulfide	4.11			
Allyl chloride	4.11			
Methylene chloride	4.40	2.06	9.27	0.03
1,1-Dichloroethene	4.57	1.57	7.83	0.12
Acetone	4.57			
trans-1,2-Dichloroethene	4.57	2.36	9.90	0.06
Acrylonitrile	5.00			
1,1-Dichloroethane	6.14	2.93	10.80	0.04
Vinyl acetate	6.43			
2,2-Dichloropropane	8.10	3.80	11.87	0.35
2-Butanone	--			
cis-1,2-Dichloroethene	8.25	3.90	11.93	0.12
Propionitrile	8.51			
Chloroform	9.01	4.80	12.60	0.03
Bromochloromethane	--	4.38	12.37	0.04
Methacrylonitrile	9.19			
1,1,1-Trichloroethane	10.18	4.84	12.83	0.08
Carbon tetrachloride	11.02	5.26	13.17	0.21
1,1-Dichloropropene	--	5.29	13.10	0.10
Benzene	11.50	5.67	13.50	0.04
1,2-Dichloroethane	12.09	5.83	13.63	0.06
Trichloroethene	14.03	7.27	14.80	0.19
1,2-Dichloropropane	14.51	7.66	15.20	0.04
Bromodichloromethane	15.39	8.49	15.80	0.08
Dibromomethane	15.43	7.93	5.43	0.24
Methyl methacrylate	15.50			
1,4-Dioxane	16.17			
2-Chloroethyl vinyl ether	--			
4-Methyl-2-pentanone	17.32			
trans-1,3-Dichloropropene	17.47	--	16.70	--
Toluene	18.29	10.00	17.40	0.11
cis-1,3-Dichloropropene	19.38	--	17.90	--

TABLE 1 (cont.)

Compound	Retention Time (minutes)			MDL[d]
	Column 1[a]	Column 2[b]	Column 2"[c]	(µg/L)
1,1,2-Trichloroethane	19.59	11.05	18.30	0.10
Ethyl methacrylate	20.01			
2-Hexanone	20.30			
Tetrachloroethene	20.26	11.15	18.60	0.14
1,3-Dichloropropane	20.51	11.31	18.70	0.04
Dibromochloromethane	21.19	11.85	19.20	0.05
1,2-Dibromoethane	21.52	11.83	19.40	0.06
1-Chlorohexane	--	13.29	--	0.05
Chlorobenzene	23.17	13.01	20.67	0.04
1,1,1,2-Tetrachloroethane	23.36	13.33	20.87	0.05
Ethylbenzene	23.38	13.39	21.00	0.06
p-Xylene	23.54	13.69	21.30	0.13
m-Xylene	23.54	13.68	21.37	0.05
o-Xylene	25.16	14.52	22.27	0.11
Styrene	25.30	14.60	22.40	0.04
Bromoform	26.23	14.88	22.77	0.12
Isopropylbenzene (Cumene)	26.37	15.46	23.30	0.15
cis-1,4-Dichloro-2-butene	27.12			
1,1,2,2-Tetrachloroethane	27.29	16.35	24.07	0.04
Bromobenzene	27.46	15.86	24.00	0.03
1,2,3-Trichloropropane	27.55	16.23	24.13	0.32
n-Propylbenzene	27.58	16.41	24.33	0.04
2-Chlorotoluene	28.19	16.42	24.53	0.04
trans-1,4-Dichloro-2-butene	28.26			
1,3,5-Trimethylbenzene	28.31	16.90	24.83	0.05
4-Chlorotoluene	28.33	16.72	24.77	0.06
Pentachloroethane	29.41			
1,2,4-Trimethylbenzene	29.47	17.70	31.50	0.13
sec-Butylbenzene	30.25	18.09	26.13	0.13
tert-Butylbenzene	30.59	17.57	26.60	0.14
p-Isopropyltoluene	30.59	18.52	26.50	0.12
1,3-Dichlorobenzene	30.56	18.14	26.37	0.12
1,4-Dichlorobenzene	31.22	18.39	26.60	0.03
Benzyl chloride	32.00			
n-Butylbenzene	32.23	19.49	27.32	0.11
1,2-Dichlorobenzene	32.31	19.17	27.43	0.03
1,2-Dibromo-3-chloropropane	35.30	21.08	--	0.26
1,2,4-Trichlorobenzene	38.19	23.08	31.50	0.04
Hexachlorobutadiene	38.57	23.68	32.07	0.11
Naphthalene	39.05	23.52	32.20	0.04
1,2,3-Trichlorobenzene	40.01	24.18	32.97	0.03

TABLE 1 (cont.)

Compound	Retention Time (minutes) Column 1[a]	Column 2[b]	Column 2"[c]	MDL[d] (µg/L)
INTERNAL STANDARDS/SURROGATES				
1,4-Difluorobenzene	13.26			
Chlorobenzene-d_5	23.10			
1,4-Dichlorobenzene-d_4	31.16			
4-Bromofluorobenzene	27.83	15.71	23.63	
1,2-Dichlorobenzene-d_4	32.30	19.08	27.25	
Dichloroethane-d_4	12.08			
Dibromofluoromethane	--			
Toluene-d_8	18.27			
Pentafluorobenzene	--			
Fluorobenzene	13.00	6.27	14.06	

[a] Column 1 - 60 meter x 0.75 mm ID VOCOL capillary. Hold at 10°C for 8 minutes, then program to 180°C at 4°C/min.

[b] Column 2 - 30 meter x 0.53 mm ID DB-624 wide-bore capillary using cryogenic oven. Hold at 10°C for 5 minutes, then program to 160°C at 6°C/min.

[c] Column 2" - 30 meter x 0.53 mm ID DB-624 wide-bore capillary, cooling GC oven to ambient temperatures. Hold at 10°C for 6 minutes, program to 70°C at 10 °C/min, program to 120°C at 5°C/min, then program to 180°C at 8°C/min.

[d] MDL based on a 25-mL sample volume.

TABLE 2

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS ON NARROW-BORE CAPILLARY COLUMNS

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
Dichlorodifluoromethane	0.88	0.11
Chloromethane	0.97	0.05
Vinyl chloride	1.04	0.04
Bromomethane	1.29	0.03
1,1-Dichloroethane	4.03	0.03
cis-1,2-Dichloroethene	5.07	0.06
2,2-Dichloropropane	5.31	0.08
Chloroform	5.55	0.04
Bromochloromethane	5.63	0.09
1,1,1-Trichloroethane	6.76	0.04
1,2-Dichloroethane	7.00	0.02
1,1-Dichloropropene	7.16	0.12
Carbon tetrachloride	7.41	0.02
Benzene	7.41	0.03
1,2-Dichloropropane	8.94	0.02
Trichloroethene	9.02	0.02
Dibromomethane	9.09	0.01
Bromodichloromethane	9.34	0.03
Toluene	11.51	0.08
1,1,2-Trichloroethane	11.99	0.08
1,3-Dichloropropane	12.48	0.08
Dibromochloromethane	12.80	0.07
Tetrachloroethene	13.20	0.05
1,2-Dibromoethane	13.60	0.10
Chlorobenzene	14.33	0.03
1,1,1,2-Tetrachloroethane	14.73	0.07
Ethylbenzene	14.73	0.03
p-Xylene	15.30	0.06
m-Xylene	15.30	0.03
Bromoform	15.70	0.20
o-Xylene	15.78	0.06
Styrene	15.78	0.27
1,1,2,2-Tetrachloroethane	15.78	0.20
1,2,3-Trichloropropane	16.26	0.09
Isopropylbenzene	16.42	0.10
Bromobenzene	16.42	0.11
2-Chlorotoluene	16.74	0.08
n-Propylbenzene	16.82	0.10
4-Chlorotoluene	16.82	0.06

TABLE 2 (cont.)

Compound	Retention Time (minutes) Column 3[a]	MDL[b] (µg/L)
1,3,5-Trimethylbenzene	16.99	0.06
tert-Butylbenzene	17.31	0.33
1,2,4-Trimethylbenzene	17.31	0.09
sec-Butylbenzene	17.47	0.12
1,3-Dichlorobenzene	17.47	0.05
p-Isopropyltoluene	17.63	0.26
1,4-Dichlorobenzene	17.63	0.04
1,2-Dichlorobenzene	17.79	0.05
n-Butylbenzene	17.95	0.10
1,2-Dibromo-3-chloropropane	18.03	0.50
1,2,4-Trichlorobenzene	18.84	0.20
Naphthalene	19.07	0.10
Hexachlorobutadiene	19.24	0.10
1,2,3-Trichlorobenzene	19.24	0.14

[a] Column 3 - 30 meter x 0.32 mm ID DB-5 capillary with 1 µm film thickness.

[b] MDL based on a 25-mL sample volume.

TABLE 3

ESTIMATED QUANTITATION LIMITS FOR VOLATILE ANALYTES[a]

Estimated Quantitation Limits		
5-mL Ground Water Purge (µg/L)	25-mL Ground water Purge (µg/L)	Low Soil/Sediment[b] µg/kg
5	1	5

[a] Estimated Quantitation Limit (EQL) - The lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The EQL is generally 5 to 10 times the MDL. However, it may be nominally chosen within these guidelines to simplify data reporting. For many analytes the EQL analyte concentration is selected for the lowest non-zero standard in the calibration curve. Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable. See the following footnote for further guidance on matrix-dependent EQLs.

[b] EQLs listed for soil/sediment are based on wet weight. Normally data are reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight in each sample.

Other Matrices	Factor[c]
Water miscible liquid waste	50
High concentration soil and sludge	125
Non-water miscible waste	500

[c] EQL = [EQL for low soil sediment (Table 3)] x [Factor].

For non-aqueous samples, the factor is on a wet-weight basis.

TABLE 4

BFB (4-BROMOFLUOROBENZENE) MASS INTENSITY CRITERIA[a]

m/z	Required Intensity (relative abundance)
50	15 to 40% of m/z 95
75	30 to 60% of m/z 95
95	Base peak, 100% relative abundance
96	5 to 9% of m/z 95
173	Less than 2% of m/z 174
174	Greater than 50% of m/z 95
175	5 to 9% of m/z 174
176	Greater than 95% but less than 101% of m/z 174
177	5 to 9% of m/z 176

[a] Alternate tuning criteria may be used, (e.g. CLP, Method 524.2, or manufacturers' instructions), provided that method performance is not adversely affected.

TABLE 5

CHARACTERISTIC MASSES (m/z) FOR PURGEABLE ORGANIC COMPOUNDS

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Acetone	58	43
Acetonitrile	41	40, 39
Acrolein	56	55, 58
Acrylonitrile	53	52, 51
Allyl alcohol	57	58, 39
Allyl chloride	76	41, 39, 78
Benzene	78	-
Benzyl chloride	91	126, 65, 128
Bromoacetone	136	43, 138, 93, 95
Bromobenzene	156	77, 158
Bromochloromethane	128	49, 130
Bromodichloromethane	83	85, 127
Bromoform	173	175, 254
Bromomethane	94	96
iso-Butanol	74	43
n-Butanol	56	41
2-Butanone	72	43
n-Butylbenzene	91	92, 134
sec-Butylbenzene	105	134
tert-Butylbenzene	119	91, 134
Carbon disulfide	76	78
Carbon tetrachloride	117	119
Chloral hydrate	82	44, 84, 86, 111
Chloroacetonitrile	48	75
Chlorobenzene	112	77, 114
1-Chlorobutane	56	49
Chlorodibromomethane	129	208, 206
Chloroethane	64 (49*)	66 (51*)
2-Chloroethanol	49	44, 43, 51, 80
Bis(2-chloroethyl) sulfide	109	111, 158, 160
2-Chloroethyl vinyl ether	63	65, 106
Chloroform	83	85
Chloromethane	50 (49*)	52 (51*)
Chloroprene	53	88, 90, 51
3-Chloropropionitrile	54	49, 89, 91
2-Chlorotoluene	91	126
4-Chlorotoluene	91	126
1,2-Dibromo-3-chloropropane	75	155, 157
Dibromochloromethane	129	127
1,2-Dibromoethane	107	109, 188
Dibromomethane	93	95, 174

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
1,2-Dichlorobenzene	146	111, 148
1,2-Dichlorobenzene-d_4	152	115, 150
1,3-Dichlorobenzene	146	111, 148
1,4-Dichlorobenzene	146	111, 148
cis-1,4-Dichloro-2-butene	75	53, 77, 124, 89
trans-1,4-Dichloro-2-butene	53	88, 75
Dichlorodifluoromethane	85	87
1,1-Dichloroethane	63	65, 83
1,2-Dichloroethane	62	98
1,1-Dichloroethene	96	61, 63
cis-1,2-Dichloroethene	96	61, 98
trans-1,2-Dichloroethene	96	61, 98
1,2-Dichloropropane	63	112
1,3-Dichloropropane	76	78
2,2-Dichloropropane	77	97
1,3-Dichloro-2-propanol	79	43, 81, 49
1,1-Dichloropropene	75	110, 77
cis-1,3-Dichloropropene	75	77, 39
trans-1,3-Dichloropropene	75	77, 39
1,2,3,4-Diepoxybutane	55	57, 56
Diethyl ether	74	45, 59
1,4-Dioxane	88	58, 43, 57
Epichlorohydrin	57	49, 62, 51
Ethanol	31	45, 27, 46
Ethyl acetate	88	43, 45, 61
Ethylbenzene	91	106
Ethylene oxide	44	43, 42
Ethyl methacrylate	69	41, 99, 86, 114
Hexachlorobutadiene	225	223, 227
Hexachloroethane	201	166, 199, 203
2-Hexanone	43	58, 57, 100
2-Hydroxypropionitrile	44	43, 42, 53
Iodomethane	142	127, 141
Isobutyl alcohol	43	41, 42, 74
Isopropylbenzene	105	120
p-Isopropyltoluene	119	134, 91
Malononitrile	66	39, 65, 38
Methacrylonitrile	41	67, 39, 52, 66
Methyl acrylate	55	85
Methyl-t-butyl ether	73	57
Methylene chloride	84	86, 49
Methyl ethyl ketone	72	43
Methyl iodide	142	127, 141

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Methyl methacrylate	69	41, 100, 39
4-Methyl-2-pentanone	100	43, 58, 85
Naphthalene	128	-
Nitrobenzene	123	51, 77
2-Nitropropane	46	-
2-Picoline	93	66, 92, 78
Pentachloroethane	167	130, 132, 165, 169
Propargyl alcohol	55	39, 38, 53
β-Propiolactone	42	43, 44
Propionitrile (ethyl cyanide)	54	52, 55, 40
n-Propylamine	59	41, 39
n-Propylbenzene	91	120
Pyridine	79	52
Styrene	104	78
1,2,3-Trichlorobenzene	180	182, 145
1,2,4-Trichlorobenzene	180	182, 145
1,1,1,2-Tetrachloroethane	131	133, 119
1,1,2,2-Tetrachloroethane	83	131, 85
Tetrachloroethene	164	129, 131, 166
Toluene	92	91
1,1,1-Trichloroethane	97	99, 61
1,1,2-Trichloroethane	83	97, 85
Trichloroethene	95	97, 130, 132
Trichlorofluoromethane	151	101, 153
1,2,3-Trichloropropane	75	77
1,2,4-Trimethylbenzene	105	120
1,3,5-Trimethylbenzene	105	120
Vinyl acetate	43	86
Vinyl chloride	62	64
o-Xylene	106	91
m-Xylene	106	91
p-Xylene	106	91
Internal Standards/Surrogates:		
Benzene-d_6	84	83
Bromobenzene-d_5	82	162
Bromochloromethane-d_2	51	131
1,4-Difluorobenzene	114	
Chlorobenzene-d_5	117	
1,4-Dichlorobenzene-d_4	152	115, 150
1,1,2-Trichloroethane-d_3	100	
4-Bromofluorobenzene	95	174, 176
Chloroform-d_1	84	
Dibromofluoromethane	113	

TABLE 5 (cont.)

Compound	Primary Characteristic Ion	Secondary Characteristic Ion(s)
Internal Standards/Surrogates		
Dichloroethane-d_4	102	
Toluene-d_8	98	
Pentafluorobenzene	168	
Fluorobenzene	96	77

* Characteristic ion for an ion trap mass spectrometer (to be used when ion-molecule reactions are observed).

TABLE 6

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A WIDE-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. Range (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1 - 10	31	97	6.5	5.7
Bromobenzene	0.1 - 10	30	100	5.5	5.5
Bromochloromethane	0.5 - 10	24	90	5.7	6.4
Bromodichloromethane	0.1 - 10	30	95	5.7	6.1
Bromoform	0.5 - 10	18	101	6.4	6.3
Bromomethane	0.5 - 10	18	95	7.8	8.2
n-Butylbenzene	0.5 - 10	18	100	7.6	7.6
sec-Butylbenzene	0.5 - 10	16	100	7.6	7.6
tert-Butylbenzene	0.5 - 10	18	102	7.4	7.3
Carbon tetrachloride	0.5 - 10	24	84	7.4	8.8
Chlorobenzene	0.1 - 10	31	98	5.8	5.9
Chloroethane	0.5 - 10	24	89	8.0	9.0
Chloroform	0.5 - 10	24	90	5.5	6.1
Chloromethane	0.5 - 10	23	93	8.3	8.9
2-Chlorotoluene	0.1 - 10	31	90	5.6	6.2
4-Chlorotoluene	0.1 - 10	31	99	8.2	8.3
1,2-Dibromo-3-Chloropropane	0.5 - 10	24	83	16.6	19.9
Dibromochloromethane	0.1 - 10	31	92	6.5	7.0
1,2-Dibromoethane	0.5 - 10	24	102	4.0	3.9
Dibromomethane	0.5 - 10	24	100	5.6	5.6
1,2-Dichlorobenzene	0.1 - 10	31	93	5.8	6.2
1,3-Dichlorobenzene	0.5 - 10	24	99	6.8	6.9
1,4-Dichlorobenzene	0.2 - 20	31	103	6.6	6.4
Dichlorodifluoromethane	0.5 - 10	18	90	6.9	7.7
1,1-Dichlorobenzene	0.5 - 10	24	96	5.1	5.3
1,2-Dichlorobenzene	0.1 - 10	31	95	5.1	5.4
1,1-Dichloroethene	0.1 - 10	34	94	6.3	6.7
cis-1,2-Dichloroethene	0.5 - 10	18	101	6.7	6.7
trans-1,2-Dichloroethene	0.1 - 10	30	93	5.2	5.6
1,2-Dichloropropane	0.1 - 10	30	97	5.9	6.1
1,3-Dichloropropane	0.1 - 10	31	96	5.7	6.0
2,2-Dichloropropane	0.5 - 10	12	86	14.6	16.9
1,1-Dichloropropene	0.5 - 10	18	98	8.7	8.9
Ethylbenzene	0.1 - 10	31	99	8.4	8.6
Hexachlorobutadiene	0.5 - 10	18	100	6.8	6.8
Isopropylbenzene	0.5 - 10	16	101	7.7	7.6
p-Isopropyltoluene	0.1 - 10	23	99	6.7	6.7
Methylene chloride	0.1 - 10	30	95	5.0	5.3

TABLE 7

SINGLE LABORATORY ACCURACY AND PRECISION DATA FOR PURGEABLE VOLATILE ORGANIC COMPOUNDS IN WATER DETERMINED WITH A NARROW-BORE CAPILLARY COLUMN (METHOD 5030)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
Benzene	0.1	7	99	6.2	6.3
Bromobenzene	0.5	7	97	7.4	7.6
Bromochloromethane	0.5	7	97	5.8	6.0
Bromodichloromethane	0.1	7	100	4.6	4.6
Bromoform	0.5	7	101	5.4	5.3
Bromomethane	0.5	7	99	7.1	7.2
n-Butylbenzene	0.5	7	94	6.0	6.4
sec-Butylbenzene	0.5	7	110	7.1	6.5
tert-Butylbenzene	0.5	7	110	2.5	2.3
Carbon tetrachloride	0.1	7	108	6.8	6.3
Chlorobenzene	0.1	7	91	5.8	6.4
Chloroethane	0.1	7	100	5.8	5.8
Chloroform	0.1	7	105	3.2	3.0
Chloromethane	0.5	7	101	4.7	4.7
2-Chlorotoluene	0.5	7	99	4.6	4.6
4-Chlorotoluene	0.5	7	96	7.0	7.3
1,2-Dibromo-3-chloropropane	0.5	7	92	10.0	10.9
Dibromochloromethane	0.1	7	99	5.6	5.7
1,2-Dibromoethane	0.5	7	97	5.6	5.8
Dibromomethane	0.5	7	93	5.6	6.0
1,2-Dichlorobenzene	0.1	7	97	3.5	3.6
1,3-Dichlorobenzene	0.1	7	101	6.0	5.9
1,4-Dichlorobenzene	0.1	7	106	6.5	6.1
Dichlorodifluoromethane	0.1	7	99	8.8	8.9
1,1-Dichloroethane	0.5	7	98	6.2	6.3
1,2-Dichloroethane	0.1	7	100	6.3	6.3
1,1-Dichloroethene	0.1	7	95	9.0	9.5
cis-1,2-Dichloroethene	0.1	7	100	3.5	3.7
trans-1,2-Dichloroethene	0.1	7	98	7.2	7.3
1,2-Dichloropropane	0.5	7	96	6.0	6.3
1,3-Dichloropropane	0.5	7	99	5.8	5.9
2,2-Dichloropropane	0.5	7	99	4.9	4.9
1,1-Dichloropropene	0.5	7	102	7.4	7.3
Ethylbenzene	0.5	7	99	5.2	5.3
Hexachlorobutadiene	0.5	7	100	6.7	6.7
Isopropylbenzene	0.5	7	102	6.4	6.3
p-Isopropyltoluene	0.5	7	113	13.0	11.5
Methylene chloride	0.5	7	97	13.0	13.4
Naphthalene	0.5	7	98	7.2	7.3

TABLE 7 (cont.)

Compound	Conc. (µg/L)	Number of Samples	% Recovery[a]	Standard Deviation of Recovery[b]	RSD
n-Propylbenzene	0.5	7	99	6.6	6.7
Styrene	0.5	7	96	19.0	19.8
1,1,1,2-Tetrachloroethane	0.5	7	100	4.7	4.7
1,1,2,2-Tetrachloroethane	0.5	7	100	12.0	12.0
Tetrachloroethene	0.1	7	96	5.0	5.2
Toluene	0.5	7	100	5.9	5.9
1,2,3-Trichlorobenzene	0.5	7	102	8.9	8.7
1,2,4-Trichlorobenzene	0.5	7	91	16.0	17.6
1,1,1-Trichloroethane	0.5	7	100	4.0	4.0
1,1,2-Trichloroethane	0.5	7	102	4.9	4.8
Trichloroethene	0.1	7	104	2.0	1.9
Trichlorofluoromethane	0.1	7	97	4.6	4.7
1,2,3-Trichloropropane	0.5	7	96	6.5	6.8
1,2,4-Trimethylbenzene	0.5	7	96	6.5	6.8
1,3,5-Trimethylbenzene	0.5	7	101	4.2	4.2
Vinyl chloride	0.1	7	104	0.2	0.2
Xylene	0.5	7	106	7.5	7.1
m-Xylene	0.5	7	106	4.6	4.3
p-Xylene	0.5	7	97	6.1	6.3

[a] Recoveries were calculated using internal standard method. Internal standard was fluorobenzene.

TABLE 8

SURROGATE SPIKE RECOVERY LIMITS FOR WATER AND SOIL/SEDIMENT SAMPLES

Surrogate Compound	Water	Soil/Sediment
4-Bromofluorobenzene[a]	86-115	74-121
Dibromofluoromethane[a]	86-118	80-120
Toluene-d_8[a]	88-110	81-117
Dichloroethane-d_4[a]	80-120	80-120

[a] Single laboratory data, for guidance only.

TABLE 9

QUANTITY OF EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SAMPLES

Approximate Concentration Range (µg/kg)	Volume of Extract[a]
500 - 10,000	100 µL
1,000 - 20,000	50 µL
5,000 - 100,000	10 µL
25,000 - 500,000	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of solvent added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of solvent is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the solvent extract and then take 100 µL for analysis.

TABLE 10

DIRECT INJECTION ANALYSIS OF NEW OIL AT 5 PPM (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone	91	14.8	1.9	5.0
Benzene	86	21.3	0.1	0.5
n-Butanol*,**	107	27.8	0.5	5.0
iso-Butanol*,**	95	19.5	0.9	5.0
Carbon tetrachloride	86	44.7	0.0	0.5
Carbon disulfide**	53	22.3	0.0	5.0
Chlorobenzene	81	29.3	0.0	5.0
Chloroform	84	29.3	0.0	6.0
1,4-Dichlorobenzene	98	24.9	0.0	7.5
1,2-Dichloroethane	101	23.1	0.0	0.5
1,1-Dichloroethene	97	45.3	0.0	0.7
Diethyl ether	76	24.3	0.0	5.0
Ethyl acetate	113	27.4	0.0	5.0
Ethylbenzene	83	30.1	0.2	5.0
Hexachloroethane	71	30.3	0.0	3.0
Methylene chloride	98	45.3	0.0	5.0
Methyl ethyl ketone	79	24.6	0.4	5.0
MIBK	93	31.4	0.0	5.0
Nitrobenzene	89	30.3	0.0	2.0
Pyridine	31	35.9	0.0	5.0
Tetrachloroethene	82	27.1	0.0	0.7
Trichlorofluoromethane	76	27.6	0.0	5.0
1,1,2-Trichlorotrifluoroethane	69	29.2	0.0	5.0
Toluene	73	21.9	0.6	5.0
Trichloroethene	66	28.0	0.0	0.5
Vinyl chloride	63	35.2	0.0	0.2
o-Xylene	83	29.5	0.4	5.0
m/p-Xylene	84	29.5	0.6	10.0

* Alternate mass employed
** IS quantitation

Data are taken from Reference 9.

TABLE 11

SINGLE LABORATORY PERFORMANCE
DATA FOR THE DIRECT INJECTION METHOD - USED OIL (METHOD 3585)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Acetone**	105	54	2.0	5.0
Benzene	3135	44	14	0.5
Benzene-d_6	56	44	2.9	0.5
n-Butanol**	100	71	12	5.0
iso-Butanol*,**	132	27	0	5.0
Carbon tetrachloride	143	68	0	0.5
Carbon tetrachloride-^{13}C	99	44	5.1	0.5
Carbon disulfide**	95	63	0	5.0
Chlorobenzene	148	71	0	5.0
Chlorobenzene-d_5	60	44	3.6	5.0
Chloroform	149	74	0	6.0
Chloroform-d_1	51	44	2.6	6.0
1,4-Dichlorobenzene	142	72	0	7.5
1,4-Dichlorobenzene-d_4	53	44	3.4	7.5
1,2-Dichloroethane**	191	54	0	0.5
1,1-Dichloroethene*	155	51	0	0.7
1,1-Dichloroethene-d_2	68	44	3.4	0.7
Diethyl ether**	95	66	0	5.0
Ethyl acetate*,**	126	39	0	5.0
Ethylbenzene	1298	44	54	5.0
Ethylbenzene-d_{10}	63	44	3.6	5.0
Hexachloroethane	132	72	0	3.0
Hexachloroethane-^{13}C	54	45	3.5	3.0
Methylene chloride**	86	65	0.3	5.0
Methyl ethyl ketone**	107	64	0	5.0
4-Methyl-2-pentanone (MIBK)**	100	74	0.1	5.0
Nitrobenzene	111	80	0	2.0
Nitrobenzene-d_5	65	53	4.0	2.0
Pyridine**	68	85	0	5.0
Pyridine-d_5	ND	--	0	5.0
Tetrachloroethene**	101	73	0	0.7
Trichlorofluoromethane**	91	70	0	5.0
1,1,2-Cl_3F_3ethane**	81	70	0	5.0
Toluene	2881	44	128	5.0
Toluene-d_8	63	44	3.6	5.0
Trichloroethene	152	57	0	0.5
Trichloroethene-d_1	55	44	2.8	0.5

TABLE 11 (cont.)

Compound	Recovery (%)	%RSD	Blank (ppm)	Spike (ppm)
Vinyl chloride**	100	69	0	0.2
o-Xylene	2292	44	105	5.0
o-Xylene-d_{10}	76	44	4.2	5.0
m-/p-Xylene	2583	44	253	10.0
p-Xylene-d_{10}	67	44	3.7	10.0

* Alternate mass employed
** IS quantitation
ND = Not Detected

Data are based on seven measurements and are taken from Reference 9.

TABLE 12

METHOD DETECTION LIMITS (METHOD 5031)

Compound	MDL (µg/L) Macro[a]	Concentration Factor Macro	Micro
Acetone	31	25-500	-
Acetonitrile	57	25-500	200
Acrolein	-	-	100
Acrylonitrile	16	25-500	100
Allyl Alcohol	7	25-500	-
1-Butanol	-	-	250
Crotonaldehyde	12	25-500	-
1,4-Dioxane	12	25-500	150
Ethyl Acetate	-	-	100
Isobutyl alcohol	7	25-500	-
Methanol	38	25-500	140
Methyl Ethyl Ketone	16	25-500	-
2-Methyl-1-propanol	-	-	250
n-Nitroso-di-n-butylamine	14	25-500	-
Paraldehyde	10	25-500	-
2-Picoline	7	25-500	-
1-Propanol	-	-	240
Propionitrile	11	25-500	200
Pyridine	4	25-500	-
o-Toluidine	13	25-500	-

[a] Produced by analysis of seven aliquots of reagent water spiked at 25 ppb at the listed compounds; calculations based on internal standard technique and use of the following equation:

MDL = 3.134 x Std. Dev. of low concentration spike (ppb).

[b] When a 40-mL sample is used, and the first 1.00 µL of distillate are collected.

TABLE 13

TARGET COMPOUNDS, SURROGATES, AND INTERNAL STANDARDS (METHOD 5031)

Target Compound	Surrogate	Internal Standard
Acetone	d_6-Acetone	d_8-Isopropyl alcohol
Acetonitrile	d_3-Acetonitrile	d_8-Isopropyl alcohol
Acrylonitrile	d_8-Isopropyl alcohol	
Allyl alcohol	d_7-Dimethyl formamide	
Crotonaldehyde	d_8-Isopropyl alcohol	
1,4-Dioxane	d_8-1,4-Dioxane	d_7-Dimethyl formamide
Isobutyl alcohol	d_7-Dimethyl formamide	
Methanol	d_3-Methanol	d_8-Isopropyl alcohol
Methyl ethyl ketone	d_8-Isopropyl alcohol	
N-Nitroso-di-n-butylamine	d_7-Dimethyl formamide	
Paraldehyde	d_7-Dimethyl formamide	
2-Picoline	d_7-Dimethyl formamide	
Propionitrile	d_8-Isopropyl alcohol	
Pyridine	d_5-Pyridine	d_7-Dimethyl formamide
o-Toluidine	d_7-Dimethyl formamide	

TABLE 14

RECOMMENDED CONCENTRATIONS FOR CALIBRATION SOLUTIONS (METHOD 5031)

Compound	Concentration(s) (ng/µL)
Internal Standards	
d_5-benzyl alcohol	10.0
d_{14}-Diglyme	10.0
d_7-Dimethyl formamide	10.0
d_8-Isopropyl alcohol	10.0
Surrogates	
d_6-Acetone	10.0
d_3-Acetonitrile	10.0
d_8-1,4-Dioxane	10.0
d_3-Methanol	10.0
d_5-Pyridine	10.0
Target Compounds	
Acetone	1.0, 5.0, 10.0, 25.0, 100.0
Acetonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Acrylonitrile	1.0, 5.0, 10.0, 25.0, 100.0
Allyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Crotonaldehyde	1.0, 5.0, 10.0, 25.0, 100.0
1,4-Dioxane	1.0, 5.0, 10.0, 25.0, 100.0
Isobutyl alcohol	1.0, 5.0, 10.0, 25.0, 100.0
Methanol	1.0, 5.0, 10.0, 25.0, 100.0
Methyl ethyl ketone	1.0, 5.0, 10.0, 25.0, 100.0
N-Nitroso-di-n-butylamine	1.0, 5.0, 10.0, 25.0, 100.0
Paraldehyde	1.0, 5.0, 10.0, 25.0, 100.0
2-Picoline	1.0, 5.0, 10.0, 25.0, 100.0
Propionitrile	1.0, 5.0, 10.0, 25.0, 100.0
Pyridine	1.0, 5.0, 10.0, 25.0, 100.0
o-Toluidine	1.0, 5.0, 10.0, 25.0, 100.0

TABLE 15

CHARACTERISTIC IONS AND RETENTION TIMES FOR VOCs (METHOD 5031)

Compound	Quantitation Ion[a]	Secondary Ions	Retention Time (min)[b]
Internal Standards			
d_8-Isopropyl alcohol	49	98,64	1.75
d_{14}-Diglyme	66	80	9.07
d_7-Dimethyl formamide	50		9.20
Surrogates			
d_6-Acetone	46	64,42	1.03
d_3-Methanol	33	35,30	1.75
d_3-Acetonitrile	44	42	2.63
d_8-1,4-Dioxane	96	64,34	3.97
d_5-Pyridine	84	56,79	6.73
d_5-Phenol[c]	99	71	15.43
Target Compounds			
Acetone	43	58	1.05
Methanol	31	29	1.52
Methyl ethyl ketone	43	72,57	1.53
Methacrylonitrile[c]	67	41	2.38
Acrylonitrile	53	52,51	2.53
Acetonitrile	41	40,39	2.73
Methyl isobutyl ketone[c]	85	100,58	2.78
Propionitrile	54	52,55	3.13
Crotonaldehyde	41	70	3.43
1,4-Dioxane	58	88,57	4.00
Paraldehyde	45	89	4.75
Isobutyl alcohol	43	33,42	5.05
Allyl alcohol	57	39	5.63
Pyridine	79	50,52	6.70
2-Picoline	93	66	7.27
N-Nitroso-di-n-butylamine	84	116	12.82
Aniline[c]	93	66,92	13.23
o-Toluidine	106	107	13.68
Phenol[c]	94	66,65	15.43

[a] These ions were used for quantitation in selected ion monitoring.

[b] GC column: DB-Wax, 30 meter x 0.53 mm, 1 µm film thickness.
Oven program: 45°C for 4 min, increased to 220°C at 12°C/min.

[c] Compound removed from target analyte list due to poor accuracy and precision.

TABLE 16

METHOD ACCURACY AND PRECISION BY MEAN PERCENT RECOVERY AND PERCENT RELATIVE STANDARD DEVIATION[a] (METHOD 5031 - MACRODISTILLATION TECHNIQUE)
(Single Laboratory and Single Operator)

Compound	25 ppb Spike		100 ppb Spike		500 ppb Spike	
	Mean %R	%RSD	Mean %R	%RSD	Mean %R	%RSD
d_6-Acetone	66	24	69	14	65	16
d_3-Acetonitrile	89	18	80	18	70	10
d_8-1,4-Dioxane	56	34	58	11	61	18
d_3-Methanol	43	29	48	19	56	14
d_5-Pyridine	83	6.3	84	7.8	85	9.0
Acetone	67	45	63	14	60	14
Acetonitrile	44	35	52	15	56	15
Acrylonitrile	49	42	47	27	45	27
Allyl alcohol	69	13	70	9.7	73	10
Crotonaldehyde	68	22	68	13	69	13
1,4-Dioxane	63	25	55	16	54	13
Isobutyl alcohol	66	14	66	5.7	65	7.9
Methanol	50	36	46	22	49	18
Methyl ethyl ketone	55	37	56	20	52	19
N-Nitroso-di-n-butylamine	57	21	61	15	72	18
Paraldehyde	65	20	66	11	60	8.9
Picoline	81	12	81	6.8	84	8.0
Propionitrile	67	22	69	13	68	13
Pyridine	74	7.4	72	6.7	74	7.3
o-Toluidine	52	31	54	15	58	12

[a] Data from analysis of seven aliquots of reagent water spiked at each concentration, using a quadrapole mass spectrometer in the selected ion monitoring mode.

TABLE 17

RECOVERIES IN SAND SAMPLES FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	8.0	7.5	6.7	5.4	6.6	6.8	13.0	34.2
Trichlorofluoromethane	13.3	16.5	14.9	13.0	10.3	13.6	15.2	68.0
1,1-Dichloroethene	17.1	16.7	15.1	14.8	15.6	15.9	5.7	79.2
Methylene chloride	24.5	22.7	19.7	19.4	20.6	21.4	9.1	107
trans-1,2-Dichloroethene	22.7	23.6	19.4	18.3	20.1	20.8	0.7	104
1,2-Dichloroethane	18.3	18.0	16.7	15.6	15.9	16.9	6.4	84.4
cis-1,2-Dichloroethene	26.1	23.1	22.6	20.3	20.8	22.6	9.0	113
Bromochloromethane	24.5	25.4	20.9	20.1	20.1	22.2	10.2	111
Chloroform	26.5	26.0	22.1	18.9	22.1	23.1	12.2	116
1,1,1-Trichloroethane	21.5	23.0	23.9	16.7	31.2	23.4	21.2	117
Carbon tetrachloride	23.6	24.2	22.6	18.3	23.3	22.4	9.4	112
Benzene	22.4	23.9	20.4	17.4	19.2	20.7	11.2	103
Trichloroethene	21.5	20.5	19.2	14.4	19.1	18.9	12.7	94.6
1,2-Dichloropropane	24.9	26.3	23.1	19.0	23.3	23.3	10.5	117
Dibromomethane	25.4	26.4	21.6	20.4	23.6	23.5	9.6	117
Bromodichloromethane	25.7	26.7	24.1	17.9	23.0	23.5	13.1	117
Toluene	28.3	25.0	24.8	16.3	23.6	23.6	16.9	118
1,1,2-Trichloroethane	25.4	24.5	21.6	17.7	22.1	22.2	12.1	111
1,3-Dichloropropane	25.4	24.2	22.7	17.0	22.2	22.3	12.8	112
Dibromochloromethane	26.3	26.2	23.7	18.2	23.2	23.5	12.5	118
Chlorobenzene	22.9	22.5	19.8	14.6	19.4	19.9	15.0	99.3
1,1,1,2-Tetrachloroethane	22.4	27.7	25.1	19.4	22.6	23.4	12.0	117
Ethylbenzene	25.6	25.0	22.1	14.9	24.0	22.3	17.5	112
p-Xylene	22.5	22.0	19.8	13.9	20.3	19.7	15.7	98.5
o-Xylene	24.2	23.1	21.6	14.0	20.4	20.7	17.3	103
Styrene	23.9	21.5	20.9	14.3	20.5	20.2	15.7	101
Bromoform	26.8	25.6	26.0	20.1	23.5	24.4	9.9	122
iso-Propylbenzene	25.3	25.1	24.2	15.4	24.6	22.9	16.6	114
Bromobenzene	19.9	21.8	20.0	15.5	19.1	19.3	10.7	96.3
1,2,3-Trichloropropane	25.9	23.0	25.6	15.9	21.4	22.2	15.8	111
n-Propylbenzene	26.0	23.8	22.6	13.9	21.9	21.6	19.0	106
2-Chlorotoluene	23.6	23.8	21.3	13.0	21.5	20.6	19.2	103
4-Chlorotoluene	21.0	19.7	18.4	12.1	18.3	17.9	17.1	89.5
1,3,5-Trimethylbenzene	24.0	22.1	22.5	13.8	22.9	21.1	17.6	105
sec-Butylbenzene	25.9	25.3	27.8	16.1	28.6	24.7	18.1	124
1,2,4-Trimethylbenzene	30.6	39.2	22.4	18.0	22.7	26.6	28.2	133
1,3-Dichlorobenzene	20.3	20.6	18.2	13.0	17.6	17.9	15.2	89.7
p-iso-Propyltoluene	21.6	22.1	21.6	16.0	22.8	20.8	11.8	104
1,4-Dichlorobenzene	18.1	21.2	20.0	13.2	17.4	18.0	15.3	90.0
1,2-Dichlorobenzene	18.4	22.5	22.5	15.2	19.9	19.7	13.9	96.6
n-Butylbenzene	13.1	20.3	19.5	10.8	18.7	16.5	23.1	82.4
1,2,4-Trichlorobenzene	14.5	14.9	15.7	8.8	12.3	13.3	18.8	66.2
Hexachlorobutadiene	17.6	22.5	21.6	13.2	21.6	19.3	18.2	96.3
1,2,3-Trichlorobenzene	14.9	15.9	16.5	11.9	13.9	14.6	11.3	73.1

Data in Tables 17, 18, and 19 are from Reference 15.

TABLE 18
RECOVERIES IN C-HORIZON SOILS FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	33.4	31.0	30.9	29.7	28.6	30.8	5.2	154
Trichlorofluoromethane	37.7	20.8	20.0	21.8	20.5	24.1	28.2	121
1,1-Dichloroethene	21.7	33.5	39.8	30.2	32.5	31.6	18.5	158
Methylene chloride	20.9	19.4	18.7	18.3	18.4	19.1	5.1	95.7
trans-1,2-Dichloroethene	21.8	18.9	20.4	17.9	17.8	19.4	7.9	96.8
1,1-Dichloroethane	23.8	21.9	21.3	21.3	20.5	21.8	5.2	109
cis-1,2-Dichloroethene	21.6	18.8	18.5	18.2	18.2	19.0	6.7	95.2
Bromochloromethane	22.3	19.5	19.3	19.0	19.2	20.0	6.0	100
Chloroform	20.5	17.1	17.3	16.5	15.9	17.5	9.2	87.3
1,1,1-Trichloroethane	16.4	11.9	10.7	9.5	9.4	11.6	22.4	57.8
Carbon tetrachloride	13.1	11.3	13.0	11.8	11.2	12.1	6.7	60.5
Benzene	21.1	19.3	18.7	18.2	16.9	18.8	7.4	94.1
Trichloroethene	19.6	16.4	16.5	16.5	15.5	16.9	8.3	84.5
1,2-Dichloropropane	21.8	19.0	18.3	18.8	16.5	18.9	9.0	94.4
Dibromomethane	20.9	17.9	17.9	17.2	18.3	18.4	6.9	92.1
Bromodichloromethane	20.9	18.0	18.9	18.2	17.3	18.6	6.6	93.2
Toluene	22.2	17.3	18.8	17.0	15.9	18.2	12.0	91.2
1,1,2-Trichloroethane	21.0	16.5	17.2	17.2	16.5	17.7	9.6	88.4
1,3-Dichloropropane	21.4	17.3	18.7	18.6	16.7	18.5	8.8	92.6
Dibromochloromethane	20.9	18.1	19.0	18.8	16.6	18.7	7.5	93.3
Chlorobenzene	20.8	18.4	17.6	16.8	14.8	17.7	11.2	88.4
1,1,1,2-Tetrachloroethane	19.5	19.0	17.8	17.2	16.5	18.0	6.2	90.0
Ethylbenzene	21.1	18.3	18.5	16.9	15.3	18.0	10.6	90.0
p-Xylene	20.0	17.4	18.2	16.3	14.4	17.3	10.9	86.3
o-Xylene	20.7	17.2	16.8	16.2	14.8	17.1	11.4	85.7
Styrene	18.3	15.9	16.2	15.3	13.7	15.9	9.3	79.3
Bromoform	20.1	15.9	17.1	17.5	16.1	17.3	8.6	86.7
iso-Propylbenzene	21.0	18.1	19.2	18.4	15.6	18.4	9.6	92.2
Bromobenzene	20.4	16.2	17.2	16.7	15.4	17.2	10.1	85.9
1,1,2,2-Tetrachloroethane	23.3	17.9	21.2	18.8	16.8	19.6	12.1	96.0
1,2,3-Trichloropropane	18.4	14.6	15.6	16.1	15.6	16.1	8.0	80.3
n-Propylbenzene	20.4	18.9	17.9	17.0	14.3	17.7	11.6	88.4
2-Chlorotoluene	19.1	17.3	16.1	16.0	14.4	16.7	9.2	83.6
4-Chlorotoluene	19.0	15.5	16.8	15.9	13.6	16.4	10.6	81.8
1,3,5-Trimethylbenzene	20.8	18.0	17.4	16.1	14.7	17.4	11.7	86.9
sec-Butylbenzene	21.4	18.3	18.9	17.0	14.9	18.1	11.8	90.5
1,2,4-Trimethylbenzene	20.5	18.6	16.8	15.3	13.7	17.0	14.1	85.0
1,3-Dichlorobenzene	17.6	15.9	15.6	14.2	14.4	15.6	7.9	77.8
p-iso-Propyltoluene	20.5	17.0	17.1	15.6	13.4	16.7	13.9	83.6
1,4-Dichlorobenzene	18.5	13.8	14.8	16.7	14.9	15.7	10.5	78.7
1,2-Dichlorobenzene	18.4	15.0	15.4	15.3	13.5	15.5	10.5	77.6
n-Butylbenzene	19.6	15.9	15.9	14.4	18.9	16.9	11.7	84.6
1,2,4-Trichlorobenzene	15.2	17.2	17.4	13.6	12.1	15.1	13.5	75.4
Hexachlorobutadiene	18.7	16.2	15.5	13.8	16.6	16.1	10.0	80.7
Naphthalene	13.9	11.1	10.2	10.8	11.4	11.5	11.0	57.4
1,2,3-Trichlorobenzene	14.9	15.2	16.8	13.7	12.7	14.7	9.5	73.2

TABLE 19
RECOVERIES IN GARDEN SOIL FORTIFIED AT 4 µg/kg (ANALYSIS BY METHOD 5035)

Compound	Recovery per Replicate (ng) 1	2	3	4	5	Mean	RSD	Mean Rec
Vinyl chloride	12.7	10.9	9.8	8.1	7.2	9.7	20.2	48.7
Trichlorofluoromethane	33.7	6.4	30.3	27.8	22.9	24.2	39.6	121
1,1-Dichloroethene	27.7	20.5	24.1	15.1	13.2	20.1	26.9	101
Methylene chloride	25.4	23.9	24.7	22.2	24.2	24.1	4.4	120
trans-1,2-Dichloroethene	2.8	3.0	3.3	2.2	2.4	2.7	15.0	13.6
1,1-Dichloroethane	24.1	26.3	27.0	20.5	21.2	23.8	11.0	119
cis-1,2-Dichloroethene	8.3	10.2	8.7	5.8	6.4	7.9	20.1	39.4
Bromochloromethane	11.1	11.8	10.2	8.8	9.0	10.2	11.2	50.9
Chloroform	16.7	16.9	17.0	13.8	15.0	15.9	7.9	79.3
1,1,1-Trichloroethane	24.6	22.8	22.1	16.2	20.9	21.3	13.4	107
Carbon tetrachloride	19.4	20.3	22.2	20.0	20.2	20.4	4.6	102
Benzene	21.4	22.0	22.4	19.6	20.4	21.2	4.9	106
Trichloroethene	12.4	16.5	14.9	9.0	9.9	12.5	22.9	62.7
1,2-Dichloropropane	19.0	18.8	19.7	16.0	17.6	18.2	7.1	91.0
Dibromomethane	7.3	8.0	6.9	5.6	6.8	6.9	11.3	34.6
Bromodichloromethane	14.9	15.9	15.9	12.8	13.9	14.7	8.3	73.3
Toluene	42.6	39.3	45.1	39.9	45.3	42.4	5.9	212
1,1,2-Trichloroethane	13.9	15.2	1.4	21.3	14.9	15.9	17.0	79.6
1,3-Dichloropropane	13.3	16.7	11.3	10.9	9.5	12.3	20.3	61.7
Dibromochloromethane	14.5	13.1	14.5	11.9	14.4	13.7	7.6	68.3
Chlorobenzene	8.4	10.0	8.3	6.9	7.8	8.3	12.1	41.3
1,1,1,2-Tetrachloroethane	16.7	16.7	15.6	15.8	15.7	16.1	3.2	80.4
Ethylbenzene	22.1	21.4	23.1	20.1	22.6	21.9	4.8	109
p-Xylene	41.4	38.4	43.8	38.3	44.0	41.2	6.1	206
o-Xylene	31.7	30.8	34.3	30.4	33.2	32.1	4.6	160
Styrene	0	0	0	0	0	0	0	0
Bromoform	8.6	8.9	9.1	7.0	7.7	8.3	9.4	41.4
iso-Propylbenzene	18.1	18.8	9.7	18.3	19.6	18.9	3.5	94.4
Bromobenzene	5.1	5.4	5.3	4.4	4.0	4.8	11.6	24.1
1,1,2,2-Tetrachloroethane	14.0	13.5	14.7	15.3	17.1	14.9	8.5	74.5
1,2,3-Trichloropropane	11.0	12.7	11.7	11.7	11.9	11.8	4.5	59.0
n-Propylbenzene	13.4	13.3	14.7	12.8	13.9	13.6	4.7	68.1
2-Chlorotoluene	8.3	9.0	11.7	8.7	7.9	9.1	14.8	45.6
4-Chlorotoluene	5.1	5.4	5.5	4.8	4.5	5.0	7.9	25.2
1,3,5-Trimethylbenzene	31.3	27.5	33.0	31.1	33.6	31.3	6.8	157
sec-Butylbenzene	13.5	13.4	16.4	13.8	15.4	14.5	8.3	72.5
1,2,4-Trimethylbenzene	38.7	32.4	40.8	34.1	40.3	37.3	9.1	186
1,3-Dichlorobenzene	3.6	3.6	3.7	3.0	3.2	3.4	8.0	17.2
p-iso-Propyltoluene	14.7	14.1	16.1	13.9	15.1	14.8	5.2	73.8
1,4-Dichlorobenzene	3.0	3.5	3.3	2.6	2.8	3.0	10.2	15.0
1,2-Dichlorobenzene	3.6	4.3	4.0	3.5	3.6	3.8	8.3	19.0
n-Butylbenzene	17.4	13.8	14.0	18.9	24.0	17.6	21.2	88.0
1,2,4-Trichlorobenzene	2.8	2.9	3.3	2.6	3.2	3.0	8.5	15.0
Hexachlorobutadiene	4.8	4.0	6.1	5.6	6.0	5.3	15.1	26.4
Naphthalene	5.5	5.1	5.5	4.7	5.6	5.3	6.2	26.5
1,2,3-Trichlorobenzene	2.2	2.3	2.4	2.2	2.3	2.3	3.5	11.4

Data in Table 19 are from Reference 15.

TABLE 20

VOLATILE ORGANIC ANALYTE RECOVERY FROM SOIL USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Soil/H_2O[b] Recovery Mean	Soil/H_2O[b] Recovery RSD	Soil/Oil[c] Recovery Mean	Soil/Oil[c] Recovery RSD	Soil/Oil/H_2O Recovery Mean	Soil/Oil/H_2O Recovery RSD
Chloromethane	61	20	40	18	108	68
Bromomethane	58	20	47	13	74	13
Vinyl chloride	54	12	46	11	72	20
Chloroethane	46	10	41	8	52	14
Methylene chloride	60	2	65	8	76	11
Acetone	INT[e]	INT	44	8		
Carbon disulfide	47	13	53	10	47	4
1,1-Dichloroethene	48	9	47	5	58	3
1,1-Dichloroethane	61	6	58	9	61	6
trans-1,2-Trichloroethane	54	7	60	7	56	5
cis-1,2-Dichloroethene	60	4	72	6	63	8
Chloroform	104	11	93	6	114	15
1,2-Dichloroethane	177	50	117	8	151	22
2-Butanone	INT	36	38	INT		
1,1,1-Trichloroethane	124	13	72	16	134	26
Carbon tetrachloride	172	122	INT	INT		
Vinyl acetate	88	11	INT			
Bromodichloromethane	93	4	91	23	104	23
1,1,2,2-Tetrachloroethane	96	13	50	12	104	7
1,2-Dichloropropane	105	8	102	6	111	6
trans-1,3-Dichloropropene	134	10	84	16	107	8
Trichloroethene	98	9	99	10	100	5
Dibromochloromethane	119	8	125	31	142	16
1,1,2-Trichloroethane	126	10	72	16	97	4
Benzene	99	7	CONT[f]	CONT		
cis-1,3-Dichloropropene	123	12	94	13	112	9
Bromoform	131	13	58	18	102	9
2-Hexanone	155	18	164	19	173	29
4-Methyl-2-pentanone	152	20	185	20	169	18
Tetrachloroethene	90	9	123	14	128	7
Toluene	94	3	CONT	CONT		
Chlorobenzene	98	7	93	18	112	5
Ethylbenzene	114	13	CONT	CONT		
Styrene	106	8	93	18	112	5
p-Xylene	97	9	CONT	CONT		
o-Xylene	105	8	112	12	144	13

TABLE 20 (cont.)

Compound	Soil/H_2O[b] Recovery Mean	RSD	Soil/Oil[c] Recovery Mean	RSD	Soil/Oil/H_2O Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	177	50	117	8	151	22
Toluene-d_8	96	6	79	12	82	6
Bromofluorobenzene	139	13	37	13	62	5

[a] Results are for 10 min. distillations times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision value reflects the propagated errors. Each analyte was spiked at 50 ppb. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may introduce bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Soil samples spiked with 0.2 mL water containing analytes and then 5 mL water added to make slurry.

[c] Soil sample + 1 g cod liver oil, spiked with 0.2 mL water containing analytes.

[d] Soil samples + 1 g cod liver oil, spiked as above with 5 mL of water added to make slurry.

[e] Interference by co-eluting compounds prevented accurate measurement of analyte.

[f] Contamination of sample matrix by analyte prevented assessment of efficiency.

TABLE 21

VACUUM DISTILLATION EFFICIENCIES FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Efficiency Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	CONT[c]	
Acetone	CONT[c]	
Carbon disulfide	79	36
1,1-Dichloroethene	122	39
1,1-Dichloroethane	126	35
trans-1,2-Trichloroethene	109	46
cis-1,2-Dichloroethene	106	22
Chloroform	111	32
1,2-Dichloroethane	117	27
2-Butanone	INT[d]	
1,1,1-Trichloroethane	106	30
Carbon tetrachloride	83	34
Vinyl acetate	INT[d]	
Bromodichloromethane	97	22
1,1,2,2-Tetrachloroethane	67	20
1,2-Dichloropropane	117	23
trans-1,3-Dichloropropene	92	22
Trichloroethene	98	31
Dibromochloromethane	71	19
1,1,2-Trichloroethane	92	20
Benzene	129	35
cis-1,3-Dichloropropene	102	24
Bromoform	58	19
2-Hexanone	INT[d]	
4-Methyl-2-pentanone	113	37
Tetrachloroethene	66	20
Toluene	CONT[c]	
Chlorobenzene	65	19
Ethylbenzene	74	19
Styrene	57	14
p-Xylene	46	13
o-Xylene	83	20

TABLE 21 (cont.)

Compound	Efficiency Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	115	27
Toluene-d_8	88	24
Bromofluorobenzene	52	15

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicate 10-g aliquots of fish spiked at 25 ppb were analyzed using GC/MS external standard quantitation. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards were replicated and results reflect 1 sigma propagated standard deviation.

[b] No analyses.

[c] Contamination of sample matrix by analyte prevented accurate assessment of analyte efficiency.

[d] Interfering by co-eluting compounds prevented accurate measurement of analyte.

TABLE 22

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN FISH TISSUE (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	7.8	7.3
Bromomethane	9.7	9.8
Vinyl chloride	9.5	9.4
Chloroethane	9.2	10.0
Methylene chloride	CONT[b]	CONT[b]
Acetone	CONT[b]	CONT[b]
Carbon disulfide	5.4	4.9
1,1-Dichloroethene	4.0	5.7
1,1-Dichloroethane	4.0	3.5
trans-1,2-Dichloroethene	4.4	4.0
cis-1,2-Dichloroethene	4.7	4.1
Chloroform	5.6	5.0
1,2-Dichloroethane	3.3	3.2
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	1.1	4.2
Carbon tetrachloride	3.2	3.5
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	3.2	2.8
1,1,2,2-Tetrachloroethane	4.4	3.8
1,2-Dichloropropane	3.8	3.7
trans-1,3-Dichloropropene	3.4	3.0
Trichloroethene	3.1	4.0
Dibromochloromethane	3.5	3.2
1,1,2-Trichloroethane	4.4	3.3
Benzene	3.6	3.2
cis-1,3-Dichloropropene	3.5	3.0
Bromoform	4.9	4.0
2-Hexanone	7.7	8.0
4-Methyl-2-pentanone	7.5	8.0
Tetrachloroethene	4.3	4.0
Toluene	3.0	2.5
Chlorobenzene	3.3	2.8
Ethylbenzene	3.6	3.5
Styrene	3.5	3.3
p-Xylene	3.7	3.5
o-Xylene	3.3	4.7

Footnotes are on the following page.

[a] Values shown are the average MDLs for studies on three non-consecutive days, involving seven replicate analyses of 10 g of fish tissue spiked a 5 ppb. Daily MDLs were calculated as three times the standard deviation. Quantitation was performed by GC/MS Method 8260 and separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] Contamination of sample by analyte prevented determination.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 23

VOLATILE ORGANIC ANALYTES RECOVERY FOR WATER USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Chloromethane	114	27	116	29	176	67
Bromomethane	131	14	121	14	113	21
Vinyl chloride	131	13	120	16	116	23
Chloroethane	110	15	99	8	96	16
Methylene chloride	87	16	105	15	77	6
Acetone	83	22	65	34	119	68
Carbon disulfide	138	17	133	23	99	47
1,1-Dichloroethene	105	11	89	4	96	18
1,1-Dichloroethane	118	10	119	11	103	25
trans-1,2-Dichloroethene	105	11	107	14	96	18
cis-1,2-Dichloroethene	106	7	99	5	104	23
Chloroform	114	6	104	8	107	21
1,2-Dichloroethane	104	6	109	8	144	19
2-Butanone	83	50	106	31	INT[c]	
1,1,1-Trichloroethane	118	9	109	9	113	23
Carbon tetrachloride	102	6	108	12	109	27
Vinyl acetate	90	16	99	7	72	36
Bromodichloromethane	104	3	110	5	99	5
1,1,2,2-Tetrachloroethane	85	17	81	7	111	43
1,2-Dichloropropane	100	6	103	2	104	7
trans-1,3-Dichloropropene	105	8	105	4	92	4
Trichloroethene	98	4	99	2	95	5
Dibromochloroethane	99	8	99	6	90	25
1,1,2-Trichloroethane	98	7	100	4	76	12
Benzene	97	4	100	5	112	10
cis-1,3-Dichloropropene	106	5	105	4	98	3
Bromoform	93	16	94	8	57	21
2-Hexanone	60	17	63	16	78	23
4-Methyl-2-pentanone	79	24	63	14	68	15
Tetrachloroethene	101	3	97	7	77	14
Toluene	100	6	97	8	85	5
Chlorobenzene	98	6	98	4	88	16
Ethylbenzene	100	3	92	8	73	13
Styrene	98	4	97	9	88	16
p-Xylene	96	4	94	8	60	12
o-Xylene	96	7	95	6	72	14

TABLE 23 (cont.)

Compound	5 mL H_2O[b] Recovery Mean	RSD	20 mL H_2O[c] Recovery Mean	RSD	20 mL H_2O/Oil Recovery Mean	RSD
Surrogates						
1,2-Dichloroethane	104	6	109	6	144	19
Toluene-d_8	104	5	102	2	76	7
Bromofluorobenzene	106	6	106	9	40	8

[a] Results are for 10 min. distillation times, and condenser temperature held at -10°C. A 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness was used for chromatography. Standards and samples were replicated and precision values reflect the propagated errors. Concentrations of analytes were 50 ppb for 5-mL samples and 25 ppb for 20-mL samples. Recovery data generated with comparison to analyses of standards without the water matrix.

[b] Sample contained 1 gram cod liver oil and 20 mL water. An emulsion was created by adding 0.2 mL of water saturated with lecithin.

[c] Interference by co-eluting compounds prevented accurate assessment of recovery.

TABLE 24

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES USING VACUUM DISTILLATION (METHOD 5032) (INTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.2	8.0	7.3	N/A[f]
Bromomethane	2.8	4.9	9.8	N/A[f]
Vinyl chloride	3.5	6.0	9.4	N/A[f]
Chloroethane	5.9	6.0	10.0	N/A[f]
Methylene chloride	3.1	4.0	CONT[g]	0.05
Acetone	5.6	CONT[g]	CONT[g]	0.06
Carbon disulfide	2.5	2.0	4.9	0.18
1,1-Dichloroethene	2.9	3.2	5.7	0.18
1,1-Dichloroethane	2.2	2.0	3.5	0.14
trans-1,2-Dichloroethene	2.2	1.4	4.0	0.10
cis-1,2-Dichloroethene	2.0	2.3	4.1	0.07
Chloroform	2.4	1.8	5.0	0.07
1,2-Dichloroethane	1.7	1.5	3.2	0.06
2-Butanone	7.4	INT[h]	INT[h]	INT[h]
1,1,1-Trichloroethane	1.8	1.7	4.2	0.10
Carbon tetrachloride	1.4	1.5	3.5	0.13
Vinyl acetate	11.8	INT[h]	INT[h]	INT[h]
Bromodichloromethane	1.6	1.4	2.8	0.06
1,1,2,2-Tetrachloroethane	2.5	2.1	3.8	0.02
1,2-Dichloropropane	2.2	2.1	3.7	0.15
trans-1,3-Dichloropropene	1.5	1.7	3.0	0.05
Trichloroethene	1.6	1.7	4.0	0.04
Dibromochloromethane	1.7	1.5	3.2	0.07
1,1,2-Trichloroethane	2.1	1.7	3.3	0.05
Benzene	0.5	1.5	3.2	0.05
cis-1,3-Dichloropropene	1.4	1.7	3.0	0.04
Bromoform	1.8	1.5	4.0	0.05
2-Hexanone	4.6	3.6	8.0	INT[h]
4-Methyl-2-pentanone	3.5	4.6	8.0	INT[h]
Tetrachloroethene	1.4	1.6	4.0	0.10
Toluene	1.0	3.3	2.5	0.05
Chlorobenzene	1.4	1.4	2.8	0.06
Ethylbenzene	1.5	2.8	3.5	0.04
Styrene	1.4	1.4	3.3	0.18
p-Xylene	1.5	2.9	3.5	0.20
o-Xylene	1.7	3.4	4.7	0.07

Footnotes are found on the following page.

[a] Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Method detection limits are the average MDLs for studies on three non-consecutive days.

[b] Method detection limits are the average MDLs for studies of three non-consecutive days. Daily studies were seven replicated analyses of 5 mL aliquots of 4 ppb soil. Daily MDLs were three times the standard deviation.

[c] Daily studies were seven replicated analyses of 10 g fish tissue spiked at 5 ppb. Daily MDLs were three times the standard deviation. Quantitation was performed using GC/MS Method 8260 and chromatographic separation with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[d] Method detection limits are estimated analyzing 1 g of cod liver oil samples spiked at 250 ppm. Five replicates were analyzed using Method 8260.

[e] No analyses.

[f] Contamination of sample by analyte prevented determination.

[g] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 25

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES (METHOD 5032) (EXTERNAL STANDARD METHOD)[a]

Compound	Water[b] (µg/L)	Soil[c] (µg/kg)	Tissue[d] (µg/kg)	Oil[e] (mg/kg)
Chloromethane	3.1	8.6[f]	7.8	N/A[g]
Bromomethane	2.5	4.9[f]	9.7	N/A[g]
Vinyl chloride	4.0	7.1[f]	9.5	N/A[g]
Chloroethane	6.1	7.5[f]	9.2	N/A[g]
Methylene chloride	3.1	3.3	CONT[h]	0.08
Acetone	33.0[f]	CONT[h]	CONT[h]	0.12
Carbon disulfide	2.5	3.2	5.4	0.19
1,1-Dichloroethene	3.4	3.8	4.0	0.19
1,1-Dichloroethane	2.3	1.7	4.0	0.13
trans-1,2-Dichloroethene	3.0	3.2	4.4	0.09
cis-1,2-Dichloroethene	2.4	2.7	4.7	0.08
Chloroform	2.7	2.6	5.6	0.06
1,2-Dichloroethane	1.6	1.7	3.3	0.06
2-Butanone	57.0[f]	INT[i]	INT[i]	INT[i]
1,1,1-Trichloroethane	1.6	2.4	1.1	0.08
Carbon tetrachloride	1.5	1.7	3.2	0.15
Vinyl acetate	23.0[f]	INT[i]	INT[i]	INT[i]
Bromodichloromethane	2.0	2.3	3.2	0.05
1,1,2,2-Tetrachloroethane	3.6	3.2	4.4	0.09
1,2-Dichloropropane	2.9	3.7	3.8	0.12
trans-1,3-Dichloropropene	2.3	2.4	3.8	0.08
Trichloroethene	2.5	3.0	3.1	0.06
Dibromochloromethane	2.1	2.9	3.5	0.04
1,1,2-Trichloroethane	2.7	2.8	4.4	0.07
Benzene	1.7	2.9	3.6	0.03
cis-1,3-Dichloropropene	2.1	2.5	3.5	0.06
Bromoform	2.3	2.5	4.9	0.10
2-Hexanone	4.6	4.6	7.7	INT[i]
4-Methyl-2-pentanone	3.8	3.9	7.5	INT[i]
Tetrachloroethene	1.8	2.6	4.3	0.12
Toluene	1.8	4.4	3.0	0.09
Chlorobenzene	2.4	2.6	3.3	0.07
Ethylbenzene	2.4	4.1	3.6	0.09
Styrene	2.0	2.5	3.5	0.16
p-Xylene	2.3	3.9	3.7	0.18
o-Xylene	2.4	4.1	3.3	0.08

[a] Method detection limits are the average MDLs for studies on three non-consecutive days. Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb. Daily MDLs were three times the standard deviation.

[b] Daily studies were seven replicate analyses of 5-mL aliquots of water spiked at 4 ppb.

[c] These studies were seven replicate analyses of 5-g aliquots of soil spiked at 4 ppb.

[d] These studies were seven replicate analyses of 10-g aliquots of fish tissue spiked at 5 ppb.

[e] Method detection limits were estimated by analyzing cod liver oil samples spiked at 250 ppb. Five replicates were analyzed using Method 8260.

[f] Method detection limits were estimated by analyzing replicate 50 ppb standards five times over a single day.

[g] No analyses.

Contamination of sample by analyte prevented determination.

Interference by co-eluting compound prevented accurate quantitation.

TABLE 26

VOLATILE ORGANIC ANALYTE RECOVERY FROM OIL USING VACUUM DISTILLATION (METHOD 5032)[a]

Compound	Recovery Mean (%)	RSD (%)
Chloromethane	N/A[b]	
Bromomethane	N/A[b]	
Vinyl chloride	N/A[b]	
Chloroethane	N/A[b]	
Methylene chloride	62	32
Acetone	108	55
Carbon disulfide	98	46
1,1-Dichloroethene	97	24
1,1-Dichloroethane	96	22
trans-1,2-Trichloroethene	86	23
cis-1,2-Dichloroethene	99	11
Chloroform	93	14
1,2-Dichloroethane	138	31
2-Butanone	INT[c]	
1,1,1-Trichloroethane	89	14
Carbon tetrachloride	129	23
Vinyl acetate	INT[c]	
Bromodichloromethane	106	14
1,1,2,2-Tetrachloroethane	205	46
1,2-Dichloropropane	107	24
trans-1,3-Dichloropropene	98	13
Trichloroethene	102	8
Dibromochloromethane	168	21
1,1,2-Trichloroethane	95	7
Benzene	146	10
cis-1,3-Dichloropropene	98	11
Bromoform	94	18
2-Hexanone	INT[c]	
4-Methyl-2-pentanone	INT[c]	
Tetrachloroethene	117	22
Toluene	108	8
Chlorobenzene	101	12
Ethylbenzene	96	10
Styrene	120	46
p-Xylene	87	23
o-Xylene	90	10

TABLE 26 (cont.)

Compound	Recovery Mean (%)	RSD (%)
Surrogates		
1,2-Dichloroethane	137	30
Toluene-d_8	84	6
Bromofluorobenzene	48	2

[a] Results are for 10 min. distillation times and condenser temperature held at -10°C. Five replicates of 10-g fish aliquots spiked at 25 ppb were analyzed. Quantitation was performed with a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness. Standards and samples were replicated and precision value reflects the propagated errors. Vacuum distillation efficiencies (Method 5032) are modified by internal standard corrections. Method 8260 internal standards may bias for some analytes. See Method 5032 to identify alternate internal standards with similar efficiencies to minimize bias.

[b] Not analyzed.

[c] Interference by co-evaluating compounds prevented accurate measurement of analyte.

TABLE 27

METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC ANALYTES IN OIL (METHOD 5032)[a]

Compound	Method Detection Limit (ppb) External Standard Method	Internal Standard Method
Chloromethane	N/A[b]	N/A[b]
Bromomethane	N/A[b]	N/A[b]
Vinyl chloride	N/A[b]	N/A[b]
Chloroethane	N/A[b]	N/A[b]
Methylene chloride	80	50
Acetone	120	60
Carbon disulfide	190	180
1,1-Dichloroethene	190	180
1,1-Dichloroethane	130	140
trans-1,2-Dichloroethene	90	100
cis-1,2-Dichloroethene	80	70
Chloroform	60	70
1,2-Dichloroethane	60	60
2-Butanone	INT[c]	INT[c]
1,1,1-Trichloroethane	80	100
Carbon tetrachloride	150	130
Vinyl acetate	INT[c]	INT[c]
Bromodichloromethane	50	60
1,1,2,2-Tetrachloroethane	90	20
1,2-Dichloropropane	120	150
trans-1,3-Dichloropropene	80	50
Trichloroethene	60	40
Dibromochloromethane	40	70
1,1,2-Trichloroethane	70	50
Benzene	30	50
cis-1,3-Dichloropropene	60	40
Bromoform	100	50
2-Hexanone	INT[c]	INT[c]
4-Methyl-2-pentanone	INT[c]	INT[c]
Tetrachloroethene	120	100
Toluene	90	50
Chlorobenzene	70	60
Ethylbenzene	90	40
Styrene	160	180
p-Xylene	180	200
o-Xylene	80	70

[a] Method detection limits are estimated as the result of five replicated analyses of 1 g cod liver oil spiked at 25 ppb. MDLs were calculated as three times the standard deviation. Quantitation was performed using a 30 m x 0.53 mm ID stable wax column with a 1 µm film thickness.

[b] No analyses.

[c] Interference by co-eluting compounds prevented accurate quantitation.

TABLE 28

INTERNAL STANDARDS FOR ANALYTES AND SURROGATES PREPARED USING EQUILIBRIUM HEADSPACE ANALYSIS (METHOD 5021)

Chloroform-d_1	1,1,2-TCA-d_3	Bromobenzene-d_5
Dichlorodifluoromethane	1,1,1-Trichloroethane	Chlorobenzene
Chloromethane	1,1-Dichloropropene	Bromoform
Vinyl chloride	Carbon tetrachloride	Styrene
Bromomethane	Benzene	iso-Propylbenzene
Chloroethane	Dibromomethane	Bromobenzene
Trichlorofluoromethane	1,2-Dichloropropane	n-Propylbenzene
1,1-Dichloroethene	Trichloroethene	2-Chlorotoluene
Methylene chloride	Bromodichloromethane	4-Chlorotoluene
trans-1,2-Dichloroethene	cis-1,3-Dichloropropene	1,3,5-Trimethylbenzene
1,1-Dichloroethane	trans-1,3-Dichloropropene	tert-Butylbenzene
cis-1,2-Dichloroethene	1,1,2-Trichloroethane	1,2,4-Trimethylbenzene
Bromochloromethane	Toluene	sec-Butylbenzene
Chloroform	1,3-Dichloropropane	1,3-Dichlorobenzene
2,2-Dichloropropane	Dibromochloromethane	1,4-Dichlorobenzene
1,2-Dichloroethane	1,2-Dibromoethane	p-iso-Propyltoluene
	Tetrachloroethene	1,2-Dichlorobenzene
	1,1,2-Trichloroethane	n-Butylbenzene
	Ethylbenzene	1,2-Dibromo-3-chloropropane
	m-Xylene	1,2,4-Trichlorobenzene
	p-Xylene	Naphthalene
	o-Xylene	Hexachlorobutadiene
	1,1,2,2-Tetrachloroethane	1,2,3-Trichlorobenzene
	1,2,3-Trichloropropane	

TABLE 29

PRECISION AND MDL DETERMINED FOR ANALYSIS OF FORTIFIED SAND[a] (METHOD 5021)

Compound	% RSD	MDL (µg/kg)
Benzene	3.0	0.34
Bromochloromethane	3.4	0.27
Bromodichloromethane	2.4	0.21
Bromoform	3.9	0.30
Bromomethane	11.6	1.3
Carbon tetrachloride	3.6	0.32
Chlorobenzene	3.2	0.24
Chloroethane	5.6	0.51
Chloroform	3.1	0.30
Chloromethane	4.1	3.5[b]
1,2-Dibromo-3-chloropropane	5.7	0.40
1,2-Dibromoethane	3.2	0.29
Dibromomethane	2.8	0.20
1,2-Dichlorobenzene	3.3	0.27
1,3-Dichlorobenzene	3.4	0.24
1,4-Dichlorobenzene	3.7	0.30
Dichlorodifluoromethane	3.0	0.28
1,1-Dichloroethane	4.5	0.41
1,2-Dichloroethane	3.0	0.24
1,1-Dichloroethene	3.3	0.28
cis-1,2-Dichloroethene	3.2	0.27
trans-1,2-Dichloroethene	2.6	0.22
1,2-Dichloropropane	2.6	0.21
1,1-Dichloropropene	3.2	0.30
cis-1,3-Dichloropropene	3.4	0.27
Ethylbenzene	4.8	0.47
Hexachlorobutadiene	4.1	0.38
Methylene chloride	8.2	0.62[c]
Naphthalene	16.8	3.4[c]
Styrene	7.9	0.62
1,1,1,2-Tetrachloroethane	3.6	0.27
1,1,2,2-Tetrachloroethane	2.6	0.20
Tetrachloroethene	9.8	1.2[c]
Toluene	3.5	0.38
1,2,4-Trichlorobenzene	4.2	0.44
1,1,1-Trichloroethane	2.7	0.27
1,1,2-Trichloroethane	2.6	0.20
Trichloroethene	2.3	0.19

Compound	% RSD	MDL (µg/kg)
Trichlorofluoromethane	2.7	0.31
1,2,3-Trichloropropane	1.5	0.11
Vinyl chloride	4.8	0.45
m-Xylene/p-Xylene	3.6	0.37
o-Xylene	3.6	0.33

[a] Most compounds spiked at 2 ng/g (2 µg/kg)
[b] Incorrect ionization due to methanol
[c] Compound detected in unfortified sand at >1 ng

TABLE 30

RECOVERIES IN GARDEN SOIL FORTIFIED AT 20 µg/kg (ANALYSIS BY METHOD 5021)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Benzene	37.6	35.2	38.4	37.1	3.7	185[a]
Bromochloromethane	20.5	19.4	20.0	20.0	2.3	100
Bromodichloromethane	21.1	20.3	22.8	21.4	4.9	107
Bromoform	23.8	23.9	25.1	24.3	2.4	121
Bromomethane	21.4	19.5	19.7	20.2	4.2	101
Carbon tetrachloride	27.5	26.6	28.6	27.6	3.0	138
Chlorobenzene	25.6	25.4	26.4	25.8	1.7	129
Chloroethane	25.0	24.4	25.3	24.9	1.5	125
Chloroform	21.9	20.9	21.7	21.5	2.0	108
Chloromethane	21.0	19.9	21.3	20.7	2.9	104[a]
1,2-Dibromo-3-chloro-propane	20.8	20.8	21.0	20.9	0.5	104
1,2-Dibromoethane	20.1	19.5	20.6	20.1	2.2	100
Dibromomethane	22.2	21.0	22.8	22.0	3.4	110
1,2-Dichlorobenzene	18.0	17.7	17.1	17.6	2.1	88.0
1,3-Dichlorobenzene	21.2	21.0	20.1	20.8	2.3	104
1,4-Dichlorobenzene	20.1	20.9	19.9	20.3	2.1	102
Dichlorodifluoromethane	25.3	24.1	25.4	24.9	2.4	125
1,1-Dichloroethane	23.0	22.0	22.7	22.6	1.9	113
1,2-Dichloroethane	20.6	19.5	19.8	20.0	2.3	100
1,1-Dichloroethene	24.8	23.8	24.4	24.3	1.7	122
cis-1,2-Dichloroethene	21.6	20.0	21.6	21.1	3.6	105
trans-1,2-Dichloroethene	22.4	21.4	22.2	22.0	2.0	110
1,2-Dichloropropane	22.8	22.2	23.4	22.8	2.1	114
1,1-Dichloropropene	26.3	25.7	28.0	26.7	3.7	133
cis-1,3-Dichloropropene	20.3	19.5	21.1	20.3	3.2	102
Ethylbenzene	24.7	24.5	25.5	24.9	1.7	125
Hexachlorobutadiene	23.0	25.3	25.2	24.5	4.3	123
Methylene chloride	26.0	25.7	26.1	25.9	0.7	130[a]
Naphthalene	13.8	12.7	11.8	12.8	6.4	63.8[a]
Styrene	24.2	23.3	23.3	23.6	1.8	118
1,1,1,2-Tetrachloroethane	21.4	20.2	21.3	21.0	2.6	105
1,1,2,2-Tetrachloroethane	18.6	17.8	19.0	18.5	2.7	92.3
Tetrachloroethene	25.2	24.8	26.4	25.5	2.7	127
Toluene	28.6	27.9	30.9	29.1	4.4	146[a]
1,2,4-Trichlorobenzene	15.0	14.4	12.9	14.1	6.3	70.5
1,1,1-Trichloroethane	28.1	27.2	29.9	28.4	4.0	142
1,1,2-Trichloroethane	20.8	19.6	21.7	20.7	4.2	104

TABLE 30 (cont.)

Compound	Recovery per Replicate (ng) Sample 1	Sample 2	Sample 3	Mean (ng)	RSD	Recovery (%)
Trichloroethene	26.3	24.9	26.8	26.0	3.1	130
Trichlorofluoromethane	25.9	24.8	26.5	25.7	2.7	129
1,2,3-Trichloropropane	18.8	18.3	19.3	18.8	2.2	94.0
Vinyl chloride	24.8	23.2	23.9	24.0	2.7	120
m-Xylene/p-Xylene	24.3	23.9	25.3	24.5	2.4	123
o-Xylene	23.1	22.3	23.4	22.9	2.0	115

[a] Compound found in unfortified garden soil matrix at >5 ng.

TABLE 31

METHOD DETECTION LIMITS AND BOILING POINTS
FOR VOLATILE ORGANICS (ANALYSIS BY METHOD 5041)[a]

Compound	Detection Limit (ng)	Boiling Point (°C)
Chloromethane	58	-24
Bromomethane	26	4
Vinyl chloride	14	-13
Chloroethane	21	13
Methylene chloride	9	40
Acetone	35	56
Carbon disulfide	11	46
1,1-Dichloroethene	14	32
1,1-Dichloroethane	12	57
trans-1,2-Dichloroethene	11	48
Chloroform	11	62
1,2-Dichloroethane	13	83
1,1,1-Trichloroethane	8	74
Carbon tetrachloride	8	77
Bromodichloromethane	11	88
1,1,2,2-Tetrachloroethane**	23	146
1,2-Dichloropropane	12	95
trans-1,3-Dichloropropene	17	112
Trichloroethene	11	87
Dibromochloromethane	21	122
1,1,2-Trichloroethane	26	114
Benzene	26	80
cis-1,3-Dichloropropene	27	112
Bromoform**	26	150
Tetrachloroethene	11	121
Toluene	15	111
Chlorobenzene	15	132
Ethylbenzene**	21	136
Styrene**	46	145
Trichlorofluoromethane	17	24
Iodomethane	9	43
Acrylonitrile	13	78
Dibromomethane	14	97
1,2,3-Trichloropropane**	37	157
total Xylenes**	22	138-144

Footnotes are found on the following page.

* The method detection limit (MDL) is defined in Chapter One. The detection limits cited above were determined according to 40 CFR, Part 136, Appendix B, using standards spiked onto clean VOST tubes. Since clean VOST tubes were used, the values cited above represent the best that the methodology can achieve. The presence of an emissions matrix will affect the ability of the methodology to perform at its optimum level.

** Boiling Point greater than 130°C. Not appropriate for quantitative sampling by Method 0030.

TABLE 32

VOLATILE INTERNAL STANDARDS WITH CORRESPONDING ANALYTES ASSIGNED FOR QUANTITATION (METHOD 5041)

Bromochloromethane	1,4-Difluorobenzene
Acetone	Benzene
Acrylonitrile	Bromodichloromethane
Bromomethane	Bromoform
Carbon disulfide	Carbon tetrachloride
Chloroethane	Chlorodibromomethane
Chloroform	Dibromomethane
Chloromethane	1,2-Dichloropropane
1,1-Dichloroethane	cis-1,3-Dichloropropene
1,2-Dichloroethane	trans-1,3-Dichloropropene
1,2-Dichloroethane-d_4 (surrogate)	1,1,1-Trichloroethane
1,1-Dichloroethene	1,1,2-Trichloroethane
Trichloroethene	
trans-1,2-Dichloroethene	
Iodomethane	
Methylene chloride	
Trichlorofluoromethane	
Vinyl chloride	

Chlorobenzene-d_5
4-Bromofluorobenzene (surrogate)
Chlorobenzene
Ethylbenzene
Styrene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Toluene
Toluene-d_8 (surrogate)
1,2,3-Trichloropropane
Xylenes

TABLE 33

METHOD 0040 - COMPOUNDS DEMONSTRATED TO BE APPLICABLE TO THE METHOD

Compound	Boiling Point (°C)	Condensation Point at 20°C (%)	Estimated Detection Limit[a] (ppm)
Dichlorodifluoromethane	-30	Gas	0.20
Vinyl chloride	-19	Gas	0.11
1,3-Butadiene	-4	Gas	0.90
1,2-Dichloro-1,1,2,2-tetrafluoroethane	4	Gas	0.14
Methyl bromide	4	Gas	0.14
Trichlorofluoromethane	24	88	0.18
1,1-Dichloroethene	31	22	0.07
Methylene chloride	40	44	0.05
1,1,2-Trichloro-trifluoroethane	48	37	0.13
Chloroform	61	21	0.04
1,1,1-Trichloroethane	75	13	0.03
Carbon tetrachloride	77	11	0.03
Benzene	80	10	0.16
Trichloroethene	87	8	0.04
1,2-Dichloropropane	96	5	0.05
Toluene	111	3	0.08
Tetrachloroethene	121	2	0.03

[a] Since this value represents a direct injection (no concentration) from the Tedlar® bag, these values are directly applicable as stack detection limits.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS

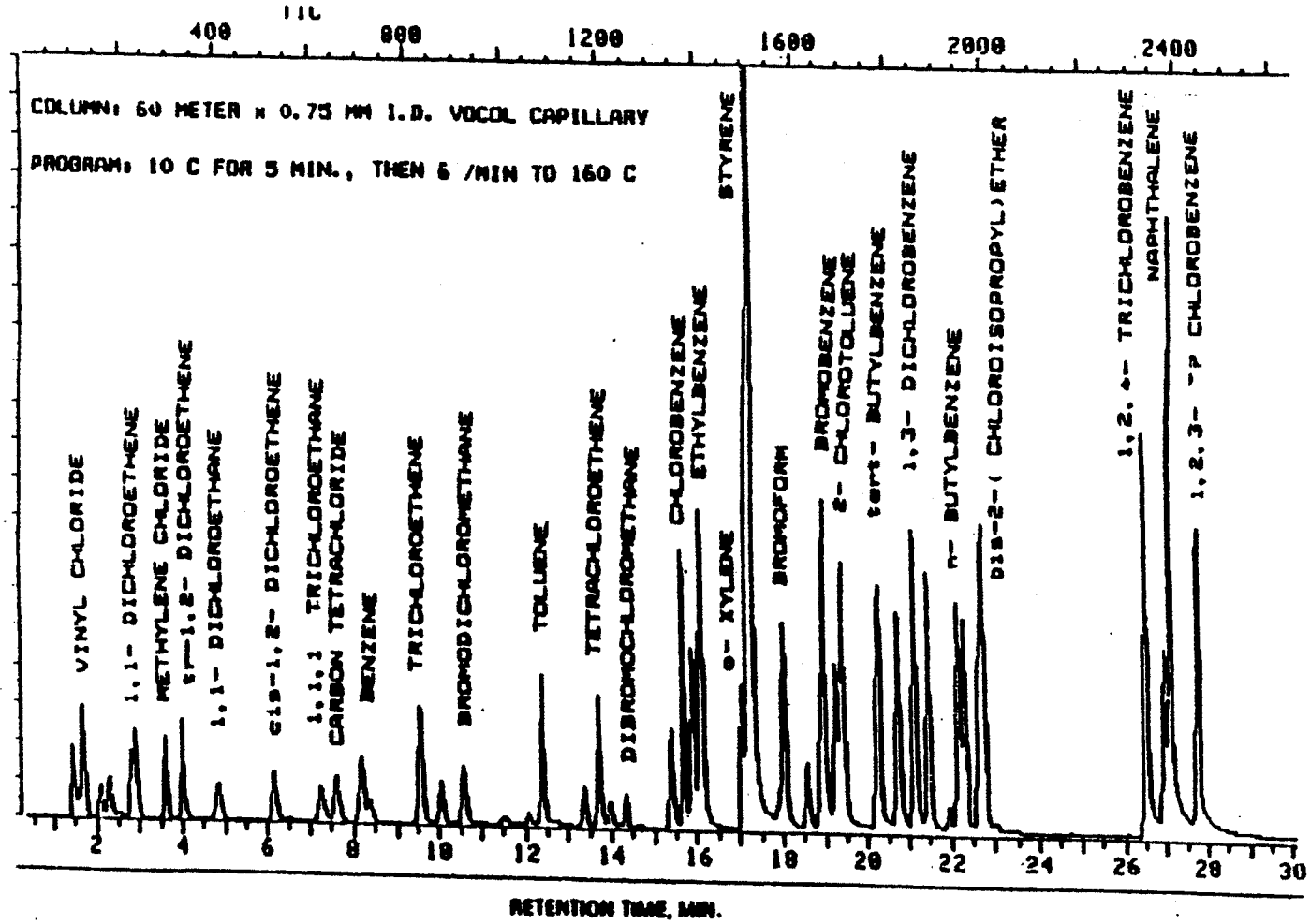


FIGURE 2
GAS CHROMATOGRAM OF VOLATILE ORGANICS

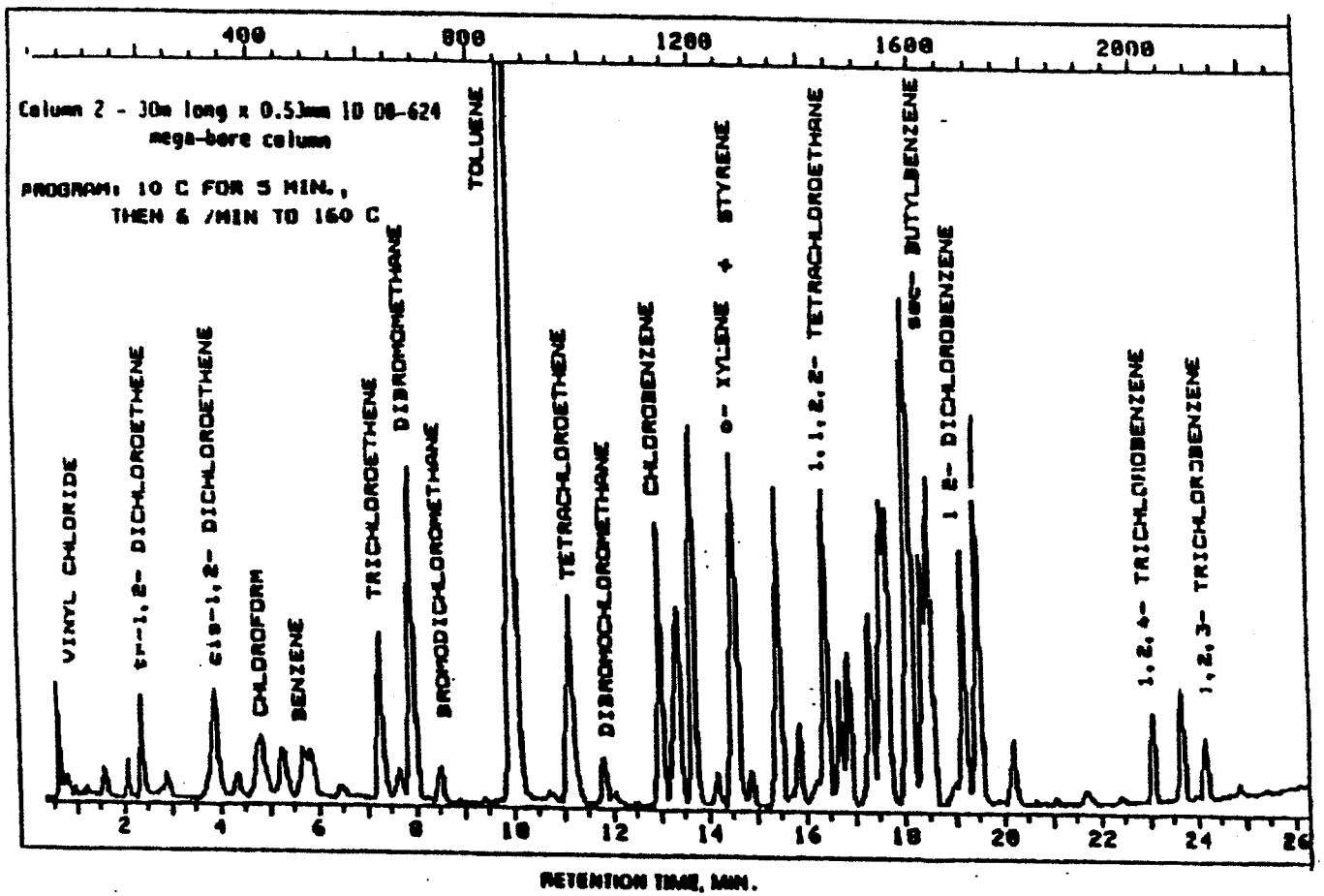


FIGURE 3
GAS CHROMATOGRAM OF VOLATILE ORGANICS

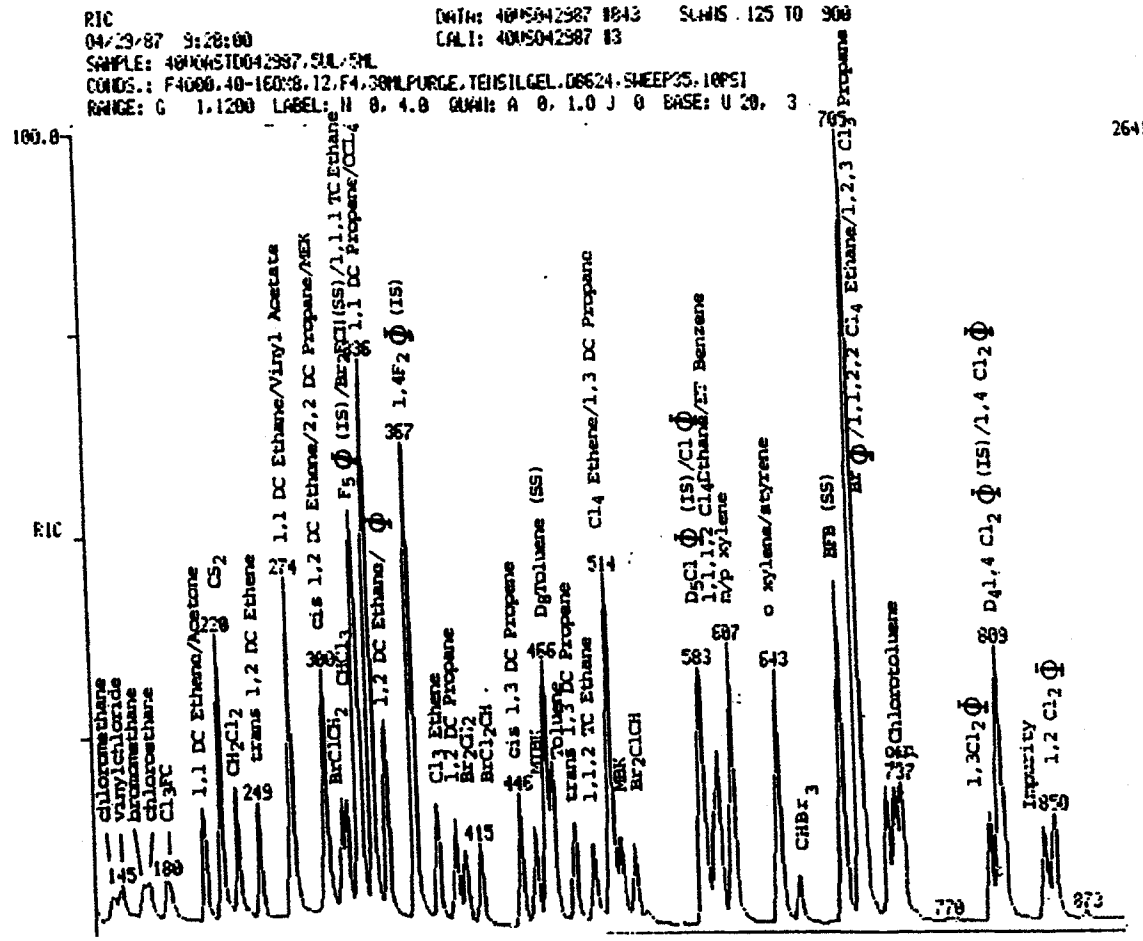
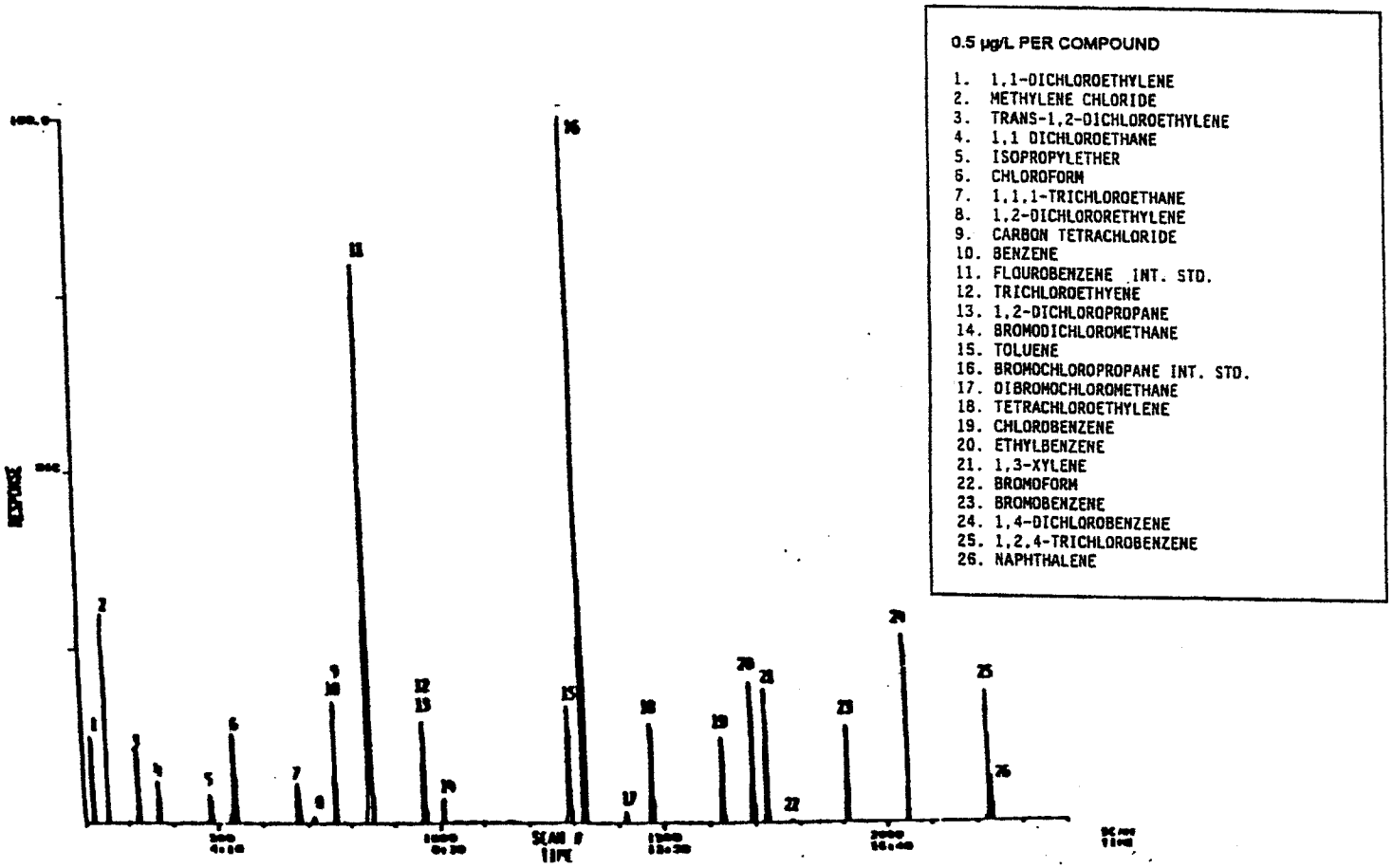
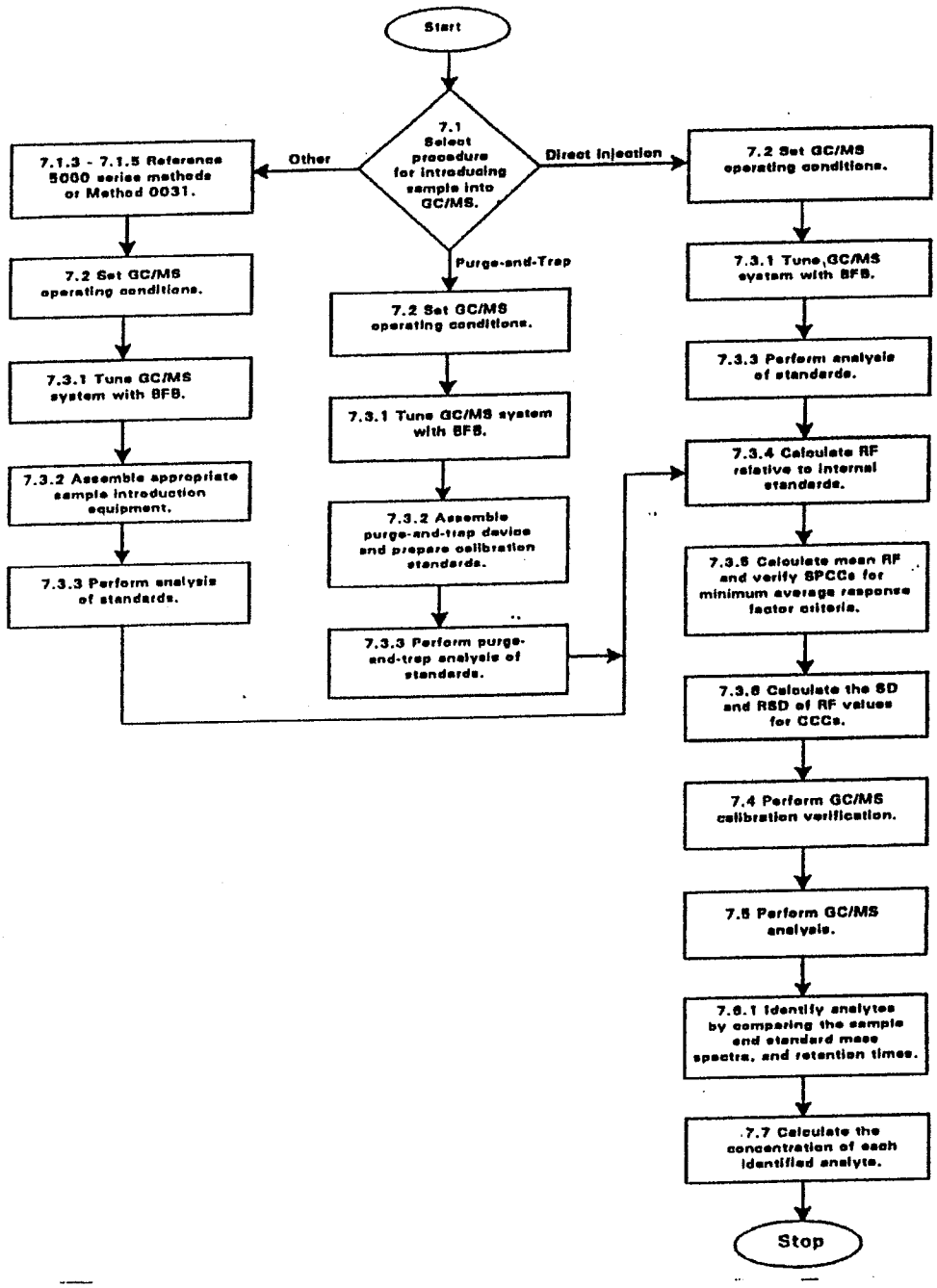


FIGURE 4
GAS CHROMATOGRAM OF TEST MIXTURE




Start
7.1 Select procedure for introducing sample into GC/MS.
Other
Purge-and-Trap
Direct injection
7.1.3 - 7.1.5 Reference 5000 series methods or Method 0031.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble appropriate sample introduction equipment.
7.3.3 Perform analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.2 Assemble purge-and-trap device and prepare calibration standards.
7.3.3 Perform purge-and-trap analysis of standards.
7.2 Set GC/MS operating conditions.
7.3.1 Tune GC/MS system with BFB.
7.3.3 Perform analysis of standards.
7.3.4 Calculate RF relative to internal standards.
7.3.5 Calculate mean RF and verify SPCCs for minimum average response factor criteria.
7.3.6 Calculate the SD and RSD of RF values for CCCs.
7.4 Perform GC/MS calibration verification.
7.5 Perform GC/MS analysis.
7.6.1 Identify analytes by comparing the sample and standard mass spectra, and retention times.
7.7 Calculate the concentration of each identified analyte.
Stop

Copper

METHOD 200.7

TRACE ELEMENTS IN WATER, SOLIDS, AND BIOSOLIDS BY INDUCTIVELY COUPLED PLASMA-ATOMIC EMISSION SPECTROMETRY

Revision 5.0

August 1998

U.S. Environmental Protection Agency
Office of Water
Office of Science and Technology
Engineering and Analysis Division (4303)
401 M Street SW
Washington, D.C. 20460

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USEPA-ICP Users Group (Edited by T.D. Martin and J.F. Kopp) - Method 200.7, Revision 1.0, (Printed 1979, Published 1982)

T.D. Martin and E.R. Martin - Method 200.7, Revision 3.0 (1990)

T.D. Martin, C.A. Brockhoff, J.T. Creed, and S.E. Long (Technology Applications Inc.) - Method 200.7, Revision 3.3 (1991)

T.D. Martin, C.A. Brockhoff, J.T. Creed, and EMMC Methods Work Group - Method 200.7, Revision 4.4 (1994)

Disclaimer

This draft method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of the U.S. Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. EPA plans further validation of this draft method. The method may be revised following validation to reflect results of the study.

EPA welcomes suggestions for improvement of this method. Suggestions and questions concerning this method or its application should be addressed to:

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Note: This method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this method are met. The laboratory may not omit any quality control analyses. The terms "shall," "must," and "may not" define procedures required for producing reliable results. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this method.

Method 200.7

Trace Elements in Water, Solids, and Biosolids by Inductively Coupled Plasma-Atomic Emission Spectrometry

1.0 Scope and Application

1.1 Inductively coupled plasma-atomic emission spectrometry (ICP-AES) is used to determine metals and some nonmetals in solution. This method is a consolidation of existing methods for water, wastewater, and solid wastes (References 1-4). For analysis of petroleum products see References 5 and 6. This method is applicable to the following analytes:

Analyte		Chemical Abstract Services Registry Number (CASRN)
Aluminum	(Al)	7429-90-5
Antimony	(Sb)	7440-36-0
Arsenic	(As)	7440-38-2
Barium	(Ba)	7440-39-3
Beryllium	(Be)	7440-41-7
Boron	(B)	7440-42-8
Cadmium	(Cd)	7440-43-9
Calcium	(Ca)	7440-70-2
Cerium[a]	(Ce)	7440-45-1
Chromium	(Cr)	7440-47-3
Cobalt	(Co)	7440-48-4
Copper	(Cu)	7440-50-8
Iron	(Fe)	7439-89-6
Lead	(Pb)	7439-92-1
Lithium	(Li)	7439-93-2
Magnesium	(Mg)	7439-95-4
Manganese	(Mn)	7439-96-5
Mercury	(Hg)	7439-97-6
Molybdenum	(Mo)	7439-98-7
Nickel	(Ni)	7440-02-0
Phosphorus	(P)	7723-14-0
Potassium	(K)	7440-09-7
Selenium	(Se)	7782-49-2
Silica[b]	(SiO_2)	7631-86-9
Silver	(Ag)	7440-22-4

Analyte		Chemical Abstract Services Registry Number (CASRN)
Sodium	(Na)	7440-23-5
Strontium	(Sr)	7440-24-6
Thallium	(Tl)	7440-28-0
Tin	(Sn)	7440-31-5
Titanium	(Ti)	7440-32-6
Vanadium	(V)	7440-62-2
Zinc	(Zn)	7440-66-6

[a]Cerium has been included as a method analyte for correction of potential interelement spectral interference.
[b]This method is not suitable for the determination of silica in solids.

1.2 To confirm approval of this method for use in compliance monitoring programs [e.g., Clean Water Act (NPDES) or Safe Drinking Water Act (SDWA)] consult both the appropriate sections of the Code of Federal Regulation (40 CFR Part 136 Table 1B for NPDES, and Part 141 § 141.23 for drinking water) and the latest Federal Register announcements.

1.3 ICP-AES can be used to determine dissolved analytes in aqueous samples after suitable filtration and acid preservation. To reduce potential interferences, dissolved solids should be <0.2% (w/v) (Section 4.2).

1.4 With the exception of silver, where this method is approved for the determination of certain metal and metalloid contaminants in drinking water, aqueous samples may be analyzed directly by pneumatic nebulization without acid digestion if the sample has been properly preserved with acid and has turbidity of <1 NTU at the time of analysis. This total recoverable determination procedure is referred to as "direct analysis." However, in the determination of some primary drinking water metal contaminants, preconcentration of the sample may be required prior to analysis in order to meet drinking water acceptance performance criteria (Sections 11.2.2 through 11.2.7).

1.5 For the determination of total recoverable analytes in aqueous, biosolids (municipal sewage sludge), and solid samples, a digestion/extraction is required prior to analysis when the elements are not in solution (e.g., soil, sludge, sediment, and aqueous samples that may contain particulate and suspended solids). Aqueous samples containing total suspended solids ≥ 1% (w/v) should be extracted as a solid type sample.

1.6 When determining boron and silica in aqueous samples, only plastic, PTFE or quartz labware should be used from time of sample collection to completion of analysis. For accurate determination of boron in solid and sludge samples, only quartz or PTFE beakers should be used

during acid extraction with immediate transfer of an extract aliquot to a plastic centrifuge tube following dilution of the extract to volume. When possible, borosilicate glass should be avoided to prevent contamination of these analytes.

1.7 Silver is only slightly soluble in the presence of chloride unless there is a sufficient chloride concentration to form the soluble chloride complex. Therefore, low recoveries of silver may occur in samples, fortified sample matrices and even fortified blanks if determined as a dissolved analyte or by "direct analysis" where the sample has not been processed using the total recoverable mixed acid digestion. For this reason it is recommended that samples be digested prior to the determination of silver. The total recoverable sample digestion procedure given in this method is suitable for the determination of silver in aqueous samples containing concentrations up to 0.1 mg/L. For the analysis of wastewater samples containing higher concentrations of silver, succeeding smaller volume, well-mixed aliquots should be prepared until the analysis solution contains <0.1 mg/L silver. The extraction of solid or sludge samples containing concentrations of silver >50 mg/kg should be treated in a similar manner.

NOTE: *When analyzing samples containing high levels of silver as might occur in the photographic manufacturing industries, EPA Method 272.1 can be used for silver determinations. Based on the use of cyanogen iodide (CNI) as a stabilizing agent, Method 272.1 can be used on samples containing up to 4 mg/L of Ag. However, it should be recognized that CNI is an extremely hazardous and environmentally toxic reagent, and should be used with the utmost caution.*

1.8 The extraction of tin from solid or sludge samples should be prepared using aliquots <1 g when determined sample concentrations exceed 1%.

1.9 The total recoverable sample digestion procedures given in this method will solubilize and hold in solution only minimal concentrations of barium in the presence of free sulfate. For the analysis of barium in samples having varying and unknown concentrations of sulfate, analysis should be completed as soon as possible after sample preparation.

1.10 The total recoverable sample digestion procedure given in this method is not suitable for the determination of volatile organo-mercury compounds. However, if digestion is not required (turbidity <1 NTU), the combined concentrations of inorganic and organo-mercury in solution can be determined by "direct analysis" pneumatic nebulization provided the sample solution is adjusted to contain the same mixed acid (HNO_3 + HCl) matrix as the total recoverable calibration standards and blank solutions.

1.11 The determination of some analytes in biosolids may require the use of an axial ICP. (More information on this point will be provided by the validation study. Currently, there are known difficulties in analyzing molybdenum in biosolids with a radial ICP).

1.12 Detection limits and linear ranges for the elements will vary with the wavelength selected, the spectrometer, and the matrices. Method detection limits (MDLs; 40 CFR 136, Appendix B) and

minimum levels (MLs) when no interferences are present will be determined for this method through a validation study. Preliminary MDL values are given in Table 4. The ML for each analyte can be calculated by multiplying the MDL by 3.18 and rounding to the nearest (2, 5, or 10 X 10") where n is an integer.

1.13 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must document and have on file the required initial demonstration performance data described in Section 9.2 prior to using the method for analysis.

2.0 Summary of Method

2.1 An aliquot of a well-mixed, homogeneous sample is accurately weighed or measured for sample processing. For total recoverable analysis of a solid or an aqueous sample containing undissolved material, analytes are solubilized by gentle refluxing with HNO_3 and HCl. For the total recoverable analysis of a sludge sample containing <1% total suspended solids, analytes are solubilized by successive refluxing with HNO_3 and HCl. For total recoverable analysis of a sludge sample containing total suspended solids ≥1% (w/v), analytes are solubilized by refluxing with HNO_3, background organic materials are oxidized with peroxide, and analytes are further solubilized by refluxing with HCl. After cooling, the sample is made up to volume, mixed and then centrifuged or allowed to settle overnight prior to analysis. For the determination of dissolved analytes in a filtered aqueous sample aliquot, or for the "direct analysis" total recoverable determination of analytes in drinking water where sample turbidity is <1 NTU, the sample is made ready for analysis by the addition of the appropriate volume of HNO_3, and then diluted to a predetermined volume and mixed before analysis.

2.2 The analysis described in this method involves multi elemental determinations by ICP-AES using sequential or simultaneous instruments. The instruments measure characteristic atomic-line emission spectra by optical spectrometry. Samples are nebulized and the resulting aerosols are transported to the plasma torch. Element specific emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed by a grating spectrometer, and the intensities of the line spectra are monitored at specific wavelengths by a photosensitive device. Photocurrents from the photosensitive device are processed and controlled by a computer system. A background correction technique is required to compensate for variable background contribution to the determination of the analytes. The background must be measured adjacent to an analyte wavelength during analysis. Interferences must be considered and addressed appropriately as discussed in Sections 4.0, 7.0, 9.0, and 11.0.

3.0 Definitions

3.1 Biosolids–A solid, semisolid, or liquid residue (sludge) generated during treatment of domestic sewage in a treatment works.

3.2 Calibration blank–A volume of reagent water acidified with the same acid matrix as the calibration standards (Section 7.11.1). The calibration blank is a zero standard and is used to calibrate the ICP instrument.

3.3 Calibration standard–A solution prepared from the dilution of stock standard solutions (Section 7.10). The calibration solutions are used to calibrate the instrument response with respect to analyte concentration.

3.4 Calibration verification (CV) solution–A solution of method analytes, used to evaluate the performance of the instrument system with respect to a defined set of method criteria (Section 7.12).

3.5 Dissolved analyte–The concentration of analyte in an aqueous sample that will pass through a 0.45 µm membrane filter assembly prior to sample acidification (Section 8.2).

3.6 Field blank–An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures (Section 8.5). The field blank is analyzed to determine if method analytes or other interferences are present in the field environment.

3.7 Internal standard–Pure analyte(s) added to a sample, extract, or standard solution in a known amount(s) and used to measure the relative responses of other method analytes that are components of the same sample or solution. The internal standard must be an analyte that is not a sample component (Section 11.6).

3.8 Linear dynamic range (LDR)–The concentration range over which the instrument response to an analyte is linear (Section 9.2.3).

3.9 Matrix spike (MS) and matrix spike duplicate (MSD)–Two aliquots of the same environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample, and their purpose is: to determine whether the sample matrix contributes bias to the analytical results, and to indicate precision associated with laboratory procedures. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations (Section 9.5).

3.10 May–This action, activity, or procedural step is neither required nor prohibited.

3.11 May not–This action, activity, or procedural step is prohibited.

3.12 Method blank–An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and internal standards that are

used with other samples. The method blank is used to determine if method analytes or other interferences are present in the laboratory environment, reagents, or apparatus (Section 7.11.2).

3.13 Method detection limit (MDL)–The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence (Section 9.2.1). The MDL is determined according to procedures described in 40 CFR Part 136, Appendix B.

3.14 Minimum level (ML)–The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point for the analyte. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specific sample weights, volumes and cleanup procedures have been employed.

3.15 Must–This action, activity, or procedural step is required.

3.16 Ongoing precision and recovery standard (OPR)–The OPR test is used to ensure that the laboratory meets performance criteria during the period that samples are analyzed. It also separates laboratory performance from method performance on the sample matrix. For aqueous samples, the OPR solution is an aliquot of method blank to which known quantities of the method analytes are added in the laboratory. For solid samples, the use of clean sand or soil to which known quantities of the method analytes are added in the laboratory is recommended. The OPR is analyzed in the same manner as samples (Section 9.7).

3.17 Plasma solution–A solution that is used to determine the optimum height above the work coil for viewing the plasma (Section 7.16).

3.18 Reference sample–A solution of method analytes of known concentrations which is used to fortify an aliquot of method blank or sample matrix (Section 7.13). The reference sample is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory and/or instrument performance.

3.19 Shall–This action, activity or procedural step is required.

3.20 Should–This action, activity, or procedural step is suggested but not required..

3.21 Solid sample–For the purpose of this method, a sample taken from material classified as either soil, sediment or industrial sludge.

3.22 Spectral interference check (SIC) solution–A solution of selected method analytes of higher concentrations which is used to evaluate the procedural routine for correcting known interelement spectral interferences with respect to a defined set of method criteria (Sections 7.14 and 9.4).

3.23 Standard addition–The addition of a known amount of analyte to the sample in order to determine the relative response of the detector to an analyte within the sample matrix. The relative response

is then used to assess either an operative matrix effect or the sample analyte concentration (Sections 9.5.3.1 and 11.6).

3.24 Standard stock solution–A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source (Section 7.9).

3.25 Total recoverable analyte–The concentration of analyte determined either by "direct analysis" of an unfiltered acid preserved drinking water sample with turbidity of <1 NTU (Section 11.2.1), or by analysis of the solution extract of a sludge, solid, or unfiltered aqueous sample following digestion by refluxing with hot dilute mineral acid(s) as specified in the method (Sections 11.2 through 11.4).

3.26 Total Solids–The residue left in the vessel after evaporation of liquid from a sample and subsequent drying in an oven at 103°C to 105°C.

3.27 Water sample–For the purpose of this method, a sample taken from one of the following sources: drinking, surface, ground, storm runoff, industrial or domestic wastewater.

4.0 Interferences

4.1 Spectral interferences are caused by background emission from continuous or recombination phenomena, stray light from the line emission of high concentration elements, overlap of a spectral line from another element, or unresolved overlap of molecular band spectra.

4.1.1 Background emission and stray light can usually be compensated for by subtracting the background emission determined by measurement(s) adjacent to the analyte wavelength peak. Spectral scans of samples or single element solutions in the analyte regions may indicate not only when alternate wavelengths are desirable because of severe spectral interference, but also will show whether the most appropriate estimate of the background emission is provided by an interpolation from measurements on both sides of the wavelength peak or by the measured emission on one side or the other. The location(s) selected for the measurement of background intensity will be determined by the complexity of the spectrum adjacent to the wavelength peak. The location(s) used for routine measurement must be free of off-line spectral interference (interelement or molecular) or adequately corrected to reflect the same change in background intensity as occurs at the wavelength peak.

4.1.2 Spectral overlaps may be avoided by using an alternate wavelength or can be compensated for by equations that correct for interelement contributions, which involves measuring the interfering elements. Some potential on-line spectral interferences observed for the recommended wavelengths are given in Table 2. When operative and uncorrected, these interferences will produce false-positive determinations and be reported as analyte concentrations. The interferences listed are only those that occur between method analytes. Only interferences of a direct overlap nature that were observed with a single

instrument having a working resolution of 0.035 nm are listed. More extensive information on interferant effects at various wavelengths and resolutions is available in Boumans' Tables (Reference 8). Users may apply interelement correction factors determined on their instruments within tested concentration ranges to compensate (off-line or on-line) for the effects of interfering elements.

4.1.3 When interelement corrections are applied, there is a need to verify their accuracy by analyzing spectral interference check solutions as described in Section 7.14. Interelement corrections will vary for the same emission line among instruments because of differences in resolution, as determined by the grating plus the entrance and exit slit widths, and by the order of dispersion. Interelement corrections will also vary depending upon the choice of background correction points. Selecting a background correction point where an interfering emission line may appear should be avoided when practical. Interelement corrections that constitute a major portion of an emission signal may not yield accurate data. Users should not forget that some samples may contain uncommon elements that could contribute spectral interferences (References 7 and 8).

4.1.4 The interference effects must be evaluated for each individual instrument whether configured as a sequential or simultaneous instrument. For each instrument, intensities will vary not only with optical resolution but also with operating conditions (such as power, viewing height and argon flow rate). When using the recommended wavelengths given in Table 1, the analyst is required to determine and document for each wavelength the effect from the known interferences given in Table 2, and to use a computer routine for their automatic correction on all analyses. To determine the appropriate location for off-line background correction, the user must scan the area on either side adjacent to the wavelength and record the apparent emission intensity from all other method analytes. This spectral information must be documented and kept on file. The location selected for background correction must either be free of off-line interelement spectral interference or a computer routine must be used for automatic correction on all determinations. If a wavelength other than the recommended wavelength is used, the user must determine and document both the on-line and off-line spectral interference effect from all method analytes and provide for automatic correction on all analyses. Tests to determine the spectral interference must be done using analyte concentrations that will adequately describe the interference. Normally, 100 mg/L single element solutions are sufficient, however, for analytes such as iron that may be found at high concentration a more appropriate test would be to use a concentration near the upper LDR limit. See Section 9.4 for required spectral interference test criteria.

4.1.5 When interelement corrections are *not* used, either ongoing SIC solutions (Section 7.14) must be analyzed to verify the absence of interelement spectral interference or a computer software routine must be employed for comparing the determinative data to limits files for notifying the analyst when an interfering element is detected in the sample at a concentration that will produce either an apparent false positive concentration greater than the analyte MDL, or false negative analyte concentration less than the 99% lower control

limit of the calibration blank. When the interference accounts for 10% or more of the analyte concentration, either an alternate wavelength free of interference or another approved test procedure must be used to complete the analysis. For example, the copper peak at 213.853 nm could be mistaken for the zinc peak at 213.856 nm in solutions with high copper and low zinc concentrations. For this example, a spectral scan in the 213.8 nm region would not reveal the misidentification because a single peak near the zinc location would be observed. The possibility of misidentification of copper for the zinc peak at 213.856 nm can be identified by measuring the copper at another emission line, e.g., 324.754 nm. Users should be aware that, depending upon the instrumental resolution, alternate wavelengths with adequate sensitivity and freedom from interference may not be available for all matrices. In these circumstances the analyte must be determined using another approved test procedure.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies, especially in samples containing high dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by such means as a high-solids nebulizer, diluting the sample, using a peristaltic pump, or using an appropriate internal standard element. Another problem that can occur with high dissolved solids is salt buildup at the tip of the nebulizer, which affects aerosol flow rate and causes instrumental drift. This problem can be controlled by a high-solids nebulizer, wetting the argon prior to nebulization, using a tip washer, or diluting the sample. Also, it has been reported that better control of the argon flow rates, especially for the nebulizer, improves instrument stability and precision; this is accomplished with the use of mass flow controllers.

4.3 Chemical interferences include molecular-compound formation, ionization effects, and solute-vaporization effects. Normally, these effects are not significant with the ICP-AES technique. If observed, they can be minimized by careful selection of operating conditions (such as incident power and observation height), by buffering of the sample, by matrix matching, and by standard-addition procedures. Chemical interferences are highly dependent on matrix type and the specific analyte element.

4.4 Memory interferences result when analytes in a previous sample contribute to the signals measured in a new sample. Memory effects can result from sample deposition on the uptake tubing to the nebulizer, and from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (Section 7.11.1). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element must be estimated prior to analysis. This may be achieved by aspirating a standard containing elements corresponding to either their LDR or a concentration ten times those usually encountered. The aspiration time should be the same as a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of two of the method detection limit, should be noted. Until the required rinse time is established, this

method requires a rinse period of at least 60 seconds between samples and standards. If a memory interference is suspected, the sample must be analyzed again after a long rinse period.

5.0 Safety

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been fully established. Each chemical should be regarded as a potential health hazard and exposure to these compounds should be as low as reasonably achievable. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method (References 9, 10, 11, and 12). A reference file of material data handling sheets should also be made available to all personnel involved in the chemical analysis. Specifically, concentrated HNO_3 and HCl present various hazards and are moderately toxic and extremely irritating to skin and mucus membranes. Use these reagents in a fume hood whenever possible and if eye or skin contact occurs, flush with large volumes of water. Always wear safety glasses or a shield for eye protection, protective clothing and observe proper mixing when working with these reagents.

5.2 The acidification of samples containing reactive materials may result in the release of toxic gases, such as cyanides or sulfides. Acidification and digestion of samples should be done in a fume hood.

5.3 All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

5.4 The inductively coupled plasma should only be viewed with proper eye protection from the ultraviolet emissions.

5.5 It is the responsibility of the user of this method to comply with relevant disposal and waste regulations. For guidance, see Sections 14.0 and 15.0.

6.0 Equipment and Supplies

NOTE: *The mention of trade names or commercial products in this method is for illustrative purposes only and does not constitute endorsement or recommendation for use by the EPA. Equivalent performance may be achievable using apparatus and materials other than those suggested here. The laboratory is responsible for demonstrating equivalent performance.*

6.1 Inductively coupled plasma emission spectrometer:

6.1.1 Computer-controlled emission spectrometer with background-correction capability. The spectrometer must be capable of meeting and complying with the requirements described and referenced in Section 2.2.

6.1.2 Radio-frequency generator compliant with FCC regulations.

6.1.3 Argon gas supply–High purity grade (99.99%). When analyses are conducted frequently, liquid argon is more economical and requires less frequent replacement of tanks than compressed argon in conventional cylinders.

6.1.4 A variable speed peristaltic pump is required to deliver both standard and sample solutions to the nebulizer.

6.1.5 (Optional) Mass flow controllers to regulate the argon flow rates, especially the aerosol transport gas, are highly recommended. Their use will provide more exacting control of reproducible plasma conditions.

6.2 Analytical balance, with capability to measure to 0.1 mg, for use in weighing solids, for preparing standards, and for determining dissolved solids in digests or extracts.

6.3 A temperature adjustable hot plate capable of maintaining a temperature of 95°C.

6.4 (Optional) A temperature adjustable block digester capable of maintaining a temperature of 95°C and equipped with 250-mL constricted digestion tubes.

6.5 (Optional) A steel cabinet centrifuge with guard bowl, electric timer and brake.

6.6 A gravity convection drying oven with thermostatic control capable of maintaining 180°C ± 5°C.

6.7 (Optional) An air displacement pipetter capable of delivering volumes ranging from 0.1-2500 µL with an assortment of high quality disposable pipet tips.

6.8 Mortar and pestle, ceramic or other nonmetallic material.

6.9 Polypropylene sieve, 5-mesh (4 mm opening).

6.10 Labware–Prevention of contamination and loss are of prime consideration for determination of trace levels of elements. Potential contamination sources include improperly cleaned laboratory apparatus and general contamination within the laboratory environment from dust, etc. A clean laboratory work area designated for trace element sample handling must be used. Sample containers can introduce positive and negative errors in the determination of trace elements by (1) contributing contaminants through surface desorption or leaching, and (2) depleting element concentrations through adsorption processes. All reusable labware (glass, quartz, polyethylene, PTFE, FEP, etc.) should be sufficiently clean for the task objectives. One recommended procedure found to provide clean labware includes washing with a detergent solution, rinsing with tap water, soaking for four hours or more in 20% (v/v) HNO_3 or a mixture of HNO_3 and HCl (1+2+9), rinsing with reagent water and storing clean (References 2 and 3). Chromic acid cleaning solutions must be avoided because chromium is an analyte.

6.10.1 Glassware--Volumetric flasks, graduated cylinders, funnels and centrifuge tubes (glass and/or metal-free plastic).

6.10.2 Assorted calibrated pipettes.

6.10.3 Conical Phillips beakers (Corning 1080-250 or equivalent), 250-mL with 50-mm watch glasses.

6.10.4 Griffin beakers, 250-mL with 75-mm watch glasses and (optional) 75-mm ribbed watch glasses.

6.10.5 (Optional) PTFE and/or quartz Griffin beakers, 250-mL with PTFE covers.

6.10.6 Narrow-mouth storage bottles, FEP (fluorinated ethylene propylene) with screw closure, 125-mL to 1-L capacities.

6.10.7 One-piece stem FEP wash bottle with screw closure, 125-mL capacity.

7.0 Reagents and Standards

7.1 Reagents may contain elemental impurities which might affect analytical data. Only high-purity reagents that conform to the American Chemical Society specifications should be used whenever possible (Reference 13). If the purity of a reagent is in question, analyze for contamination. All acids used for this method must be of ultra high-purity grade or equivalent. Suitable acids are available from a number of manufacturers. Redistilled acids prepared by sub-boiling distillation are acceptable.

7.2 Hydrochloric acid, concentrated (specific gravity=1.19).

7.2.1 Hydrochloric acid (1+1)--Add 500 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.2 Hydrochloric acid (1+4)--Add 200 mL concentrated HCl to 400 mL reagent water and dilute to 1 L.

7.2.3 Hydrochloric acid (1+20)--Add 10 mL concentrated HCl to 200 mL reagent water.

7.3 Nitric acid, concentrated (specific gravity=1.41).

7.3.1 Nitric acid (1+1)--Add 500 mL concentrated HNO_3 to 400 mL reagent water and dilute to 1 L.

7.3.2 Nitric acid (1+2)--Add 100 mL concentrated HNO_3 to 200 mL reagent water.

7.3.3 Nitric acid (1+5)–Add 50 mL concentrated HNO_3 to 250 mL reagent water.

7.3.4 Nitric acid (1+9)–Add 10 mL concentrated HNO_3 to 90 mL reagent water.

7.4 Reagent water–All references to water in this method refer to ASTM Type I grade water (Reference 14).

7.5 Ammonium hydroxide, concentrated (specific gravity=0.902).

7.6 Tartaric acid–ACS reagent grade.

7.7 Hydrogen peroxide–H_2O_2

7.7.1 Hydrogen peroxide, 50%, stabilized certified reagent grade.

7.7.2 Hydrogen peroxide, 30%, stabilized certified reagent grade.

7.8 Clean sand or soil–All references to clean sand or soil in this method refer to sand or soil certified to be free of the analytes of interest at or above their MDLs or to contain those analytes at certified levels.

7.9 Standard Stock Solutions–Stock standards may be purchased or prepared from ultra-high purity grade chemicals (99.99-99.999% pure). All compounds must be dried for one hour at 105°C, unless otherwise specified. It is recommended that stock solutions be stored in FEP bottles. Replace stock standards when succeeding dilutions for preparation of calibration standards cannot be verified.

CAUTION: *Many of these chemicals are extremely toxic if inhaled or swallowed (Section 5.1). Wash hands thoroughly after handling.*

Typical stock solution preparation procedures follow for 1-L quantities (Equations 1 and 2), but for the purpose of pollution prevention, the analyst is encouraged to prepare smaller quantities when possible. Concentrations are calculated based upon the weight of the pure element or upon the weight of the compound multiplied by the fraction of the analyte in the compound.

Equation 1

From pure element,

$$C = \frac{m}{V}$$

where:

C=concentration (mg/L)
m=mass (mg)
V=volume (L)

Equation 2

From pure compound,

$$C = \frac{m * g_f}{V}$$

where:

C=concentration (mg/L)
m=mass (mg)
V=volume (L)
g_f=gravimetric factor (the weight fraction of the analyte in the compound)

7.9.1 Aluminum solution, stock, 1 mL = 1000 µg Al–Dissolve 1.000 g of aluminum metal, weighed accurately to at least four significant figures, in an acid mixture of 4.0 mL of (1+1) HCl and 1 mL of concentrated $HN0_3$ in a beaker. Warm beaker slowly to effect solution. When dissolution is complete, transfer solution quantitatively to a 1-L flask, add an additional 10.0 mL of (1+1) HCl and dilute to volume with reagent water.

7.9.2 Antimony solution, stock, 1 mL = 1000 µg Sb–Dissolve 1.000 g of antimony powder, weighed accurately to at least four significant figures, in 20.0 mL (1+1) HNO_3 and 10.0 mL concentrated HCl. Add 100 mL reagent water and 1.50 g tartaric acid. Warm solution slightly to effect complete dissolution. Cool solution and add reagent water to volume in a 1-L volumetric flask.

7.9.3 Arsenic solution, stock, 1 mL = 1000 µg As–Dissolve 1.320 g of As_2O_3 (As fraction = 0.7574), weighed accurately to at least four significant figures, in 100 mL of reagent water containing 10.0 mL concentrated NH_4OH. Warm the solution gently to effect dissolution. Acidify the solution with 20.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.4 Barium solution, stock, 1 mL = 1000 µg Ba–Dissolve 1.437 g $BaCO_3$ (Ba fraction = 0.6960), weighed accurately to at least four significant figures, in 150 mL (1+2) HNO_3

with heating and stirring to de-gas and dissolve compound. Let solution cool and dilute with reagent water in 1-L volumetric flask.

7.9.5 Beryllium solution, stock, 1 mL = 1000 µg Be–DO NOT DRY. Dissolve 19.66 g $BeSO_4 \cdot 4H_2O$ (Be fraction = 0.0509), weighed accurately to at least four significant figures, in reagent water, add 10.0 mL concentrated HNO_3, and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.6 Boron solution, stock, 1 mL = 1000 µg B–DO NOT DRY. Dissolve 5.716 g anhydrous H_3BO_3 (B fraction = 0.1749), weighed accurately to at least four significant figures, in reagent water and dilute in a 1-L volumetric flask with reagent water. Transfer immediately after mixing to a clean FEP bottle to minimize any leaching of boron from the glass volumetric container. Use of a non-glass volumetric flask is recommended to avoid boron contamination from glassware.

7.9.7 Cadmium solution, stock, 1 mL = 1000 µg Cd–Dissolve 1.000 g Cd metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask.

7.9.8 Calcium solution, stock, 1 mL = 1000 µg Ca–Suspend 2.498 g $CaCO_3$ (Ca fraction = 0.4005), dried at 180°C for one hour before weighing, weighed accurately to at least four significant figures, in reagent water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.9 Cerium solution, stock, 1 mL = 1000 µg Ce–Make a slurry of 1.228 g CeO_2 (Ce fraction = 0.8141), weighed accurately to at least four significant figures, in 100 mL concentrated HNO_3 and evaporate to dryness. Make another slurry of the residue in 20 mL H_2O, add 50 mL concentrated HNO_3, with heat and stirring add 60 mL 50% H_2O_2 drop-wise in 1 mL increments allowing periods of stirring between the 1 mL additions. Boil off excess H_2O_2 before diluting to volume in a 1-L volumetric flask with reagent water.

7.9.10 Chromium solution, stock, 1 mL = 1000 µg Cr–Dissolve 1.923 g CrO_3 (Cr fraction = 0.5200), weighed accurately to at least four significant figures, in 120 mL (1+5) HNO_3. When solution is complete, dilute to volume in a 1 L volumetric flask with reagent water.

7.9.11 Cobalt solution, stock, 1 mL = 1000 µg Co–Dissolve 1.000 g Co metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1) HNO_3. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.12 Copper solution, stock, 1 mL = 1000 µg Cu–Dissolve 1.000 g Cu metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50.0 mL (1+1)

HNO_3 with heating to effect dissolution. Let solution cool and dilute in a 1-L volumetric flask with reagent water.

7.9.13 Iron solution, stock, 1 mL = 1000 µg Fe–Dissolve 1.000 g Fe metal, acid cleaned with (1+1) HCl, weighed accurately to four significant figures, in 100 mL (1+1) HCl with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask.

7.9.14 Lead solution, stock, 1 mL = 1000 µg Pb–Dissolve 1.599 g $Pb(NO_3)_2$ (Pb fraction = 0.6256), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HNO_3. Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.15 Lithium solution, stock, 1 mL = 1000 µg Li–Dissolve 5.324 g Li_2CO_3 (Li fraction = 0.1878), weighed accurately to at least four significant figures, in a minimum amount of (1+1) HCl and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.16 Magnesium solution, stock, 1 mL = 1000 µg Mg–Dissolve 1.000 g cleanly polished Mg ribbon, accurately weighed to at least four significant figures, in slowly added 5.0 mL (1+1) HCl (**CAUTION:** reaction is vigorous). Add 20.0 mL (1+1) HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.17 Manganese solution, stock, 1 mL = 1000 µg Mn–Dissolve 1.000 g of manganese metal, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.18 Mercury solution, stock, 1 mL = 1000 µg Hg–DO NOT DRY. **CAUTION:** highly toxic element. Dissolve 1.354 g $HgCl_2$ (Hg fraction = 0.7388) in reagent water. Add 50.0 mL concentrated HNO_3 and dilute to volume in 1-L volumetric flask with reagent water.

7.9.19 Molybdenum solution, stock, 1 mL = 1000 µg Mo–Dissolve 1.500 g MoO_3 (Mo fraction = 0.6666), weighed accurately to at least four significant figures, in a mixture of 100 mL reagent water and 10.0 mL concentrated NH_4OH, heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask.

7.9.20 Nickel solution, stock, 1 mL = 1000 µg Ni–Dissolve 1.000 g of nickel metal, weighed accurately to at least four significant figures, in 20.0 mL hot concentrated HNO_3, cool, and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.21 Phosphorus solution, stock, 1 mL = 1000 µg P–Dissolve 3.745 g $NH_4H_2PO_4$ (P fraction = 0.2696), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.22 Potassium solution, stock, 1 mL = 1000 µg K–Dissolve 1.907 g KCl (K fraction = 0.5244) dried at 110°C, weighed accurately to at least four significant figures, in reagent water, add 20 mL (1+1) HCl and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.23 Selenium solution, stock, 1 mL = 1000 µg Se–Dissolve 1.405 g SeO_2 (Se fraction = 0.7116), weighed accurately to at least four significant figures, in 200 mL reagent water and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.24 Silica solution, stock, 1 mL = 1000 µg SiO_2–DO NOT DRY. Dissolve 2.964 g $(NH_4)_2SiF_6$, weighed accurately to at least four significant figures, in 200 mL (1+20) HCl with heating at 85°C to effect dissolution. Let solution cool and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.25 Silver solution, stock, 1 mL = 1000 µg Ag–Dissolve 1.000 g Ag metal, weighed accurately to at least four significant figures, in 80 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water in a 1-L volumetric flask. Store solution in amber bottle or wrap bottle completely with aluminum foil to protect solution from light.

7.9.26 Sodium solution, stock, 1 mL = 1000 µg.Na–Dissolve 2.542 g NaCl (Na fraction = 0.3934), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.27 Strontium solution, stock, 1 mL = 1000 µg Sr–Dissolve 1.685 g $SrCO_3$ (Sr fraction = 0.5935), weighed accurately to at least four significant figures, in 200 mL reagent water with drop-wise addition of 100 mL (1+1) HCl. Dilute to volume in a 1-L volumetric flask with reagent water.

7.9.28 Thallium solution, stock, 1 mL = 1000 µg Tl–Dissolve 1.303 g $TlNO_3$ (Tl fraction = 0.7672), weighed accurately to at least four significant figures, in reagent water. Add 10.0 mL concentrated HNO_3 and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.29 Tin solution, stock, 1 mL = 1000 µg Sn–Dissolve 1.000 g Sn shot, weighed accurately to at least four significant figures, in an acid mixture of 10.0 mL concentrated HCl and 2.0 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool, add 200 mL concentrated HCl, and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.30 Titanium solution, stock, 1 mL = 1000 µg Ti–DO NOT DRY. Dissolve 6.138 g $(NH_4)_2TiO(C_2O_4)_2 \cdot H_2O$ (Ti fraction = 0.1629), weighed accurately to at least four significant figures, in 100 mL reagent water. Dilute to volume in a 1-L volumetric flask with reagent water.

7.9.31 Vanadium solution, stock, 1 mL = 1000 µg V–Dissolve 1.000 g V metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1)

HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1-L volumetric flask.

7.9.32 Yttrium solution, stock 1 mL = 1000 µg Y–Dissolve 1.270 g Y_2O_3 (Y fraction = 0.7875), weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3, heating to effect dissolution. Cool and dilute to volume in a 1-L volumetric flask with reagent water.

7.9.33 Zinc solution, stock, 1 mL = 1000 µg Zn–Dissolve 1.000 g Zn metal, acid cleaned with (1+9) HNO_3, weighed accurately to at least four significant figures, in 50 mL (1+1) HNO_3 with heating to effect dissolution. Let solution cool and dilute with reagent water to volume in a 1-L volumetric flask.

7.10 Mixed calibration standard solutions–For the analysis of total recoverable digested samples, prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in 500 mL volumetric flasks containing 20 mL (1+1) HNO_3 and 20 mL (1+1) HCl and dilute to volume with reagent water. Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interferences or the presence of impurities. Care should be taken when preparing the mixed standards to ensure that the elements are compatible and stable together. To minimize the opportunity for contamination by the containers, it is recommended that the mixed-standard solutions be transferred to acid-cleaned, never-used FEP fluorocarbon bottles for storage. Fresh mixed standards should be prepared, as needed, with the realization that concentrations can change on aging. Calibration standards not prepared from primary standards must be initially verified using a certified reference solution. For the recommended wavelengths listed in Table 1, some typical calibration standard combinations are given in Table 3.

NOTE: *If the addition of silver to the recommended mixed-acid calibration standard results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. For this acid combination, the silver concentration should be limited to 0.5 mg/L.*

7.11 Blanks–Three types of blanks are required for the analysis. The calibration blank is used in establishing the analytical curve, the method blank is used to assess possible contamination from the sample preparation procedure, and a rinse blank is used to flush the sample uptake system and nebulizer between standards, check solutions, and samples to reduce memory interferences.

7.11.1 The calibration and rinse blanks are prepared by acidifying reagent water to the same concentrations of the acids as used for the standards. The blanks should be stored separately in FEP bottles.

7.11.2 The method blank is reagent water that is carried through the same entire preparation scheme as the samples including sample digestion, when applicable. When the method blank is analyzed, it will contain all the reagents in the same volumes as the samples.

7.12 Calibration verification (CV) solution–The CV solution is used to verify instrument performance during analysis. It should be prepared in the same acid mixture as the calibration standards by combining method analytes at appropriate concentrations. Silver must be limited to <0.5 mg/L; while potassium and phosphorus, because of higher MDLs, and silica, because of potential contamination, should be at concentrations of 10 mg/L. For other analytes a concentration of 2 mg/L is recommended. The CV solution should be prepared from the same standard stock solutions used to prepare the calibration standards and stored in an FEP bottle. Agency programs may specify or request that additional CV solutions be prepared at specified concentrations in order to meet particular program needs.

7.13 Reference sample–Analysis of a reference sample is required for initial and periodic verification of calibration standards or stock standard solutions in order to verify instrument performance. The reference sample must be obtained from an outside source different from the standard stock solutions and prepared in the same acid mixture as the calibration standards. The concentration of the analytes in the reference sample solution should be ≥ 1 mg/L, except silver, which must be limited to a concentration of 0.5 mg/L for solution stability. The reference sample solution should be stored in a FEP bottle and analyzed as needed to meet data-quality needs. A fresh solution should be prepared quarterly or more frequently as needed. Alternatively, the reference sample may be a standard or certified reference material traceable to the National Institute of Standards and Technology.

7.14 Spectral interference check (SIC) solutions–SIC solutions containing (a) 300 mg/L Fe; (b) 200 mg/L Al; (c) 50 mg/L Ba; (d) 50 mg/L Be; (e) 50 mg/L Cd; (f) 50 mg/L Ce; (g) 50 mg/L Co; (h) 50 mg/L Cr; (I) 50 mg/L Cu; (j) 50 mg/L Mn; (k) 50 mg/L Mo; (l) 50 mg/L Ni; (m) 50 mg/L Sn; (n) 50 mg/L SiO_2; (o) 50 mg/L Ti; (p) 50 mg/L Tl and (q) 50 mg/L V should be prepared in the same acid mixture as the calibration standards and stored in FEP bottles. These solutions can be used to periodically verify a partial list of the on-line (and possible off-line) interelement spectral correction factors for the recommended wavelengths given in Table 1. Other solutions could achieve the same objective as well. Multielement SIC solutions may be prepared and substituted for the single element solutions provided an analyte is not subject to interference from more than one interferant in the solution (Reference 3).

NOTE: *If wavelengths other than those recommended in Table 1 are used, solutions other than those above (a through q) may be required.*

7.15 Plasma solution–The plasma solution is used for determining the optimum viewing height of the plasma above the work coil prior to using the method (Section 10.2). The solution is prepared by adding a 5 mL aliquot from each of the stock standard solutions of arsenic, lead, selenium, and thallium to a mixture of 20 mL (1+1) HNO_3 and 20 mL (1+1) HCl and diluting to 500 mL with reagent water. Store in a FEP bottle.

8.0 Sample Collection, Preservation, and Storage

8.1 Prior to the collection of an aqueous sample, consideration should be given to the type of data required, (i.e., dissolved or total recoverable), so that appropriate preservation and pretreatment steps can be taken. The pH of all aqueous samples **must** be tested immediately prior to withdrawing an aliquot for processing or "direct analysis" to ensure the sample has been properly preserved. If properly acid preserved, the sample can be held up to six months before analysis.

NOTE: *Do not dip pH paper or a pH meter into the sample; remove a small aliquot with a clean pipette and test the aliquot.*

8.2 For the determination of the dissolved elements, a sample must be filtered through a 0.45 µm pore diameter membrane filter at the time of collection or as soon thereafter as practically possible. (Glass or plastic filtering apparatus is recommended to avoid possible contamination. Only plastic apparatus should be used when the determinations of boron and silica are critical). Use a portion of the filtered sample to rinse the filter flask, discard this portion and collect the required volume of filtrate. Acidify the filtrate with (1+1) HNO_3 to pH <2 immediately following filtration.

8.3 For the determination of total recoverable elements in aqueous samples, samples are **not** filtered, but acidified with (1+1) HNO_3 to pH <2 (normally, 3 mL of (1+1) acid per liter of sample is sufficient for most ambient and drinking water samples). Preservation may be done at the time of collection. However, to avoid the hazards of strong acids in the field, transport restrictions, and possible contamination, it is recommended that samples be returned to the laboratory within two weeks of collection and acid preserved upon receipt in the laboratory. Following acidification, the sample should be mixed, held for 16 hours, and then verified to be pH <2 just prior to withdrawing an aliquot for processing or "direct analysis." If, for some reason such as high alkalinity, the sample pH is verified to be >2, more acid must be added, and the sample held for 16 hours until verified to be pH <2.

NOTE: *When the nature of the sample is either unknown or is known to be hazardous, acidification should be done in a fume hood.*

8.4 Solid samples require no preservation prior to analysis other than storage at 4°C. There is no established holding time limitation for solid samples.

8.5 A field blank should be prepared and analyzed as required by the data user. Use the same conditions (i.e., container, filtration and preservation) as used in sample collection.

8.6 If a total solids determination is required, then a separate aliquot should be collected following the procedure given in Section 8.0 of Appendix A.

9.0 Quality Assurance/Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program (Reference 24). The minimum requirements of this program consist of an initial demonstration of laboratory capability, analysis of samples spiked with analyte(s) of interest to evaluate and document data quality, and analysis of standards and blanks as tests of continued performance. Laboratory performance is compared to established performance criteria to determine that results of the analysis meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted to exercise certain options to eliminate interferences or lower the costs of measurements. These options include alternate digestion, preconcentration, cleanup procedures, and changes in instrumentation. Alternate determinative techniques, such as the substitution of a colorimetric technique or changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, then that technique must have a specificity equal to or better than the specificity of the techniques in this method for the analytes of interest.

9.1.2.1 Each time the method is modified, the analyst is required to repeat the procedure in Section 9.2. If the change will affect the detection limit of the method, the laboratory is required to demonstrate that the MDL (40 *CFR* Part 136, Appendix B) is lower than the MDL for that analyte in this method, or one-third the regulatory compliance level, whichever is higher. If the change will affect calibration, the analyst must recalibrate the instrument according to Section 10.0.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2 A listing of analytes measured, by name and CAS Registry number.

9.1.2.2.3 A narrative stating the reason(s) for the modification(s).

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

(a) Method detection limit
(b) Calibration
(c) Calibration verification
(d) Initial precision and recovery
(e) Ongoing precision and recovery
(f) Analysis of blanks
(g) Matrix spike and matrix spike duplicate analyses

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (peak height, area, or other signal) to the final result. These data are to include, where possible:

(a) Sample numbers and other identifiers
(b) Digestion/preparation or extraction dates
(c) Analysis dates and times
(d) Analysis sequence/run chronology
(e) Sample weight or volume
(f) Volume before the extraction/concentration step
(g) Volume after each extraction/concentration step
(h) Final volume before analysis
(I) Injection volume
(j) Dilution data, differentiating between dilution of a sample or extract
(k) Instrument and operating conditions (make, model, revision, modifications)
(l) Sample introduction system (ultrasonic nebulizer, flow injection system, etc.)
(m) Preconcentration system
(n) Operating conditions (background corrections, temperature program, flow rates, etc.)
(o) Detector (type, operating conditions, etc.)
(p) Mass spectra, printer tapes, and other recordings of raw data
(q) Quantitation reports, data system outputs, and other data to link raw data to results reported

9.1.3 Analyses of blanks are required to demonstrate freedom from contamination. Section 9.6 describes the required types, procedures, and criteria for analysis of blanks.

9.1.4 Analyses of MS and MSD samples are required to demonstrate the accuracy and precision of the method and to monitor for matrix interferences (Section 9.5). When results of these spikes indicate atypical method performance for samples, an alternative extraction or cleanup technique must be used to bring method performance within acceptable limits. If method performance cannot be brought within the limits given in this method, the result may not be reported for regulatory compliance purposes.

9.1.5 The laboratory shall, on an ongoing basis, demonstrate through calibration verification (Section 9.3) and through analysis of the OPR standard (Section 9.7) that the analytical system is meeting the performance criteria.

9.1.6 The laboratory shall maintain records to define the quality of data that are generated. Development of accuracy statements is described in Sections 9.1.6 and 9.8.6.

9.1.7 All samples must be associated with an acceptable OPR, MS/MSD, IPR, and uncontaminated blanks.

9.2 Initial demonstration of laboratory capability.

9.2.1 Method detection limit–To establish the ability to detect the analyte(s) of interest, the analyst shall determine the MDL for each analyte according to the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. The laboratory must produce an MDL that is less than or equal to the MDL specified in Section 1.11 or one-third the regulatory compliance limit, whichever is greater. MDLs must be determined when a new operator begins work or whenever a change in instrument hardware or operating conditions is made that may affect the MDL. MDLs must be determined for solids with clean sand or soil matrix if solid or sludge samples are to be run and/or with a reagent water matrix if aqueous samples are to be run.

9.2.2 Initial precision and recovery (IPR)–To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

9.2.2.1 Spike four aliquots of reagent water (for aqueous samples) or clean sand or soil (for solid and sludge samples) with the analyte(s) of interest at one to five times the ML. Analyze the four aliquots according to the procedures in Section 11.0. This test must use the containers, labware, and reagents that will be used with samples and all digestion, extraction, and concentrations steps.

9.2.2.2 Using the results of the four analyses, compute the average percent recovery (X) for the analyte(s) in each aliquot and the standard deviation of the recovery (s) for each analyte.

9.2.2.3 For each analyte, compare s and X with the corresponding limits for IPR in (Table 5- to be determined in validation study). If s and X for all analyte(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may begin. If, however, any individual s exceeds the precision limit or any individual X falls outside the range for accuracy, system performance is unacceptable for that analyte. Correct the problem and repeat the test.

9.2.3 Linear dynamic range (LDR)–The upper limit of the LDR must be established for each wavelength used. It must be determined from a linear calibration prepared in the normal manner using the established analytical operating procedure for the instrument. The LDR should be determined by analyzing successively higher standard concentrations of the analyte until the observed analyte concentration is no more than 10% below the stated concentration of the standard. LDRs must be documented and kept on file. The LDR which may be used for the analysis of samples should be judged by the analyst from the resulting data. Calculated sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and analyzed again. The LDRs should be verified annually or whenever, in the judgement of the analyst, a change in analytical performance caused by either a change in instrument hardware or operating conditions would dictate they should be redetermined.

9.2.4 Reference sample–When beginning the use of this method, quarterly, and as needed to meet data quality requirements, the analyst must verify the calibration standards and acceptable instrument performance with the preparation and analysis of a reference sample (Section 7.13). To verify the calibration standards, the determined mean concentration from three analyses of the reference sample must be within ±5% of the stated reference sample value. If the reference sample is not within the required limits, an immediate second analysis of the reference sample is recommended to confirm unacceptable performance. If both the calibration standards and acceptable instrument performance cannot be verified, the source of the problem must be identified and corrected before proceeding with further analyses.

9.3 Calibration verification–A laboratory must analyze a CV solution (Section 7.12) and a calibration blank (Section 7.11.1) immediately following daily calibration, after every 10th sample (or more frequently, if required) and at the end of the sample run. The analysis data of the calibration blank and CV solution must be kept on file with the sample analyses data.

9.3.1 The result of the calibration blank should be less than the analyte ML or one-third the regulatory compliance level, whichever is greater.

9.3.2 Analysis of the CV solution immediately following calibration must verify that the instrument is within performance criteria to be determined by the validation study (Table 5).

9.3.3 If the calibration cannot be verified within the specified limits, both the CV solution and the calibration blank should be analyzed again. If the second analysis of the CV solution or the calibration blank confirm calibration to be outside the limits, sample analysis must be discontinued, the cause determined, corrected, and/or the instrument recalibrated. All samples following the last acceptable CV solution must be analyzed again.

9.4 Spectral interference check (SIC) solution–For all determinations the laboratory must periodically verify the interelement spectral interference correction routine by analyzing SIC solutions (Section 7.14).

9.4.1 For interferences from iron and aluminum, only those correction factors (positive or negative) which, when multiplied by 100, exceed the analyte ML, or one-third the regulatory compliance, whichever is greater, or fall below the lower limit for the calibration blank, need be tested on a daily basis. The lower calibration blank control limit is determined by subtracting the ML, or one-third the regulatory compliance limit, whichever is greater, from zero.

9.4.2 For the other interfering elements, only those correction factors (positive or negative) when multiplied by 10 to calculate apparent analyte concentrations that exceed the analyte ML, or one-third the regulatory compliance, whichever is greater, or fall below the lower limit for the calibration blank, need be tested on a daily basis.

9.4.3 If the correction routine is operating properly, the determined apparent analyte(s) concentration from analysis of each interference solution (a through q) should fall within a specific concentration range bracketing the calibration blank. This concentration range is calculated by multiplying the concentration of the interfering element by the value of the correction factor being tested and dividing by 10. If, after subtraction of the analyte ML, or one-third the regulatory compliance, whichever is greater, the apparent analyte concentration is outside (above or below) this range, a change in the correction factor of more than 10% should be suspected. The cause of the change should be determined and corrected and the correction factor should be updated.

NOTE: *The SIC solution should be analyzed more than once to confirm a change has occurred with adequate rinse time between solutions and before subsequent analysis of the calibration blank.*

9.4.4 If the correction factors as tested on a daily basis are found to be within the 10% criteria for five consecutive days, the required verification frequency of those factors in compliance may be extended to a weekly basis. Also, if the nature of the samples analyzed is such (e.g., finished drinking water) that they do not contain concentrations of the interfering elements at the 10 mg/L level, daily verification is not required; however, all interelement spectral correction factors must be verified annually and updated if necessary.

9.4.5 All interelement spectral correction factors must be verified whenever there is a change in instrument operating conditions. Examples of changes requiring rigorous verification of spectral correction factors are: changes in incident power, changes in nebulizer gas flow rate, or installation of a new torch injector with a different orifice.

9.4.6 If the instrument does not display negative concentration values, fortify the SIC solutions with the elements of interest at 1 mg/L and test for analyte recoveries that are below 95%. In the absence of measurable analyte, over-correction could go undetected because a negative value could be reported as zero.

9.4.7 For instruments without interelement correction capability or when interelement corrections are not used, SIC solutions (containing similar concentrations of the major components in the samples, e.g., ≥ 10 mg/L) can serve to verify the absence of effects at the wavelengths selected. These data must be kept on file with the sample analysis data. If the SIC solution confirms an operative interference that is ≥ 10% of the analyte concentration, the analyte must be determined using a wavelength and background correction location free of the interference or by another approved test procedure. Users are advised that high salt concentrations can cause analyte signal suppressions and confuse interference tests.

9.5 Matrix spike (MS) and matrix spike duplicates (MSD)-To assess the performance of the method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (one sample in 10) of the samples from a given sampling site or, if for compliance monitoring, from a given discharge. Blanks may not be used for MS/MSD analysis.

9.5.1 The concentration of the MS and MSD shall be determined as follows:

9.5.1.1 If, as in compliance monitoring, the concentration of analytes in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample, whichever is greater. (For notes on Ag, Ba, and Sn see Sections 1.7 and 1.8).

9.5.1.2 If the concentration of analytes in a sample is not being checked against a regulatory concentration limit, the spike shall be at 1-5 times the background concentration.

9.5.1.3 For solid and sludge samples, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor 100 (mg/L x 0.1L/0.001kg = 100, Section 12.5). (For notes on Ag, Ba, and Sn see Sections 1.7 and 1.8).

9.5.2 Assessing spike recovery

9.5.2.1 To determine the background concentration (B), analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established a priori.

NOTE: *The concentrations of calcium, magnesium, sodium and strontium in environmental waters, along with iron and aluminum in solids and sludge can vary greatly and are not necessarily predictable. Major constituents should not be spiked to >25 mg/L so that the sample matrix is not altered and the analysis is not affected.*

9.5.2.2 Prepare a standard solution to produce an appropriate concentration in the sample (Section 9.5.1).

9.5.2.3 Spike two additional sample aliquots with the spiking solution and analyze these aliquots as described in Section 11 to determine the concentration after spiking (A).

9.5.2.4 Calculate the percent recovery (P) in each aliquot (Equation 3).

Equation 3

$$P = 100 * \frac{(A - B)}{T}$$

where:

P=Percent recovery
A=Measured concentration of analyte after spiking
B=Measured concentration of analyte before spiking
T=True concentration of the spike

9.5.3 Compare the percent recovery with the QC acceptance criteria in Table 5 (to be determined in validation study).

9.5.3.1 If P falls outside the designated range for recovery in Table 5, the results have failed to meet the established performance criteria. If P is unacceptable, analyze the OPR standard (Section 9.7). If the OPR is within established performance criteria (Table 5), the analytical system is within specification and the problem can be attributed to interference by the sample matrix. The data user should be informed that the result for that analyte in the unfortified sample is suspect due to either the heterogeneous nature of the sample or matrix effects, and analysis by method of standard addition or the use of an internal standard(s) (Section 11.6) should be considered.

9.5.3.2 If the results of both the spike and the OPR test fall outside the acceptance criteria, the analytical system is judged to be outside specified limits. The analyst must identify and correct the problem and analyze the sample batch again.

9.5.4 Assess the possible need for the method of standard additions (MSA) or internal standard elements by the following tests. Directions for using MSA or internal standard(s) are given in Section 11.6.

9.5.4.1 Analyte addition test: An analyte(s) standard added to a portion of a prepared sample, or its dilution, should have a recovery of 85% to 115% of the known value. The analyte(s) addition should produce a minimum level of 20 times and a maximum level of 100 times the method detection limit. If the analyte addition is <20% of the sample analyte concentration, the dilution test described in Section 9.5.4.2 should be used. If recovery of the analyte(s) is not within the specified limits, a matrix effect should be suspected, and the associated data flagged accordingly. The method of additions or the use of an appropriate internal standard element may provide more accurate data.

9.5.4.2 Dilution test: If the analyte concentration is sufficiently high (minimally, a factor of 50 above the instrument detection limit in the original solution but <90% of the linear limit), an analysis of a 1+4 dilution should agree (after correction for the fivefold dilution) within ±10% of the original determination. If not, a chemical or physical interference effect should be suspected and the associated data flagged accordingly. The method of standard additions or the use of an internal-standard element may provide more accurate data for samples failing this test.

9.5.5 Recovery for samples should be assessed and records maintained.

9.5.5.1 After the analysis of five samples of a given matrix type (river water, lake water, etc.). For which the analyte(s) pass the tests in Section 9.5.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (SR) for the analyte(s). Express the accuracy assessment as a percent recovery interval from R - 2SR to R + 2SR for each matrix. For example, if R=90% and SR = 10% for five analyses of river water, the accuracy interval is expressed as 70-110%.

9.5.5.2 Update the accuracy assessment for each metal in each matrix regularly (e.g., after each five to ten new measurements).

9.5.6 Precision of matrix spike and duplicate

9.5.6.1 Relative percent difference between duplicates–Compute the relative percent difference (RPD) between the MS and MSD results according to Equation 4 using the concentrations found in the MS and MSD. Do not use the recoveries calculated in Section 9.5.2 for this calculation because the RPD is inflated when the background concentration is near the spike concentration.

Equation 4

$$RPD = 200 * \frac{(|D_1 - D_2|)}{D_1 + D_2}$$

where:

RPD=Relative percent different
D_1=Concentration of the analyte in the MS sample
D_2=Concentration of the analyte in the MS sample

9.5.6.2 The RPD for the MS/MSD pair must not exceed the acceptance criterion in Table 5 (to be determined in validation study). If the criterion is not met, the system is judged to be outside accepted limits of performance. The problem must be identified and corrected, and the analytical batch must be analyzed again.

9.5.6.3 Reference material analysis can provide additional interference data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably. Reference materials containing high concentrations of analytes can provide additional information on the performance of the spectral interference correction routine.

9.6 Blanks

9.6.1 Method blank

9.6.1.1 Prepare a method blank with each sample batch (samples of the same matrix started through the sample preparation process (Section 11.0) on the same 12-hour shift, to a maximum of 20 samples). Analyze the blank immediately after the OPR is analyzed (Section 9.7) to demonstrate freedom from contamination.

9.6.1.2 If the analyte(s) of interest or any potentially interfering substance is found in the method blank at a concentration equal to or greater than the ML (Table 4) or 1/3 the regulatory compliance level, whichever is greater, sample analysis must be halted, the source of the contamination

determined, the samples must be prepared again with a fresh method blank and OPR and analyzed again.

9.6.1.3 Alternatively, if a sufficient number of blanks (three minimum) are analyzed to characterize the nature of a blank, the average concentration plus two standard deviations must be less than the regulatory compliance level.

9.6.1.4 If the result for a single blank remains above the ML or if the result for the average concentration plus two standard deviations of three or more blanks exceeds the regulatory compliance level, results for samples associated with those blanks may not be reported for regulatory compliance purposes.

9.6.2 Field blank

9.6.2.1 Analyze the field blank(s) shipped with each set of samples (samples collected from the same site at the same time, to a maximum of 20 samples). Analyze the blank immediately before analyzing the samples in the batch.

9.6.2.2 If the analyte(s) of interest or any potentially interfering substance is found in the field blank at a concentration equal to or greater than the ML or greater than one-fifth the level in the associated sample, whichever is greater, results for associated samples may be the result of contamination and may not be reported for regulatory compliance purposes.

9.6.2.3 Alternatively, if a sufficient number of field blanks (three minimum) are analyzed to characterize the nature of the field blank, the average concentration plus two standard deviations must be less than the regulatory compliance level or less than one-half the level in the associated sample, whichever is greater.

9.6.2.4 If contamination of the field blanks and associated samples is known or suspected, the laboratory should communicate this to the sampling team so that the source of contamination can be identified and corrective measures taken prior to the next sampling event.

9.6.3 Equipment blanks--Before any sampling equipment is used at a given site, it is recommended that the laboratory or cleaning facility generate equipment blanks to demonstrate that the sampling equipment is free from contamination. Two types of equipment blanks are recommended: bottle blanks and sampler check blanks.

9.6.3.1 Bottle blanks–After undergoing appropriate cleaning procedures (Section 6.1.2), bottles should be subjected to conditions of use to verify the effectiveness of the cleaning procedures. A representative set of sample bottles should be filled with reagent water acidified to pH < 2 and allowed to stand for a minimum of 24 hours. Ideally, the time that the bottles are allowed to stand should be as close as possible to the actual time that sample will be in contact with the bottle. After standing, the water should be analyzed for any signs of contamination. If any bottle shows signs of contamination, the problem must be identified, the cleaning procedures corrected or cleaning solutions changed, and all affected bottles cleaned again.

9.6.3.2 Sampler check blanks–Sampler check blanks are generated in the laboratory or at the equipment cleaning contractor's facility by processing reagent water through the sampling devices using the same procedures that are used in the field.

9.6.3.2.1 Sampler check blanks are generated by filling a large carboy or other container with reagent water (Section 7.1) and processing the reagent water through the equipment using the same procedures that are used in the field. For example, manual grab sampler check blanks are collected by directly submerging a sample bottle into the water, filling the bottle, and capping. Subsurface sampler check blanks are collected by immersing the sampler into the water and pumping water into a sample container. Whatever precautions and equipment are used in the field should also be used to generate these blanks.

9.6.3.2.2 The sampler check blank should be analyzed using the procedures in this method. If the target analyte(s) or any potentially interfering substance is detected in the blank, the source of contamination or interference must be identified and the problem corrected. The equipment should be demonstrated to be free from contamination before the equipment is used in the field.

9.6.3.2.3 Sampler check blanks should be run on *all* equipment that will be used in the field. If, for example, samples are to be collected using both a grab sampling device and a subsurface sampling device, a sampler check blank must be run on both pieces of equipment.

9.7 Ongoing precision and recovery

9.7.1 For aqueous samples, prepare an OPR sample (laboratory fortified method blank) identical to the IPR aliquots (Section 9.2.2.1) with each preparation batch (samples of the same matrix started through the sample preparation process (Section 11.0) on the same 12-hour shift, to a maximum of 20 samples) by spiking an aliquot of reagent water with the analyte(s) of interest.

9.7.2 For solid and sludge samples, the use of clean sand or soil fortified as in Section 9.8.1 is recommended.

9.7.3 Analyze the OPR sample immediately before the method blank and samples from the same batch.

9.7.4 Compute the percent recovery of each analyte in the OPR sample.

9.7.5 For each analyte, compare the concentration to the limits for ongoing recovery in (Table 5 - to be determined in validation study). If all analyte(s) meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, any individual recovery falls outside of the range given, the analytical processes are not being performed properly for that analyte. Correct the problem, prepare the sample batch again with fresh OPR and method blank, and reanalyze the QA/QC and samples.

9.7.6 Add results that pass the specifications in Section 9.8.5 to IPR and previous OPR data for each analyte in each matrix. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each analyte in each matrix type by calculating the average percent recovery (R) and the standard deviation of percent recovery (SR). Express the accuracy as a recovery interval from R-2SR to R+2SR. For example, if R = 95% and SR = 5%, the accuracy is 85-105%.

10.0 Calibration and Standardization

10.1 For initial and daily operation, calibrate the instrument according to the instrument manufacturer's recommended procedures, using mixed calibration standard solutions (Section 7.10) and the calibration blank (Section 7.11.1). The lowest calibration point (excluding calibration blanks) must be equal to the ML (Section 1.11).

10.2 The calibration line should include a calibration blank and a high standard near the upper limit of the linear dynamic range. The lowest calibration standard must contain the analyte(s) of interest at the ML. Replicates of the blank and highest standard provide an optimal distribution of calibration standards to minimize the confidence band for a straight-line calibration in a response region with uniform variance (Reference 20).

10.3 Calculate the response factor (RF) of the analytes for each of the standards (Equation 5).

Equation 5

$$RF = \frac{R_x}{C_x}$$

where:

R_x=*Peak height or area*
C_x=*Concentration of standard x*

10.3.1 Calculate the mean response factor (RF_m), the standard deviation of the RF_m, and the relative standard deviation (RSD) of the mean (Equation 6).

Equation 6

$$RSD = 100 * \frac{SD}{RF_m}$$

where:

RSD=Relative standard deviation of the mean
SD=Standard deviation of the RF_m
RF_m=*the mean response factor*

10.3.2 Performance criteria for the calibration will be set after the validation of the method.

11.0 Procedure

11.1 Aqueous sample preparation (Dissolved analytes)–For the determination of dissolved analytes in ground, drinking and surface waters, pipet an aliquot (≥20 mL) of the filtered, acid preserved sample into a 50-mL polypropylene centrifuge tube. Add an appropriate volume of (1+1) HNO_3 to adjust the acid concentration of the aliquot to approximate a 1% (v/v) HNO_3 solution (e.g., add 0.4 mL (1+1) HNO_3 to a 20 mL aliquot of sample). Cap the tube and mix. The sample is now ready for analysis. Allowance for sample dilution should be made in the calculations (Section 12). If mercury is to be determined, a separate aliquot must be additionally acidified to contain 1% (v/v) HCl to match the signal response of mercury in the calibration standard and reduce memory interference effects.

NOTE: *If a precipitate is formed during acidification, transport, or storage, the sample aliquot must be treated using the procedure described in Sections 11.2.2 through 11.2.7 prior to analysis.*

11.2 Aqueous Sample Preparation–Total Recoverable Analytes

11.2.1 For the "direct analysis" of total recoverable analytes in drinking water samples containing turbidity <1 NTU, treat an unfiltered, acid preserved sample aliquot using the sample preparation procedure described in Section 11.1 while making allowance for sample dilution in the data calculation (Section 12.0). For the determination of total recoverable analytes in all other aqueous samples or for preconcentrating drinking water samples prior to analysis, follow the procedure given in Sections 11.2.2 through 11.2.7.

11.2.2 For the determination of total recoverable analytes in aqueous samples of >1 NTU turbidity, transfer a 100 mL (±1 mL) aliquot from a well mixed, acid preserved sample to a 250-mL Griffin beaker. (When necessary, smaller sample aliquot volumes may be used).

NOTE: *If the sample contains undissolved solids >1%, a well mixed, acid preserved aliquot containing no more than 1 g particulate material should be cautiously evaporated to near 10 mL and extracted using the acid-mixture procedure described in Sections 11.3.3 through 11.3.6.*

11.2.3 Add 2 mL (1+1) HNO_3 and 1.0 mL of (1+1) HCl to the beaker containing the measured volume of sample. Place the beaker on the hot plate for solution evaporation. The hot plate should be located in a fume hood and previously adjusted to provide evaporation at a temperature of approximately but no higher than 85°C. (See the following note). The beaker should be covered with an elevated watch glass or other necessary steps should be taken to prevent sample contamination from the fume hood environment.

NOTE: *For proper heating, adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass, the temperature of the water will rise to approximately 95°C).*

11.2.4 Reduce the volume of the sample aliquot to about 20 mL by gentle heating at 85°C. DO NOT BOIL. This step takes about two hours for a 100 mL aliquot with the rate of evaporation rapidly increasing as the sample volume approaches 20 mL. (A spare beaker containing 20 mL of water can be used as a gauge).

11.2.5 Cover the lip of the beaker with a watch glass to reduce additional evaporation and gently reflux the sample for 30 minutes. (Slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope).

11.2.6 Allow the beaker to cool. Quantitatively transfer the sample solution to a 50-ml volumetric flask, dilute to volume with reagent water, stopper and mix.

11.2.7 Allow any undissolved material to settle overnight, or centrifuge a portion of the prepared sample until clear. (If after centrifuging or standing overnight, the sample contains

suspended solids that would clog the nebulizer, a portion of the sample may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration). The sample is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.3 Solid sample preparation–Total recoverable analytes

11.3.1 For the determination of total recoverable analytes in solid samples, mix the sample thoroughly and transfer a portion to a tared weighing dish. For samples with <35% estimated moisture, a 20 g portion is sufficient. For samples with estimated moisture >35%, a larger aliquot 50-100 g is required. Dry the sample to a constant weight at 60°C. The sample is dried at 60°C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.

11.3.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples). From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250-ml Phillips beaker for acid extraction (Sections 1.6, 1.7, 1.8, and 1.9).

11.3.3 To the beaker, add 4 mL of (1+1) HNO_3 and 10 mL of (1+4) HCl. Cover the lip of the beaker with a watch glass. Place the beaker on a hot plate for reflux extraction of the analytes. The hot plate should be located in a fume hood and previously adjusted to provide a reflux temperature of approximately 95°C (See the following note).

NOTE: *For proper heating, adjust the temperature control of the hot plate such that an uncovered Griffin beaker containing 50 mL of water placed in the center of the hot plate can be maintained at a temperature approximately but no higher than 85°C. (Once the beaker is covered with a watch glass the temperature of the water will rise to approximately 95°C). Also, a block digester capable of maintaining a temperature of 95°C and equipped with 250 mL constricted volumetric digestion tubes may be substituted for the hot plate and conical beakers in the extraction step.*

11.3.4 Heat the sample and gently reflux for 30 minutes. Very slight boiling may occur, but vigorous boiling must be avoided to prevent loss of the HCl-H_2O azeotrope. Some solution evaporation will occur (3-4 mL).

11.3.5 Allow the sample to cool and quantitatively transfer the extract to a 100-ml volumetric flask. Dilute to volume with reagent water, stopper and mix.

11.3.6 Allow the sample extract solution to stand overnight to separate insoluble material or centrifuge a portion of the sample solution until clear. (If after centrifuging or standing

overnight, the extract solution contains suspended solids that would clog the nebulizer, a portion of the extract solution may be filtered for their removal prior to analysis. However, care should be exercised to avoid potential contamination from filtration). The sample extract is now ready for analysis. Because the effects of various matrices on the stability of diluted samples cannot be characterized, all analyses should be performed as soon as possible after the completed preparation.

11.3.7 Determine the total solids content of the sample using the procedure in Appendix A.

11.4 Sludge sample preparation–Total recoverable analytes

NOTE: *It may be possible to use the solids digestion (Section 11.3) for sludge samples, depending on the composition of the sludge sample and the analyte(s) of interest. Under this performance-based method, it is admissible to change the digestion technique as long as all quality control and assurance tests meet the criteria published in Tables 4 and 5. This method has been validated using the sludge sample digestion in Section 11.4 of this method, and it works for all the analytes listed in Section 1.1.*

11.4.1 Determination of total recoverable analytes in sludge samples containing total suspended solids ≥ 1% (w/v).

11.4.1.1 Mix the sample thoroughly and transfer a portion to a tared weighing dish. For samples with <35% estimated moisture a 20 g portion is sufficient. For samples with estimated moisture >35% a larger aliquot of 50-100 g is required. Dry the sample to a constant weight at 60°C. The sample is dried at 60°C to prevent the loss of mercury and other possible volatile metallic compounds, to facilitate sieving, and to ready the sample for grinding.

11.4.1.2 To achieve homogeneity, sieve the dried sample using a 5-mesh polypropylene sieve and grind in a mortar and pestle. (The sieve, mortar and pestle should be cleaned between samples). From the dried, ground material weigh accurately a representative 1.0 ± 0.01 g aliquot (W) of the sample and transfer to a 250-mL Phillips beaker for acid extraction (Sections 1.6, 1.7, 1.8, and 1.9).

11.4.1.3 Add 10 mL of (1+1) HNO_3 to the beaker and cover the lip of the beaker with a watch glass. Place the beaker on a hot plate and reflux the sample for 10 minutes. Remove the sample from the hot plate and allow to cool. Add 5 mL of concentrated HNO_3 to the beaker, replace the watch glass, place on a hot plate, and reflux for 30 minutes. Repeat this last step once. Remove the beaker from the hot plate and allow the sample to cool. Add 2 mL of reagent water and 3 mL of 30% H_2O_2. Place the beaker on a hot plate and heat the sample until a gentle effervescence is observed. Once

the reaction has subsided, additional 1 mL aliquots of the 30% H_2O_2 should be added until no effervescence is observed, but to no more than a total of 10 mL. Add 2 mL concentrated HCl and 10 mL of reagent water to the sample, cover with a watch glass and reflux for 15 minutes.

11.4.1.4 Cool the sample and dilute to 100 mL with reagent water. Any remaining solid material should be allowed to settle, or an aliquot of the final sample volume may be centrifuged.

11.4.1.5 Determine the total solids content of the sample using the procedure in Appendix A.

11.4.2 Determination of total recoverable analytes in sludge samples containing total suspended solids < 1% (w/v).

11.4.2.1 Transfer 100 mL of well-mixed sample to a 250-ml Griffin beaker.

11.4.2.2 Add 3 mL of concentrated HNO_3 and place the beaker on a hot plate. Heat the sample and cautiously evaporate to a volume of 5 mL. If the sample contains large amounts of dissolved solids, adjust this volume upwards to prevent the sample from going to dryness. Remove the beaker from the hot plate and allow the sample to cool. Add 3 mL of concentrated HNO_3, cover with a watch glass and gently reflux the sample until the sample is completely digested or no further changes in appearance occur, adding additional aliquots of acid if necessary to prevent the sample from going to dryness. Then remove the watch glass and reduce the sample volume to 3 mL, again adjusting upwards if necessary.

11.4.2.3 Cool the beaker, then add 10 mL of reagent water and 4 mL of (1+1) HCl to the sample and reflux for 15 minutes. Cool the sample and dilute to 100 mL with reagent water. Any remaining solid material should be allowed to settle, or an aliquot of the final sample volume may be centrifuged.

11.4.2.4 Determine the total solids content of the sample using the procedure in Appendix A.

11.5 Sample analysis

11.5.1 Prior to daily calibration of the instrument, inspect the sample introduction system including the nebulizer, torch, injector tube and uptake tubing for salt deposits, dirt and debris that would restrict solution flow and affect instrument performance. Clean the system when needed or on a daily basis.

11.5.2 Configure the instrument system.

11.5.2.1 Specific wavelengths are listed in Table 1. Other wavelengths may be substituted if they can provide the needed sensitivity and are corrected for spectral interference. However, because of the difference among various makes and models of spectrometers, specific instrument operating conditions cannot be given. The instrument and operating conditions utilized for determination must be capable of providing data of acceptable quality to the program and data user. The analyst should follow the instructions provided by the instrument manufacturer unless other conditions provide similar or better performance for a task. Operating conditions for aqueous solutions usually vary from 1100-1200 watts forward power, 15-16 mm viewing height, 15-19 L/min. argon coolant flow, 0.6-1 L/min. argon aerosol flow, 1-1.8 mL/min. sample pumping rate with a one minute preflush time and measurement time near 1 s per wavelength peak (for sequential instruments) and near 10 s per sample (for simultaneous instruments). Use of the Cu/Mn intensity ratio at 324.754 nm and 257.610 nm (by adjusting the argon aerosol flow) has been recommended as a way to achieve repeatable interference correction factors (Reference 17).

11.5.2.2 Prior to using this method, optimize the plasma operating conditions. The following procedure is recommended for vertically configured plasmas. The purpose of plasma optimization is to provide a maximum signal-to-background ratio for the least sensitive element in the analytical array. The use of a mass flow controller to regulate the nebulizer gas flow rate greatly facilitates the procedure.

11.5.2.3 Ignite the plasma and select an appropriate incident rf power with minimum reflected power. Allow the instrument to become thermally stable before beginning. This usually requires at least 30 to 60 minutes of operation. While aspirating the 1000 µg/mL solution of yttrium (Section 7.9.32), follow the instrument manufacturer's instructions and adjust the aerosol carrier gas flow rate through the nebulizer so a definitive blue emission region of the plasma extends approximately from 5-20 mm above the top of the work coil (Reference 18). Record the nebulizer gas flow rate or pressure setting for future reference.

11.5.2.4 After establishing the nebulizer gas flow rate, determine the solution uptake rate of the nebulizer in mL/min. by aspirating a known volume calibration blank for a period of at least three minutes. Divide the spent volume by the aspiration time (in minutes) and record the uptake rate. Set the peristaltic pump to deliver the uptake rate in a steady even flow.

11.5.2.5 After horizontally aligning the plasma and/or optically profiling the spectrometer, use the selected instrument conditions from Sections 11.5.2.3 and 11.5.2.4, and aspirate the plasma solution (Section 7.15), containing 10 µg/mL each of As, Pb, Se and Tl. Collect intensity data at the wavelength peak for each analyte at 1 mm intervals from 14-18 mm above the top of the work coil. This region of the plasma is commonly referred to as the analytical zone (Reference 19). Repeat the process using the calibration blank. Determine the net signal to blank intensity ratio for each analyte for each viewing height setting. Choose the height for viewing the plasma that provides the largest intensity ratio for the least sensitive element of the four analytes. If more than one position provides the same ratio, select the position that provides the highest net intensity for the least sensitive element or accept a compromise position of the intensity ratios of all four analytes.

11.5.2.6 The instrument operating condition finally selected as optimum should provide the lowest reliable method detection limits.

11.5.2.7 If either the instrument operating conditions, such as incident power and/or nebulizer gas flow rate are changed, or a new torch injector tube having a different orifice i.d. is installed, the plasma and plasma viewing height should be reoptimized.

11.5.2.8 Before daily calibration and after the instrument warmup period, the nebulizer gas flow must be reset to the determined optimized flow. If a mass flow controller is being used, it should be reset to the recorded optimized flow rate. In order to maintain valid spectral interelement correction routines the nebulizer gas flow rate should be the same from day-to-day (<2% change). The change in signal intensity with a change in nebulizer gas flow rate for both "hard" (Pb 220.353 nm) and "soft" (Cu 324.754) lines is illustrated in Figure 1.

11.5.3 The instrument must be allowed to become thermally stable before calibration and analyses. This usually requires at least 30 to 60 minutes of operation. After instrument warmup, complete any required optical profiling or alignment particular to the instrument.

11.5.4 Prior to and during the analysis of samples, the laboratory must comply with the required QA/QC procedures (Section 9). QA/QC data must be generated using the same instrument operating conditions (Section 11.5) and calibration routine (Section 10) in effect for sample analysis. The data must be documented and kept on file so that they are available for review by the data user.

11.5.5 A peristaltic pump must be used to introduce all solutions to the nebulizer. To allow equilibrium to be reached in the plasma, aspirate all solutions for 30 seconds after reaching the plasma before beginning integration of the background corrected signal to accumulate data. When possible, use the average value of replicate integration periods of the signal to be correlated to the analyte concentration. Flush the system with the rinse blank (Section 7.11.1) for a minimum of 60 seconds (Section 4.4) between all standard or sample solutions, OPRs, MS, MSD, and check solutions.

11.5.6 Determined sample analyte concentrations that are 90% or more of the upper limit of the analyte LDR must be diluted with reagent water that has been acidified in the same manner as calibration blank and analyzed again.

11.5.7 Also, for the interelement spectral interference correction routines to remain valid during sample analysis, the interferant concentration must not exceed its LDR. If the interferant LDR is exceeded, analyte detection limits are raised and determination by another approved test procedure that is either more sensitive and/or interference free is recommended. If another approved method is unavailable, the sample may be diluted with acidified reagent water and reanalyzed.

11.5.8 When it is necessary to assess an operative matrix interference (e.g., signal reduction due to high dissolved solids), the tests described in Section 9.5.4 and 11.6 are recommended.

11.5.9 Report data as directed in Section 12.0.

11.6 If the method of standard additions (MSA) is used, standards are added at one or more levels to portions of a prepared sample. This technique compensates for enhancement or depression of an analyte signal by a matrix (Reference 21). It will not correct for additive interferences such as contamination, interelement interferences, or baseline shifts. This technique is valid in the linear range when the interference effect is constant over the range, the added analyte responds the same as the endogenous analyte, and the signal is corrected for additive interferences. The simplest version of this technique is the single-addition method. This procedure calls for two identical aliquots of the sample solution to be taken. To the first aliquot, a small volume of standard is added; while to the second aliquot, a volume of acid blank is added equal to the standard addition. The sample concentration is calculated with Equation 7.

Equation 7

$$C_s = \frac{S_2 * V_1 * C}{(S_1 - S_2) * V_2}$$

where:

C_s=*Sample concentration (mg/L)*
C =*Concentration of the standard solution (mg/L)*
S_1=*Signal for fortified aliquot*
S_2=*Signal for unfortified aliquot*
V_1=*Volume of the standard addition (L)*
V_2=*Volume of the sample aliquot (L) used for MSA*

For more than one fortified portion of the prepared sample, linear regression analysis can be applied using a computer or calculator program to obtain the concentration of the sample solution. An alternative to using the method of standard additions is use of the internal standard technique by adding one or more elements (not in the samples and verified not to cause an uncorrected interelement spectral interference) at the same concentration (which is sufficient for optimum precision) to the prepared samples (blanks and standards) that are affected the same as the analytes by the sample matrix. Use the ratio of analyte signal to the internal standard signal for calibration and quantitation.

12.0 Data Analysis and Calculations

12.1 Sample data should be reported in units of mg/L for aqueous samples and mg/kg dry weight for solid and sludge samples.

12.2 For dissolved aqueous analytes (Section 11.1) report the data generated directly from the instrument with allowance for sample dilution. Do not report analyte concentrations below the MDL.

12.3 For total recoverable aqueous analytes (Section 11.2), multiply solution analyte concentrations by the dilution factor 0.5, when 100 mL aliquot is used to produce the 50 mL final solution, and report data as instructed in Section 12.4. If an aliquot volume other than 100 mL is used for sample preparation, adjust the dilution factor accordingly. Also, account for any additional dilution of the prepared sample solution needed to complete the determination of analytes exceeding 90% or more of the LDR upper limit. Do not report data below the determined analyte MDL concentration.

12.4 For analytes with MDLs <0.01 mg/L, round the data values to the thousandth place and report analyte concentrations up to three significant figures. For analytes with MDLs ≥0.01 mg/L, round the data values to the hundredth place and report analyte concentrations up to three significant

figures. Extract concentrations for solids and sludge data should be rounded in a similar manner before calculations in Section 12.5 are performed.

12.5 For total recoverable analytes in solid and sludge samples (Sections 11.3 and 11.4), round the solution analyte concentrations (mg/L) as instructed in Section 12.4. Report the data up to three significant figures as mg/kg dry-weight basis unless specified otherwise by the program or data user. Calculate the concentration using Equation 8.

Equation 8

$$C_s = \frac{C * V * D}{W}$$

where:

C_s=*Sample concentration (mg/kg, dry-weight basis)*
C=*Concentration in extract (mg/L)*
V=*Volume of extract (L, 100 mL = 0.1L)*
D=*Dilution factor (undiluted = 1)*
W=*Weight of sample aliquot extracted (kg, 1g=0.001kg)*

Do not report analyte data below the solids MDL.

12.6 To report percent solids or mg/kg of solid and sludge samples, use the procedure in Appendix A.

12.7 The QC data obtained during the analyses provide an indication of the quality of the sample data and should be provided with the sample results.

13.0 Method Performance

13.1 MDLs and MLs will be determined in a validation study. Preliminary MDL values are given in Table 4. The ML for each analyte can be calculated by multiplying the MDL by 3.18 and rounding to the number nearest (2, 5, or 10 X 10^n) where n is a positive or negative integer.

14.0 Pollution Prevention

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation (e.g., Section 7.9). When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036, (202)872-4477.

15.0 Waste Management

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in the Section 14.2.

16.0 References

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24. *Handbook of Analytical Quality Control in Water and Wastewater Laboratories*; U.S. Environmental Protection Agency. EMSL-Cincinnati, OH, March 1979.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

TABLE 1: WAVELENGTHS, ESTIMATED INSTRUMENT DETECTION LIMITS, AND RECOMMENDED CALIBRATION

Analyte	Wavelength[a] (nm)	Estimated Detection Limit[b] (µg/L)	Calibrate[c] to (mg/L)
Aluminum	308.215	45	10
Antimony	206.833	32	5
Arsenic	193.759	53	10
Barium	493.409	2.3	1
Beryllium	313.042	0.27	1
Boron	249.678	5.7	1
Cadmium	226.502	3.4	2
Calcium	315.887	30	10
Cerium	413.765	48	2
Chromium	205.552	6.1	5
Cobalt	228.616	7.0	2
Copper	324.754	5.4	2
Iron	259.940	6.2	10
Lead	220.353	42	10
Lithium	670.784	3.7[d]	5
Magnesium	279.079	30	10
Manganese	257.610	1.4	2
Mercury	194.227	2.5	2
Molybdenum	203.844	12	10
Nickel	231.604	15	2
Phosphorus	214.914	76	10
Potassium	766.491	700[e]	20
Selenium	196.090	75	5
Silica (SiO_2)	251.611	26[d] (SiO_2)	10
Silver	328.068	7.0	0.5
Sodium	588.995	29	10
Strontium	421.552	0.77	1
Thallium	190.864	40	5
Tin	189.980	25	4
Titanium	334.941	3.8	10
Vanadium	292.402	7.5	2
Zinc	213.856	1.8	5

[a]The wavelengths listed are recommended because of their sensitivity and overall acceptability. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference (see Section 4.1).

[b]These estimated 3-sigma instrumental detection limits are provided only as a guide to instrumental limits (Reference 16). The method detection limits are sample dependent and may vary as the sample matrix varies. Detection limits for solids can be estimated by dividing these values by the grams extracted per liter, which depends upon the extraction procedure. Divide solution detection limits by 10 for 1 g extracted to 100 mL for solid detection limits.

[c]Suggested concentration for instrument calibration (Reference 2). Other calibration limits in the linear ranges may be used.

[d]Calculated from 2-sigma data (Reference 5).

[e]Highly dependent on operating conditions and plasma position.

TABLE 2: ON-LINE METHOD INTERELEMENT SPECTRAL INTERFERENCES ARISING FROM INTERFERANTS AT THE 100 mg/L LEVEL

Analyte	Wavelength (nm)	Interferant[a]
Ag	328.068	Ce, Ti, Mn
Al	308.215	V, Mo, Ce, Mn
As	193.759	V, Al, Co, Fe, Ni
B	249.678	None
Ba	493.409	None
Be	313.042	V, Ce
Ca	315.887	Co, Mo, Ce
Cd	226.502	Ni, Ti, Fe, Ce
Ce	413.765	None
Co	228.616	Ti, Ba, Cd, Ni, Cr, Mo, Ce
Cr	205.552	Be, Mo, Ni
Cu	324.754	Mo, Ti
Fe	259.940	None
Hg	194.227	V, Mo
K	766.491	None
Li	670.784	None
Mg	279.079	Ce
Mn	257.610	Ce
Mo	203.844	Ce
Na	588.995	None
Ni	231.604	Co, Tl
P	214.914	Cu, Mo
Pb	220.353	Co, Al, Ce, Cu, Ni, Ti, Fe
Sb	206.833	Cr, Mo, Sn, Ti, Ce, Fe
Se	196.099	Fe
SiO_2	251.611	None
Sn	189.980	Mo, Ti, Fe, Mn, Si
Sr	421.552	None
Tl	190.864	Ti, Mo, Co, Ce, Al, V, Mn
Ti	334.941	None
V	292.402	Mo, Ti, Cr, Fe, Ce
Zn	213.856	Ni, Cu, Fe

[a]These on-line interferences from method analytes and titanium only were observed using an instrument with 0.035 nm resolution (see Section 4.1.2). Interferant ranked by magnitude of intensity with the most severe interferant listed first in the row.

TABLE 3: MIXED STANDARD SOLUTIONS

Solution	Analytes
I	Ag, As, B, Ba, Ca, Cd, Cu, Mn, Sb, and Se
II	K, Li, Mo, Na, Sr, and Ti
III	Co, P, V, and Ce
IV	Al, Cr, Hg, SiO_2, Sn, and Zn
V	Be, Fe, Mg, Ni, Pb, and Tl

TABLE 4: TOTAL RECOVERABLE METHOD DETECTION LIMITS (MDL)[a]

	MDLs	
Analyte	**Aqueous, mg/L[b]**	**Solids, mg/kg[c]**
Ag	0.002	0.3
Al	0.02	3
As	0.008	2
B[d]	0.003	–
Ba	0.001	0.2
Be	0.0003	0.1
Ca	0.01	2
Cd	0.001	0.2
Ce	0.02	3
Co	0.002	0.4
Cr	0.004	0.8
Cu	0.003	0.5
Fe	0.03[e]	6
Hg	0.007	2
K	0.3	60
Li	0.001	0.2
Mg	0.02	3
Mn	0.001	0.2
Mo	0.004	1
Na	0.03	6
Ni	0.005	1
P	0.06	12
Pb	0.01	2
Sb	0.008	2
Se	0.02	5
SiO_2	0.02	–
Sn	0.007	2
Sr	0.0003	0.1
Tl	0.001	0.2
Ti	0.02	3
V	0.003	1
Zn	0.002	0.3

[a]Table will be changed after interlaboratory validation of Method 200.7.

[b]MDL concentrations are computed for original matrix with allowance for 2x sample preconcentration during preparation. Samples were processed in PTFE and diluted in 50-mL plastic centrifuge tubes.

[c]Estimated, calculated from aqueous MDL determinations.

[d]Boron not reported because of glassware contamination. Silica not determined in solid samples.

[e]Elevated value due to fume-hood contamination.

TABLE 5: PERFORMANCE CRITERIA FOR METHOD 200.7 (TO BE DETERMINED DURING INTERLABORATORY VALIDATION)

Appendix A: Total Solids in Solid and Semisolid Matrices

1.0 Scope and Application

1.1 This procedure is applicable to the determination of total solids in such solid and semisolid samples as soils, sediments, biosolids (municipal sewage sludge) separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other biosolids dewatering processes.

1.2 This procedure is taken from EPA Method 1684: *Total, Fixed, and Volatile Solids in Solid and Semi-Solid Matrices.*

1.3 Method detection limits (MDLs) and minimum levels (MLs) have not been formally established for this draft procedure. These values will be determined during the validation of Method 1684.

1.4 This procedure is performance based. The laboratory is permitted to omit any step or modify any procedure (e.g. to overcome interferences, to lower the cost of measurement), provided that all performance requirements in this procedure are met. Requirements for establishing equivalency are given in Section 9.1.2 of Method 200.7.

1.5 Each laboratory that uses this procedure must demonstrate the ability to generate acceptable results using the procedure in Section 9.2.

2.0 Summary of Method

2.1 Sample aliquots of 25-50 g are dried at 103°C to 105°C to drive off water in the sample.

2.3 The mass of total solids in the sample is determined by comparing the mass of the sample before and after each drying step.

3.0 Definitions

3.1 Total Solids–The residue left in the vessel after evaporation of liquid from a sample and subsequent drying in an oven at 103°C to 105°C.

3.2 Additional definitions are given in Sections 3.0 and 18.0 of Method 200.7.

4.0 Interferences

4.1 Sampling, subsampling, and pipeting multi-phase samples may introduce serious errors (Reference 13.1). Make and keep such samples homogeneous during transfer. Use special handling to ensure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If visible

suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, intensive homogenization is required to ensure accurate results. When dried, some samples form a crust that prevents evaporation; special handling such as extended drying times are required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

4.2 The temperature and time of residue drying has an important bearing on results (Reference 1). Problems such as weight losses due to volatilization of organic matter, and evolution of gases from heat-induced chemical decomposition, weight gains due to oxidation, and confounding factors like mechanical occlusion of water and water of crystallization depend on temperature and time of heating. It is therefore essential that samples be dried at a uniform temperature, and for no longer than specified. Each sample requires close attention to desiccation after drying. Minimize the time the desiccator is open because moist air may enter and be absorbed by the samples. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

4.3 Residues dried at 103°C to 105°C may retain some bound water as water of crystallization or as water occluded in the interstices of crystals. They lose CO_2 in the conversion of bicarbonate to carbonate. The residues usually lose only slight amounts of organic matter by volatilization at this temperature. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.

4.4 Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.

4.5 The determination of total solids is subject to negative error due to loss of ammonium carbonate and volatile organic matter during the drying step at 103°C to 105°C. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem.

5.0 Safety

5.1 Refer to Section 5.0 of Method 200.7 for safety precautions.

6.0 Equipment and Supplies

NOTE: *Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

6.1 Evaporating Dishes–Dishes of 100-mL capacity. The dishes may be made of porcelain (90-mm diameter), platinum, or high-silica glass.

6.2 Watch glass–Capable of covering the evaporating dishes (Section 6.1).

6.3 Steam bath.

6.4 Desiccator–Moisture concentration in the desiccator should be monitored by an instrumental indicator or with a color-indicator desiccant.

6.5 Drying oven–Thermostatically-controlled, capable of maintaining a uniform temperature of 103°C to 105°C throughout the drying chamber.

6.6 Analytical balance–Capable of weighing to 0.1 mg for samples having a mass up to 200 g.

6.7 Container handling apparatus–Gloves, tongs, or a suitable holder for moving and handling hot containers after drying.

6.8 Bottles–Glass or plastic bottles of a suitable size for sample collection.

6.9 Rubber gloves (Optional).

6.10 No. 7 Cork borer (Optional).

7.0 Reagents and Standards

7.1 Reagent water–Deionized, distilled, or otherwise purified water.

7.2 Sodium chloride-potassium hydrogen phthalate standard (NaCl-KHP).

7.2.1 Dissolve 0.10 g sodium chloride (NaCl) in 500 mL reagent water. Mix to dissolve.

7.2.2 Add 0.10 g potassium hydrogen phthalate (KHP) to the NaCl solution (Section 7.2.1) and mix. If the KHP does not dissolve readily, warm the solution while mixing. Dilute to 1 L with reagent water. Store at 4°C. Assuming 100% volatility of the acid phthalate ion, this solution contains 200 mg/L total solids, 81.0 mg/L volatile solids, and 119 mg/L fixed solids.

8.0 Sample Collection, Preservation, and Storage

8.1 Use resistant-glass or plastic bottles to collect sample for solids analysis, provided that the material in suspension does not adhere to container walls. Sampling should be done in accordance with Reference 13.2. Begin analysis as soon as possible after collection because of the impracticality of preserving the sample. Refrigerate the sample at 4°C up to the time of analysis to minimize microbiological decomposition of solids. Preferably do not hold samples more than 24 hours. Under no circumstances should the sample be held more than seven days. Bring samples to room temperature before analysis.

9.0 Quality Control

9.1 Quality control requirements and requirements for performance-based methods are given in Section 9.1 of Method 200.7.

9.2 Initial demonstration of laboratory capability - The initial demonstration of laboratory capability is used to characterize laboratory performance and method detection limits.

9.2.1 Method detection limit (MDL) - The method detection limit should be established for the analyte, using diluted NaCl-KHP standard (Section 7.2). To determine MDL values, take seven replicate aliquots of the diluted NaCl-KHP solution and process each aliquot through each step of the analytical method. Perform all calculations and report the concentration values in the appropriate units. MDLs should be determined every year or whenever a modification to the method or analytical system is made that will affect the method detection limit.

9.2.2 Initial Precision and Recovery (IPR) - To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.2.1 Prepare four samples by diluting NaCl-KHP standard (Section 7.2) to 1-5 times the MDL. Using the procedures in Section 11, analyze these samples for total solids.

9.2.2.2 Using the results of the four analyses, compute the average percent recovery (x) and the standard deviation (s, Equation 1) of the percent recovery for total solids.

Equation 1

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x^2)}{n}}{n-1}}$$

Where:

n = *number of samples*
x = *% recovery in each sample*
s = *standard deviation*

9.2.2.3 Compare s and x with the corresponding limits for initial precision and recovery in Table 2 (to be determined in validation study). If s and x meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or x falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.3 Laboratory blanks

9.3.1 Prepare and analyze a laboratory blank initially (i.e. with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample, and will consist of approximately 25 g of reagent water.

9.3.2 If material is detected in the blank at a concentration greater than the MDL (Section 1.3), analysis of samples must be halted until the source of contamination is eliminated and a new blank shows no evidence of contamination. All samples must be associated with an uncontaminated laboratory blank before the results may be reported for regulatory compliance purposes.

9.4 Ongoing Precision and Recovery

9.4.1 Prepare an ongoing precision and recovery (OPR) solution identical to the IPR solution described in Section 9.2.2.1.

9.4.2 An aliquot of the OPR solution must be analyzed with each sample batch (samples started through the sample preparation process (Section 11) on the same 12-hour shift, to a maximum of 20 samples).

9.4.3 Compute the percent recovery of total solids in the OPR sample.

9.4.4 Compare the results to the limits for ongoing recovery in Table 2 (to be determined in validation study). If the results meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, the recovery of total solids falls outside of the range given, the analytical processes are not being performed properly. Correct the problem, reprepare the sample batch, and repeat the OPR test. All samples must be associated with an OPR analysis that passes acceptance criteria before the sample results can be reported for regulatory compliance purposes.

9.4.5 results that pass the specifications in Section 9.4.4 to IPR and previous OPR data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery (SR). Express the accuracy as a recovery interval from R-2SR to R+2SR. For example, if R=05% and SR=5%, the accuracy is 85-115%.

9.5 Duplicate analyses

9.5.1 Ten percent of samples must be analyzed in duplicate. The duplicate analyses must be performed within the same sample batch (samples whose analysis is started within the same 12-hour period, to a maximum of 20 samples).

9.5.2 The total solids of the duplicate samples must be within 10%.

10.0 Calibration and Standardization

10.1 Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights.

10.2 Calibration shall be within ± 10% (i.e. ±0.2 mg) at 2 mg and ± 0.5% (i.e. ±5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.

11.0 Procedure

11.1 Preparation of evaporating dishes–Heat dishes and watch glasses at 103°C to 105°C for 1 hour in an oven. Cool and store the dried equipment in a desiccator. Weigh each dish and watch glass prior to use (record combined weight as "W_{dish}").

11.2 Preparation of samples

11.2.1 Fluid samples–If the sample contains enough moisture to flow readily, stir to homogenize, place a 25 to 50 g sample aliquot on the prepared evaporating dish. If the sample is to be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Evaporate the samples to dryness on a steam bath. Cover each sample with a watch glass, and weigh (record weight as "W_{sample}").

NOTE: *Weigh wet samples quickly because wet samples tend to lose weight by evaporation. Samples should be weighed immediately after aliquots are prepared.*

11.2.2 Solid samples–If the sample consists of discrete pieces of solid material (dewatered sludge, for example), take cores from each piece with a No. 7 cork borer or pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves. Place a 25 to 50 g sample aliquot of the pulverized sample on the prepared evaporating dish. If the sample is to be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Cover each sample with a watch glass, and weigh (record weight as "W_{sample}").

11.3 Dry the samples at 103°C to 105°C for a minimum of 12 hours, cool to balance temperature in an individual desiccator containing fresh desiccant, and weigh. Heat the residue again for 1 hour, cool it to balance temperature in a desiccator, and weigh. Repeat this heating, cooling, desiccating, and weighing procedure until the weight change is less than 5% or 50 mg, whichever is less. Record the final weight as "W_{total}."

NOTE: *It is imperative that dried samples weighed quickly since residues often are very hygroscopic and rapidly absorb moisture from the air. Samples must remain in the dessicator until the analyst is ready to weigh them.*

12.0 Data Analysis and Calculations

12.1 Calculate the % solids or the mg solids/kg sludge for total solids (Equation 2).

Equation 2

$$\% \ total\ solids = \frac{W_{total} - W_{dish}}{W_{sample} - W_{dish}} * 100$$

or

$$\frac{mg\ total\ solids}{kg\ sludge} = \frac{W_{total} - W_{dish}}{W_{sample} - W_{dish}} * 1{,}000{,}000$$

Where:

W_{dish} = *Weight of dish (mg)*
W_{sample} = *Weight of wet sample and dish (mg)*
W_{total} = *Weight of dried residue and dish (mg)*

12.2 Sample results should be reported as % solids or mg/kg to three significant figures. Report results below the ML as < the ML, or as required by the permitting authority or in the permit.

13.0 Method Performance

13.1 Method performance (MDL and quality control acceptance criteria) will be determined during the multi-lab validation of this method.

13.2 Total solids duplicate determinations must agree within 10% to be reported for permitting purposes. If duplicate samples do not meet this criteria, the problem must be discovered and the sample must be run over.

14.0 Pollution Prevention

14.2 Pollution prevention details are given in Section 14 of Method 200.7.

15.0 Waste Management

15.1 Waste management details are given in Section 15 of Method 200.7.

16.0 References

16.1 "Standard Methods for the Examination of Water and Wastewater," 18th ed. and later revisions, American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 1-35: Section 1090 (Safety), 1992.

16.2 U.S. Environmental Protection Agency, 1992. Control of Pathogens and Vector Attraction in Sewage Sludge. Publ 625/R-92/013. Office of Research and Development, Washington, DC.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Tables containing method requirements for QA/QC will be added after the validation study has been performed.

ATTACHMENT E

Laboratory Quality Assurance Manual

Insert Manual

QUALITY ASSURANCE
QUALITY CONTROL DOCUMENT
FOR
WATER AND WASTE WATER

AND

ADDENDUM
FOR
SOIL AND PLANT ANALYSIS

DELLAVALLE LABORATORY, INC.
1910 W. McKinley Avenue, Suite 110
Fresno, CA 93728

Revised
May 1999

Approved By _____
Laboratory Director

2. TABLE OF CONTENTS

3. ORGANIZATION & RESPONSIBILITIES

A. MANAGER (LABORATORY DIRECTOR) - Nat B. Dellavalle
B.S., Soil Science 1961, California State Polytechnic University, San Luis Obispo, CA.

Thirty years experience in analytical laboratory operation and management, Brown & Bryant, Inc., Shafter, CA 1964-68; TMT Chemical Co. Inc., Five Points, CA 1968-78; Dellavalle Laboratory, Inc., Fresno, CA 1978-Present.

The Manager has a primary responsibility for laboratory operations. Responsibilities include overseeing laboratory operation, periodic review of analytical results, QA/QC practices and specific analytical results prior to release. He provides consultation/training for laboratory personnel and direct supervision of the Laboratory Supervisor.

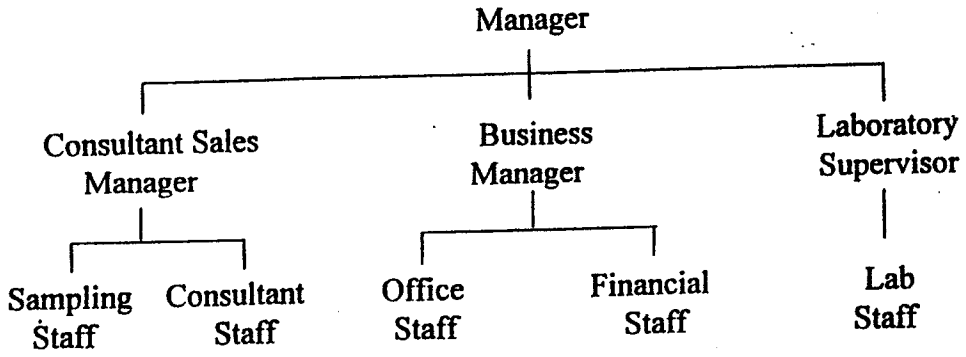
B. LABORATORY SUPERVISOR (PRINCIPAL ANALYST) - Scott Fridlund
B.S., Microbiology/Biochemistry, 1987, California State University Chico; M.S., Agricultural Chemistry, 1992, University of California, Davis.

Nearly four years experience in laboratory operation and analytical chemistry at Division of Agricultural and Natural Resources Analytical Laboratory at the University of California, Davis, CA, 5/90-11/93 and Dellavalle Laboratory, Inc., Fresno, CA, 11/93 to present.

The Laboratory Supervisor is responsible for laboratory organization, maintaining daily production and QA/QC records. He supervises the laboratory staff and provides training. The Supervisor is also responsible for development of procedures, problem solving and analyses as directed and reports to the Manager.

D. CONSULTANT STAFF
B.S. or M.S. degrees in Pomology, Biology, Soil Science, Agronomy or related areas.

Consultants review data, make judgments as to accuracy and write comments or recommendations. Consultants also perform or supervise sampling.



Revised 9/97

4. QA OBJECTIVES FOR MEASURED DATA

Measured data is to be of the type and accuracy appropriate for, and adequate to meet, the needs of the clients.

Specific procedures selected are those that provide results that meet the objectives of the client. Precision and accuracy are to be as good as, or better than, required by the appropriate regulatory agency or professional organization, or where none is available, as established by Dellavalle Laboratory.

5. SAMPLING PROCEDURES

Samples are submitted by clients or are collected by company personnel.

A. Sampling instruction, Attachment 1, are provided to the clients and personnel.

B. Sampling containers of the proper type with proper treatment or preservation are provided to clients and employees. Sterilized bottles treated with sodium thiosulfate are available for bacteriological samples. Containers may be obtained from contracting laboratories when analysis is to be subcontracted. Containers will be as indicated on Attachment 2. Labels are placed on each container, Attachment 5.

C. Laboratory Work Request forms, Attachment 3, are completed by the client when submitting samples or by a consultant when ordering sampling. The following information is included on the form:
   1. Date of receipt
   2. Client name, address & phone number
   3. Sample type
   4. Type of analysis requested
   5. Date of sampling
   6. Sample identification/description
   7. Sampler

E. Transportation of samples, when under direction of the company, will be in ice chests with Blue Ice or other suitable coolant or containers capable of maintaining proper temperature and conditions.

F. Sample Reception - Laboratory Work Request forms are completed as needed. Each sample is assigned a unique sample identification number. The number is used to document the sample in the laboratory log and on records of analysis.

G. Storage will be in a refrigerator specifically dedicated to storage of water and waste water samples. Access to storage is limited to company employees.

H. A daily log is maintained to document reception of samples and completion of analysis. Information includes the following:

1. Sample identification number
2. Client name
3. Consultant
4. Type of material
5. Number of samples in the group
6. Analysis required
7. Date analysis is mailed

6. SAMPLE CUSTODY, HOLDING AND DISPOSAL

The Laboratory Work Request form serves as a chain of custody record. A more detailed form, Attachment 4, is used when a more extensive record is required by the client.

The sample is received by a receptionist, who places it in a sample reception area. A technician reviews the Laboratory Work Request, assigns a unique sample number, places the number on the form and sample container. The technician refers to the Procedures for Sample Receiving Drinking and Waste Water manual (See attachment 2) for proper disposition. The sample is preserved accordingly by a Laboratory Technician. The sample is stored in a 4-6°C refrigerated storage area. Samples are held or preserved according to Table 1060:I in Standard Methods 18th Edition, pg 1-22. The Laboratory Work Request form is delivered to the scheduler.

The scheduler prepares worksheets, Attachment 6, or work assignments and distributes them to laboratory technicians.

Samples are disposed of after recommended/regulatory holding times have expired.

7. CALIBRATION PROCEDURES

Laboratory equipment is calibrated as follows:

A. When in use, analytical balances are inspected and cleaned by technicians and are inspected, cleaned, repaired and calibrated twice per year by a balance repair service. In addition to the repair service, an internal calibration using Class S/S-1 reference weights is performed twice per year.

B. Spectrophotometers, when in use, are calibrated several times daily with analytical standards. The wavelength indicator is calibrated when submitted for repair.

C. The ICP spectrophotometer, when in use, is calibrated several times daily with analytical standards. Wavelengths are peaked each time the analyte is changed.

D. Mechanical diluters, dispensers and pipetters are calibrated volumetrically and gravimetrically quarterly.

8. ANALYTICAL PROCEDURES

Analytical procedures for water and waste water are derived from Standard Methods for the Examination of Water and Waste Water, 18th Edition.

9. ACQUISITION, DATA REDUCTION, VALIDATION AND REPORTING

Data is acquired on worksheets (Attachment 6), printed computer reports or in analysts' journals.

Calculations based upon parameters from each method are used to reduce the acquired data for the reported results.

Results are validated through the use of internal and external check samples, duplicate samples, reagent blanks, internal consistency and reasonableness of the result.

Check samples are discussed in Sections 10 and 11. Checks of internal consistency include:

A. Anion:cation balance
B. TDS:Mass balance
C. Electrical conductivity:Cation balance
D. pH vs. Alkalinity concentration/species

The technician, laboratory supervisor and the consultant evaluate reasonableness of the result based on their knowledge of the sample, history of the site sampled, etc. Results judged unreasonable are rejected.

10. INTERNAL QUALITY CONTROL CHECKS

REPLICATE SAMPLE ANALYSIS - Replicate samples are analyzed with a minimum frequency of ten percent of samples per matrix, per group of samples (samples processed at a single time). If there are fewer than ten samples in a group, at least one duplicate sample per matrix, per group is analyzed. In the event the analyte is not detected in the sample, replicate matrix spike samples are analyzed.

MATRIX SPIKE ANALYSIS - Spiked samples are analyzed with a minimum frequency of ten percent of samples per matrix, per group of samples. If there are less than ten samples in a group, at least one per matrix, per group is analyzed. Recommended practices are to spike the sample with analyte; in a concentration at or near the same level as found in the sample; to the midrange concentration of the appropriate calibration curve; or equal to the Maximum Contaminant Level (MCL) of the analyte.

EXTERNAL REFERENCE OR CONTROL SAMPLE ANALYSIS - Two or more times per year a reference sample. The concentration of the samples are normally within the working range of the method. The samples do not require extensive pretreatment, dilution or concentration prior to analysis. Sources of these samples include, but are not limited to, quality control samples from USEPA, Environmental Research Associates, samples prepared by other laboratories or samples prepared inhouse but from different sources of analyte.

METHOD BLANKS - If a method requires sample pretreatment which is not applied to calibration standards, a method blank is processed along with the samples. Method blanks are analyzed with a minimum frequency of ten percent of the samples per matrix, per batch of samples. If there are less than ten samples in a batch, at least one per matrix per batch is analyzed. The use of method blanks provide a measurement of laboratory contamination.

11. PERFORMANCE AND SYSTEM AUDITS

External check samples are treated as unknown samples. Analysis is reported to the organization providing the samples. Results are compared to values returned by the organization.

Blind duplicate samples are submitted as unknowns and results are checked for agreement.

Internal check samples are submitted and results are checked with established values.

12. PREVENTIVE MAINTENANCE

Balances are checked and cleaned by laboratory personnel daily and twice per year by a balance service. Repair and calibration are performed at that time as needed.

There is no maintenance agreement for the Inductively Coupled Plasma Atomic Emission Spectrophotometer. It is inspected, cleaned and repaired on a regular basis by laboratory personnel.

Hoods are cleaned and serviced at least once per year.

Other laboratory equipment and facilities are cleaned on a regular basis and/or are monitored for performance and are repaired as needed.

13. ASSESSMENT OF PRECISION AND ACCURACY

Internal reference samples are analyzed with each group of samples. Periodically results are analyzed statistically. Based on standard deviations, control limits are established.

External reference samples provided by Environmental Resource Associates are analyzed periodically. Results are compared with certified values and advisory ranges.

External reference samples from EPA, DOHS or other sources are analyzed periodically. Results are reported to the appropriate organization. Upon receipt of analyzed data the laboratory results are evaluated.

14. CORRECTIVE ACTION

When a result is rejected, one or more of the following steps occur:

A. The data is reviewed for calculation or transcription error.
B. The analysis is repeated.
C. Quality of reagents and standards are checked and/or replaced.
D. Instrument calibration/reliability is checked.
E. Technician technique is reviewed.
F. The sample or a replacement sample is submitted to another laboratory.

The source of the error is corrected, or it is determined that it was random, before the result is reported.

15. QUALITY ASSURANCE REPORT

There are no formal quality assurance reports. Quality assurance records are available for review.

16. ADDENDUM FOR SOIL AND PLANT ANALYSIS QUALITY ASSURANCE/QUALITY CONTROL DOCUMENT

Measures taken to assure quality of laboratory results for soil and plant analysis involve the same subjects listed in the Table of Contents. QA/QC methods specific to soil and plant analysis are discussed below. Items not discussed are very similar if not identical to those discussed earlier for water and waste water samples.

A. SAMPLING PROCEDURES

Sampling methods vary based upon substrate and purpose of the analysis. Sampling, in general, is discussed in H.M. Reisenauer. 1983. Soil and Plant Tissue Testing in California. Bull. #1879. (Rev. Ed.). Div. of Ag. Sci. University of California, Berkeley, CA. Guidelines are not available for all situations, in which case, sampling methods are designed by a staff soil or plant scientist. Soil and plant sampling guidelines provided clients are in Attachment 7.

B. ANALYTICAL PROCEDURES

Analytical procedures for soil and plant analysis are derived from those referenced in Soil and Plant Tissue Testing in California. Additional references are:

Chapman, H.D., and P.K. Pratt. 1961. Methods of Analysis for Soils, Plants, and Waters. University of California, Berkeley, CA.

Miller, R.O., and J. Kotuby-Amacher. 1994. Summary of Western States Sample Exchange Program. University of California, Davis, CA; Utah State University, Utah.

Page, A.L. (ed.). 1982. Methods of Soil Analysis Part 2. 2nd. ed. Agronomy 9. American Society of Agronomy. Madison, WI.

Rible, J.M. and J. Quick. 1960. Water, Soil, Plant Tissue: Tentative Methods of Analysis for Diagnostic Purposes. Analytical Extension Laboratory. Agricultural Extension Service. University of California, Davis, CA.

Soil and Plant Analysis Council, Inc. 1992. Handbook on Reference Methods for Soil Analysis, Soil and Plant Analysis Council, Inc. Athens, GA.

In addition, methods are taken from articles published in the Agronomy Journal American Society of Agronomy. Madison, WI.; the Proceedings of the Soil Science Society of America. SSSA. Madison, WI; Communications in Soil Science and Plant Analysis. Marcel Dekker, Inc. NY, NY; and the Journal of Plant Nutrition. Marcel Dekker, Inc. NY, NY.

C. INTERNAL QUALITY CONTROL CHECKS

- External reference control for soil and plant samples are obtained from the Western States Agricultural Exchange Program administered by the Utah State University and the University of California at Davis.

ATTACHMENTS

1. Sampling Instructions
2. Procedures for Sample Receiving Drinking and Waste Water
3. Laboratory Request Form
4. Chain of Custody
5. Label Example
6. Analytical Worksheets
7. Soil & Plant Analysis Sampling Instructions

ATTACHMENT 1

DELLAVALLE®
Laboratory, Inc.
Chemists and Consultants
McKinley, Suite 110 • Fresno, CA 93728
(209) 233-6129 • (800) 228-9896

COLIFORM INSTRUCTIONS

- Sterilized bottles are available at no charge. For regulatory purposes samples must be collected in autoclaved-bottles. Each bottle contains a very small amount of sodium thiosulfate (chlorine inhibitor).

DO NOT open sterile bottle until sample is to be taken. DO NOT sample from leaking taps.
Outside: Choose the cleanest tap available; one that is frequently used and at least 1 1/2 feet above the ground. Avoid sampling sites that have dirty taps, are surrounded by excessive foliage or might be contaminated by humans or animals. Never sample from a hose.
Inside: Choose a tap from a service pipe directly connected to the water main or well. DO NOT sample from restroom taps, drinking fountains or taps with individual treatment unit.

1. Remove screen from faucet.
2. Let tap or well run for several minutes to clear the system.
3. Open bottle and fill leaving a small air space at the top of the bottle.
   a. DO NOT place bottle cap on ground or anywhere it can be contaminated.
   b. DO NOT TOUCH the inside of bottle with the tap or hand.
   c. DO NOT let water flow over your hands or objects and then into bottle.
   d. DO NOT rinse out sampling bottle prior to filling.
4. Replace the cap and immediately place in container with coolant and transport to lab.
5. Sample is to arrive at the lab immediately after sampling as the lab needs time to initialize the test and testing MUST begin within 24 hours of sampling. Completely fill out the information on the label.

Verbal results can be expected in approximately four to seven working days,

DBCP INSTRUCTIONS

Sampling containers are available from the laboratory at no cost. Each bottle contains a very small amount of sodium thiosulfate (chlorine inhibitor).

1. Let water run for approximately 10 minutes for temperature to stablize.
2. DO NOT rinse glass container with water. Fill completely leaving NO airspace.
3. Replace lid and refrigerate.
4. Deliver sample to laboratory as soon as possible.

Verbal results can be expected in approximately ten working days.

PROCEDURES FOR SAMPLE RECEIVING DRINKING AND WASTE WATER

All drinking and waste water samples must be kept cold in route to laboratory as well as refrigerated when received at the laboratory. Strict adherence to sample collection, preservation and holding times is a MUST.

When the sample(s) are received:

1. Verify that samples are in appropriate containers* for the analysis requested.
2. Verify that holding times* are not exceeded.
3. Sign the Chain of Custody, enter date and time of receipt;
4. Assign a unique identification number (Lab No.) generated by the computer;
5. Mark the Laboratory Work Request form with the Lab No. and the bottles appropriately;
6. Refrigerate.

If sample must be preserved:

- Notify Laboratory Supervisor or Lead Laboratory Technician;
- Refrigerate after preservation.

*See attached for Sample Preservation, Handling and Collection.

sampling:cpeg

SAMPLING REQUIREMENTS

DRINKING WATER:

TEST, VOLUME & CONTAINER	PRESERVATION	SAMPLING PROCEDURE	HOLDING TIME/ COMMENTS*
General Mineral: 1 liter plastic	Refrigerate	Completely fill	pH: 2 hrs
General Physical: 1-500 ml glass	Refrigerate	Completely fill	Must be completed within 24 hrs.
Coliform: 1-6 oz. square plastic	Sterilized, sodium thiosulfate, refrigerate	See procedure	To meet time constraints, take sample after 10 a.m. & submit the same day.
Inorganic Chemical Scan: 1 liter plastic & 500 ml plastic w/NaOH (CN)	Refrigerate	Completely fill	NO_3-N must be done within 48 hrs.
Cyanide: 1-500 ml plastic	Sodium Hydroxide	Completely fill	
Asbestos: 1 liter plastic or glass, 48 hours holding time.	Refrigerate	See procedure	See Scheduler. Testing must start within 24 hours.
Radioactivity:			
Gross Alpha: 1 liter plastic	Refrigerate	Completely fill	Acidified after sampling
Total Radium: 1 liter plastic	Refrigerate	Completely fill	Acidified after sampling
Uranium: 1 liter plastic	Refrigerate	Completely fill	Acidified after sampling
Synthetic Organic Chemicals (SOC):			
EPA 504: 1-500 ml amber glass	Refrigerate	See procedure	
EPA 505: Request EPA 525.2 and sample accordingly (see next page).			

*Holding Time/Comments - Length of time lab must begin test/submission time and pertinent information regarding sampling. For Internal Use Only.

sampling:cpeg9/9

SAMPLING REQUIREMENTS

DRINKING WATER (continued):

TEST, VOLUME & CONTAINER	PRESERVATION	SAMPLING PROCEDURE	HOLDING TIME/ COMMENTS*
Synthetic Organic Chemicals (SOC) (continued):			
EPA 507:			
Request EPA 525.2 and sample accordingly.			
EPA 508:			
1 liter amber glass	Refrigerate	Completely fill	
EPA 515.1:			
1 liter amber glass	Refrigerate	Completely fill	
EPA 525.2:			
1 liter amber glass	Refrigerate	Completely fill	
EPA 531.1:			
1-100 ml amber glass	Monochloroacetic acid, refrigerate	Completely fill	
EPA 547:			
1 liter amber glass	2 mg/l sodium thiosulfate, refrigerate	Completely fill	
EPA 548:			
1 liter amber glass	Refrigerate	Completely fill	
EPA 549:			
1-500 ml amber plastic	1 ml sodium thiosulfate, refrigerate	Completely fill	
EPA 513 or 1613:			
1 liter amber glass	80 mg/l sodium thiosulfate, refrigerate	Completely fill	
EPA 632:			
1 liter amber glass	Refrigerate	Completely fill	7 Days
Volatile Organic Chemicals (VOC):			
EPA 502.2:			
1 set VOA plus Trip Blank	Refrigerate	See procedure	

*Holding Time/Comments - Length of time lab must begin test/submission time and pertinent information regarding sampling. For Internal Use Only.

sampling:cpeg9/97

SAMPLING REQUIREMENTS

WASTE WATER:

TEST, VOLUME & CONTAINER	PRESERVATION	SAMPLING PROCEDURE	HOLDING TIME/ COMMENTS*
BOD: 1 liter plastic	Refrigerate	Completely fill	On Friday submit before 10:30 a.m. to meet time constraints (48 hrs).
COD: 1 liter plastic	Sulfuric Acid, refrigerate	Completely fill	
TOC: 1 liter amber glass	Sulfuric Acid, refrigerate	Completely fill	
Inorganic Chemicals: 1 liter plastic	Refrigerate	Completely fill	NO_3-N must be done within 48 hrs.

*Holding Time/Comments - Length of time lab must begin test/submission time and pertinent information regarding sampling. For Internal Use Only.

sampling:cpeg9/97

TABLE 1060:I. SUMMARY OF SPECIAL SAMPLING OR HANDLING REQUIREMENTS*

Determination	Container	Minimum Sample Size *mL*	Preservation	Maximum Storage Recommended/ Regulatory†
...ity	P, G(B)	100	Refrigerate	24 h/14 d
Alkalinity	P, G	200	Refrigerate	24 h/14 d
BOD	P, G	1000	Refrigerate	6 h/48 h
Boron	P	100	None required	28 d/6 months
Bromide	P, G	—	None required	28 d/28 d
Carbon, organic, total	G	100	Analyze immediately; or refrigerate and add HCl to pH<2	7 d/28 d
Carbon dioxide	P, G	100	Analyze immediately	stat/N.S.
COD	P, G	100	Analyze as soon as possible, or add H_2SO_4 to pH<2; refrigerate	7 d/28 d
Chlorine, residual	P, G	500	Analyze immediately	0.5 h/stat
Chlorine dioxide	P, G	500	Analyze immediately	0.5 h/N.S.
Chlorophyll	P, G	500	30 d in dark	30 d/N.S.
Color	P, G	500	Refrigerate	48 h/48 h
Conductivity	P, G	500	Refrigerate	28 d/28 d
Cyanide:				
Total	P, G	500	Add NaOH to pH>12, refrigerate in dark	24 h/14 d; 24 h if sulfide present
Amenable to chlorination	P, G	500	Add 100 mg $Na_2S_2O_3$/L	stat/14 d; 24 h if sulfide present
Fluoride	P	300	None required	28 d/28 d
Hardness	P, G	100	Add HNO_3 to pH<2	6 months/6 months
Iodine	P, G	500	Analyze immediately	0.5 h/N.S.
Metals, general	P(A), G(A)	—	For dissolved metals filter immediately, add HNO_3 to pH<2	6 months/6 months
Chromium VI	P(A), G(A)	300	Refrigerate	24 h/24 h
Copper by colorimetry*				
Mercury	P(A), G(A)	500	Add HNO_3 to pH<2, 4°C, refrigerate	28 d/28 d
N...gen:				
...nonia	P, G	500	Analyze as soon as possible or add H_2SO_4 to pH<2, refrigerate	7 d/28 d
...trate	P, G	100	Analyze as soon as possible or refrigerate	48 h/48 h (28 d for chlorinated samples)
...rate + nitrite	P, G	200	Add H_2SO_4 to pH<2, refrigerate	none/28 d
Nitrite	P, G	100	Analyze as soon as possible or refrigerate	none/48 h
Organic, Kjeldahl	P, G	500	Refrigerate; add H_2SO_4 to pH<2	7 d/28 d
Odor	G	500	Analyze as soon as possible; refrigerate	6 h/N.S.
Oil and grease	G, wide-mouth calibrated	1000	Add H_2SO_4 to pH<2, refrigerate	28 d/28 d
Organic compounds:				
Pesticides	G(S), TFE-lined cap	—	Refrigerate; add 1000 mg ascorbic acid/L if residual chlorine present	7 d/7 d until extraction; 40 d after extraction
Phenols	P, G	500	Refrigerate, add H_2SO_4 to pH<2	*/28 d
Purgeables by purge and trap	G, TFE-lined cap	50	Refrigerate; add HCl to pH < 2; add 1000 mg ascorbic acid/L if residual chlorine present	7 d/14 d
Oxygen, dissolved:	G, BOD bottle	300		
Electrode			Analyze immediately	0.5 h/stat
Winkler			Titration may be delayed after acidification	8 h/8 h
Ozone	G	1000	Analyze immediately	0.5 h/N.S.
pH	P, G	—	Analyze immediately	2 h/stat
Phosphate	G(A)	100	For dissolved phosphate filter immediately; refrigerate	48 h/N.S.
Salinity	G, wax seal	240	Analyze immediately or use wax seal	6 months/N.S.
Silica	P	—	Refrigerate, do not freeze	28 d/28 d
Sludge digester gas	G, gas bottle	—	—	N.S.
Solids	P, G	—	Refrigerate	7 d/2–7 d; see cited reference
Sulfate	P, G	—	Refrigerate	28 d/28 d
Sulfide	P, G	100	Refrigerate; add 4 drops 2*N* zinc acetate/100 mL; add NaOH to pH>9	28 d/7 d
	G	500	Analyze as soon as possible; refrigerate	24 h/N.S.
...perature Temperature	P, G	—	Analyze immediately	stat/stat
...idity - Turbidity	P, G	—	Analyze same day; store in dark up to 24 h, refrigerate	24 h/48 h

...text for additional details. For determinations not listed, use glass or plastic containers; preferably refrigerate during storage and analyze as soon as possible. Refrigerate = storage at 4°C, in the dark. P = plastic (polyethylene or equivalent); G = glass; G(A) or P(A) = rinsed with 1 + 1 HNO_3; G(B) = glass, borosilicate; G(S) = glass, rinsed with organic solvents; N.S. = not stated in cited reference; stat = no storage allowed; analyze immediately.

† Environmental Protection Agency, Rules and Regulations, *Federal Register* 49: No. 209, October 26, 1984. See this citation for possible differences regarding container and preservation requirements.

ATTACHMENT 3

LABORATORY WORK REQUEST

DELLAVALLE Laboratory, Inc.
Chemists and Consultants
1910 W. McKinley, Suite 110
Fresno, CA 93728

LAB NUMBER _____ Logged By

DATE _____

BILL TO: Acc. No. Cons.

_____
Firm Name

_____
Address

_____
City, State Zip

_____
Telephone

SUBMITTED BY _____

RANCH _____

NUMBER OF SAMPLES _____

MATERIAL SUBMITTED _____
(Soil, Water, Petiole, Leaf, etc.)

ANALYSIS NEEDED _____

_____

_____

ID CROP: _____ _____
Present Stage of Growth

_____
Intended

PURCHASE ORDER NO. _____

RESULTS NEEDED BY _____

COPY OF REPORT TO: (If different than billing address)

_____
Firm Name

_____
Address

_____
City, State, Zip

_____
Telephone

Invoice # _____
Invoice Date _____
Sampling Requested _____
To be Sampled _____
Observations and Comments:

Sampled by _____

DATE SAMPLED _____ TIME SAMPLED _____

DESCRIPTION OF SAMPLES

1. _____
2. _____
3. _____
4. _____
5. _____
6. _____
7. _____
8. _____
9. _____
10. _____
11. _____
12. _____
13. _____
14. _____
15. _____
16. _____
17. _____
18. _____
19. _____
20. _____

LIST ADDITIONAL SAMPLES, HISTORY OR COMMENTS ON REVERSE.

I guarantee that as the client, or on behalf of client named, I have the authority to contract the above requested services. Should it be found that I do not have such authority, I agree to be personally liable for all costs and, if there should be action against me for this breach, reasonable attorneys' fees. It is understood that payment is expected to be cash with samples unless terms have been previously arranged. Terms are net 30 days; overdue accounts will be charged a liquidated damage fee of 2% per month (annually 24%) or $5.00 per month whichever is greater. If default is made in the payment of the account, I agree to pay all costs of collection, including reasonable attorneys' fees and court costs.

AMT. PAID	REC. BY	CK. #	DATE

_____
(Signature)

DELLAVALLE LABORATORY, INC. 1910 W. McKinley Avenue, Suite 110 • Fresno, CA 93728

ATTACHMENT 3.1

LABORATORY WORK REQUEST/DRINKING WATER

NUMBER _____ Logged By _____

DATE _____

BILL TO: Acct No _____ Cons _____

_____
Firm Name

_____
Address

_____
City, State Zip

_____ _____
Telephone Fax

SUBMITTED BY _____

RANCH _____

No. of Samples _____ MATERIAL _____

Date Sampled _____ Time Sampled _____

Sampled By _____

DESCRIPTION OF SAMPLES

1. _____
2. _____
3. _____
4. _____
5. _____
6. _____
7. _____
8. _____
9. _____
10. _____

Invoicing Information:

Shipping
$_____ In
$_____ Out

Amt Paid _____ Rec By _____ Check # _____ Date _____

_____ _____
Purchase Order No. Results Needed By

COPY TO: _____

Check boxes for test required:

VOC (Volatile Organic Chemicals):
[ ] 502.2 OR 524.2: 1 set VOA & Trip Blank

SOC (Synthetic Organic Chemicals):
[ ] 504: 500 ml amber glass
[ ] 508: 1 liter amber glass
[ ] 515.1: 1 liter amber glass
[ ] 525.2 (505, 507): 1 liter amber glass
[ ] 531.1: 100 ml amber glass w/monochloracetic acid
[ ] 547: 1 liter amber glass w/2mg/l NaThio
[ ] 548: 1 liter amber glass
[ ] 549: 500 ml amber plastic w/4% solution NaThio
[ ] 632: 1 liter amber glass
[ ] 1613: 1 liter amber glass w/80 mg/l NaThio

Inorganic Chemicals:
[ ] Inorganic Scan: 1 liter plastic & 500 ml plastic w/NaOH
[ ] Cyanide: 500 ml plastic w/NaOH
[ ] NO_3, NO_2: 1 ag suit bottle
[ ] Asbestos: **SPECIAL, Call Scheduler <u>before</u> Sampling:**
[ ] First Draw Cu, Pb: 1 liter plastic

Radiological: 1 liter plastic each isotopic element
[ ] Gross Alpha [ ] Gross Alpha & Beta
[ ] Uranium [ ] Total Radium

Other Tests:
[ ] Realtor Package: NO_3, DBCP, Coliform
[ ] General Mineral: 1 liter plastic
[ ] General Physical: 500 ml glass
[ ] Bacteriological: 6 oz sterilized plastic w/NaThio
[ ] T. Coliform [ ] Coliform/fecal [ ] E. coli
[ ] Household: 1 liter plastic
[ ] Ag Suit
[ ] Other, Specify _____

Special Instructions:
Preservation: [Y] or [N] State Forms: [Y] or [N]

I guarantee that as the client, or on behalf of client named, I have the authority to contract the above requested services. Should it be found that I do not have such authority, I agree to be personally liable for all costs and, if there should be action against me for this breach, reasonable attorneys' fees. It is understood that payment is expected to be cash with samples unless terms have been previously arranged. Terms are net 30 days; overdue accounts will be charged a liquidated damage fee of 2% per month (annually 24%) or $5.00 per month whichever is greater.

If payment is not made when due and a legitimate dispute exists concerning the product or services of Dellavalle Laboratory, Inc., it will be submitted to mediation under the Rules and Procedures of Creative Alternative to Litigation, Inc. (*cal*). If the dispute is not resolved in mediation, then the dispute will be submitted to binding arbitration through *cal* under its Rules and Procedures. The parties will equally bear the costs of mediation/arbitration. If, however, the mediator declares that no legitimate dispute exists, then debtor will pay all mediation and arbitration costs, and in the event of arbitration, reasonable attorneys' fees of Dellavalle Laboratory.

_____
Signature

ATTACHMENT 4

DELLAVALLE LABORATORY, INC.
1910 W. McKinley, Suite 110
Fresno, CA 93728

CHAIN OF CUSTODY

To: _____ P.O. # _____

_____ Requested by: _____

_____ Date/Time: _____

Lab #	SAMPLE IDENTIFICATION	SAMPLE TYPE	SAMPLE DATE/TIME	ANALYSIS

Sampled By: _____

Relinquished By	Affiliation	Date / Time
Received By	Affiliation	Date / Time
Relinquished By	Affiliation	Date / Time
Received By	Affiliation	Date / Time
Relinquished By	Affiliation	Date / Time
Received By	Affiliation	Date / Time
Relinquished By	Affiliation	Date / Time
Received By	Affiliation	Date / Time

ATTACHMENT 5

Lab No. Sample Date_____ Time _____

Sampled By_____

Sample Description _____

Client _____

Analysis Required: Acidified: HNO_3 H_2SO_4 HCL

Dellavalle Laboratory, Inc.
1910 W. McKinley Ave., #110, Fresno 93728 • 800 228-9896 • 559 233-6129

ppm 23.00 = Na meq/l

Domestic Waste, Calculate EC to umhos

	Round to		0.1	Ag Only 0.01 mmhos	1 umhos	0.1 mg/l	0.1 mg/l	0.1 mg/l	0.1 mg/l	0.1 mg/l	0.01 mg/l	0.1 mg/l	0.1 mg/l	0.1 mg/l		
	Lab No.	Type	pH	EC	EC	B	Ca	Mg	Na	Fe	Mn	Zn	Cu	K		
1																
2																
3																
4																
5																
6																
7																
8																
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22																
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24																
25																
26																
27																
28																
29																
30																

Date:
Completed

General Mineral

Sample	Total Alkalinity as CaCO3 (mg/l) 0.1	Bicarbonate HCO3 (mg/l) 0.1	Carbonate CO3 (mg/l) 0.1	Hydroxide OH- (mg/l) 0.1	Surfactants MBAS (mg/l) 0.1	Residue Filterable TDS (mg/l) 1.0	Total Hardness as CaCO3 (mg/l) 0.1	Sulfate SO4 (mg/l) 1.0	Chloride Cl (mg/l) 0.1	pH 0.01	EC (umhos/cm) 1.0	Ca (mg/l) 0.1	Mg (mg/l) 0.1	Na (mg/l) 0.1	Fe (mg/l) 0.1	Mn (mg/l) 0.01	Zn (mg/l) 0.1	Cu (mg/l) 0.1	L.I. Calculated Corrosivity 0.1

Light shaded cells are for Household Analysis.

General Physical

Sample	NO3-N	NO3 Nitrate (mg/l) 1.0	NO2-N	NO2 Nitrite (mg/l) 1.0	Fluoride F (mg/l) 0.1		Color (APHA) 1.0	Odor (TON) 1.0	Turbidity (NTU) 1.0										

Wastewater Worksheet

	Sample	pH	EC (umhos/cm)	TN (mg/l)	NO_3-N (mg/l)	NH_4-N (mg/l)	Org-N (mg/l)	TKN (mg/l)	Acidity (mg/l)	Alkali (mg/l)
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										

	Sample	TDS (mg/l)	IDS (mg/l)	VDS (mg/l)	TSS (mg/l)	TS (mg/l)	SS (mg/l)	COD (mg/l)	BOD* (mg/l)	TOC* (mg/l)
1										
2										
3										
6										
7										
8										
9										
10										

* By Laborato

	Sample	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)	TP (mg/l)				
1										
2										
3										
4										
5										
6										
7										
8										

ATTACHMENT 6.2

Date	TS (mg/l)								
Group									
Analyst									
	50 ml or							Diff	
	Sample		First	Second	Thrid	Fourth	Fifth	final dry	
	aliquot	Tare	Tare+samp	Tare+samp	Tare+samp	Tare+samp	Tare+samp	weight	
	Size	Weight	dry weight	dry weight	dry weight	dry weight	dry weight	- tare wt	TS
Lab ID	(ml)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(mg/l)
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

Calculations when weights are in milligrams:

mg Total Solids/L = ((A - B)-(C-D)) * 1000/mL sample

where:

A = final weight of dried residue + dish. mg

B= weight of dish.mg

1000 = converts mL to L

C = final flask weight and residue for the blank (mg)

D = tared flask weight for blank (mg)

Calculation when weights are in grams:

mg Total Solids/L = ((A - B)-(C-D)) * 1000 * 1000/mL sample

where:

A = final flask weight and residue for sample (g)

B = tared flask weight for sample (g)

C = final flask weight and residue for the blank (g)

D = tared flask weight for blank (g)

First 1000 = converts mL to L

Second 1000 converts from g to mg.

Date			TDS (mg/l)							
Group										
Analyst										
		50 ml							Diff	
		Sample		First	Second	Thrid	Fourth	Fifth	final dry	
		aliquot	Tare	Tare+samp	Tare+samp	Tare+samp	Tare+samp	Tare+samp	weight	
		Size	Weight	dry weight	dry weight	dry weight	dry weight	dry weight	- tare wt	TDS
	Lab ID	(ml)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg)	(mg/l)
1										
2										
3										
4										
5										
6										
7										
8										
9										
10										
11										
12										
13										
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
Calculations:										
		mg Total Dissolved Solids/L = (A - B) * 1000/mL sample								
	where:									
		A = final weight of dried residue + dish, mg								
		B= weight of dish,mg								
		1000 = converts mL to L								
Calculation when weights are in grams:										
		mg Total Dissolved Solids/L = (A - B) * 1000 * 1000/mL sample								
	where:									
		A = flask weight and residue for sample (mg)								
		B = tared flask weight for sample (mg)								
		C = flask weight and residue for the blank (mg)								
		D = tared flask weight for blank (mg)								
		First 1000 = converts mL to L								
		Second 1000 converts from g to mg.								

Date			TSS (mg/l)						
Group									
Analyst									
	50 ml or							Diff	
	Sample		First	Second	Thrid	Fourth	Fifth	final dry	
	aliquot	Tare	Tare+samp	Tare+samp	Tare+samp	Tare+samp	Tare+samp	weight	
	Size	Weight	dry weight	dry weight	dry weight	dry weight	dry weight	- tare wt	TSS
Lab ID	(ml)	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(mg/l)
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
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16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

Calculations when weights are in milligrams:

mg Total Suspended Solids/L = ((A - B)-(C-D)) * 1000/mL sample

where:

A = final weight of dried residue + dish. mg

B= weight of dish.mg

1000 = converts mL to L

C = final flask weight and residue for the blank (mg)

D = tared flask weight for blank (mg)

Calculation when weights are in grams:

mg Total Suspended Solids/L = ((A - B)-(C-D)) * 1000 * 1000/mL sample

where:

A = final flask weight and residue for sample (g)

B = tared flask weight for sample (g)

C = final flask weight and residue for the blank (g)

D = tared flask weight for blank (g)

First 1000 = converts mL to L

Second 1000 converts from g to mg.

Date		Oil and Grease (mg/l)						
Group								
Analyst								
						Net		
		Sample	Tare	Tare +	Net	residue -	Oil and	
		Size	Weight	Residue	Residue	blank	Grease	
	Lab ID	(ml)	(g)	(g)	(g)	(g)	(mg/l)	
1	Blank							
2								
3								
4								
5								
6								
7								
8								
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16								
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18								
19								
20								
21								
22								
23								
24								
25								
26								
27								
28								
29								
30								
Calculations								
	mg oil and grease/L = ((A - B) - (C - D)) * 1000/mL sample							
where:								
	A = flask weight and residue for sample (mg)				C = flask weight and residue for the blank (mg)			
	B = tared flask weight for sample (mg)				D = tared flask weight for blank (mg)			
	1000 = converts mL to L							
Calculation when weights are in grams:								
mg oil and grease/L = ((A - B) - (C - D)) * 1000* 1000/mL sample								
where:								
	A = flask weight and residue for sample (mg)				C = flask weight and residue for the blank (mg)			
	B = tared flask weight for sample (mg)				D = tared flask weight for blank (mg)			
	First 1000 = converts mL to L							
	Second 1000 converts from g to mg.							

Sample	Sample size (ml)	H2SO4 Phenol	H2SO4 Bromocesol Green	AgNO3 Pot Chr.						
Blk										
		Acid (N)	Acid (N)	AgNO3 (N)	——————meq/l——————			——————mg/l——————		
Sample	Sample size (ml)	H2SO4 Phenol	H2SO4 Bromocesol Green	AgNO3 Pot Chr.	(CO3) "P"	(CO3+ HCO3) "T"	(Cl) "Cl"	(CO3)	(CO3+ HCO3).	(Cl)
1										
2										
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5										
6										
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27										
28										
29										
30										
Calculations:										
"P. (CO3)", (meq/l)			=((ml H2SO4 to reach ph 8.3 - ml H2SO4 to reach pH 8.3 for blk)*Normaity of H2SO4*1000/ml of sample)							
"T. (CO3 -HCO3)", (meq/l)			=((ml H2SO4 to reach pH 8.3 + ml H2SO4 to reach pH 4.5) -(ml H2SO4 to reach pH 8.3 +ml H2SO4 to reach pH 4.5 for blk)*Normaity of H2SO4*1000/ml of sample)							
Cl. (meq/l)			=(ml ofAgNO3 to reach a reddish-brown endpoint of the same intensity and color as the blank- ml of AgNO3 for blk) * normality of AgNO3 * 1000/ ml of sample)							
CO3. (mg/l)			=CO3 (meq/l)*30							
CO3 - HCO3. (mg/l)			=CO3 + HCO3 (meq/l)*50							
Cl. (mg/l)			=Cl (meq/l)*35.45							

Sulfate

Date analyzed:

Analyst:

						Instrument	Calc	Calc	As
				Extract		Reading	Blank	SO4	SO4-S
	Group #	Lab #	Weight (g)	Vol (ml)	Dilution	400 nm	Correction	ppm	ppm
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
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32									
33									
34									
35									
36									

Std ppm		*Conc.*	**Calculations using standanrd protocol.**		
0.0			*Soil:*	*Water :*	
5.0			SO4-S mg/kg=	SO4 mg/l =	
10.0			6.66 x reading x dilution	4 x reading x dilution	
15.0					
20.0			*Plant tissue:*		
30.0			SO4-S mg/kg =		
			133.2 x reading x dilution		

ATTACHMENT 7.1

DELLAVALLE®
Laboratory, Inc.
Chemists and Consultants
McKinley, Suite 110 • Fresno, CA 93728
(209) 233-6129 • (800) 228-9696

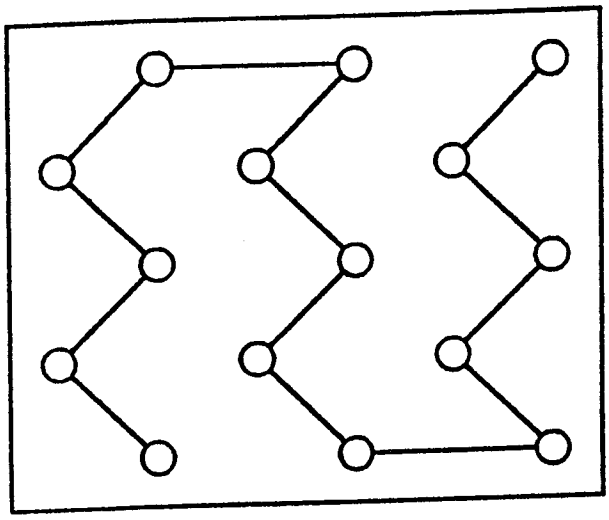
GENERAL NEMATODE SAMPLING GUIDELINES

When sampling a fallow field for nematodes, a minimum of one composite sample for 10 acres should be taken. Each sample consists of about 12-15 subsamples taken from a depth of 6 inches to 24 inches. Use a sampling tube with about a one-inch diameter so sample size will not be too large. Discard the top 6 inches of soil, as it is not needed. When sampling, run a pattern similar to the one below. Be sure to include any soil differences, especially sandy areas, even if it means deviating some from the pattern. Also, if there are plants or weeds in various spots of the field, be sure to sample from those areas. There may be nematodes living and reproducing in those areas. It may be of value to collect a separate sample from such areas. Put soil in airtight plastic bags and keep cool. Refrigerate if storing before shipping. Do not freeze the soil.

When sampling a field with a growing crop, collect soil cores near plants at the edges of weak areas. From 24 inch long cores, collect moist soil containing roots. Include as many roots as possible.

Do not use these sampling methods for cysts of the cyst nematode or for Ditylenchus nematodes.

SUGGESTED COLLECTION PATTERN



SHIPPING SAMPLES: Samples are to be packed in plastic-lined bags or plastic bags. The bags should be placed in a container so that soil will not spill if the package is damaged. A sturdy carton lined with a four ml plastic bag will do. For out of state sample, the carton should be labeled "Soil Samples for Analysis Do Not Sterilize. To be opened only in the presence of an official agricultural inspector."

You may ship samples to us via Greyhound, UPS, US mail or other common carrier. Samples should be maintained cool and moist if nematodes are to survive for detection.

Attachment F

ATTACHMENT F

Example Data Review Checklist

Analyte	Sample #	Sample Date	Test Date	Criteria	Test MDL	Pass/Fail
Acrolien				**2.641 ug/L**		
Copper				**.0017 mg/L.**		
Sulfate				**.0516 mg/L.**		

Signed: _____

Woodbridge Irrigation District

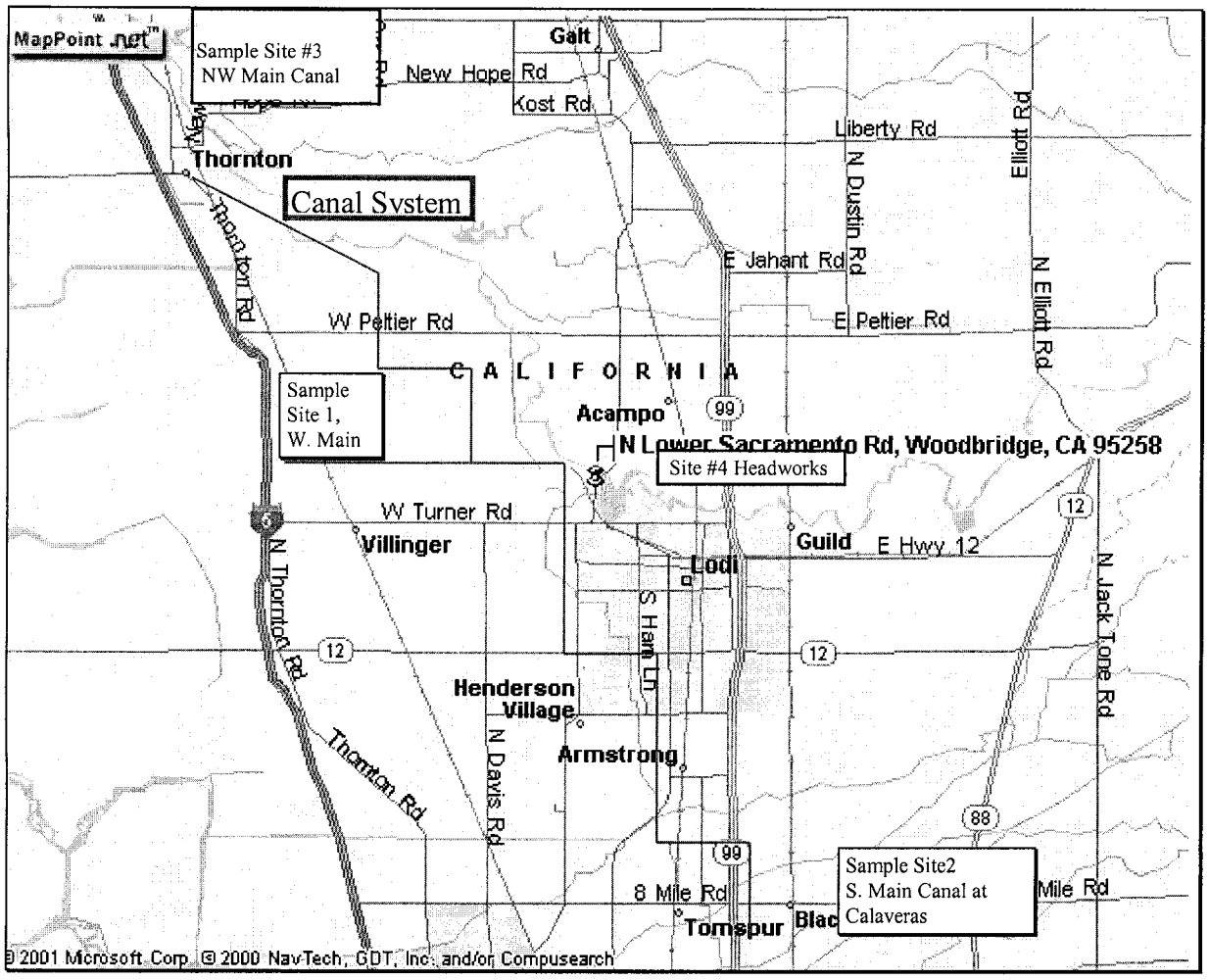
Example Field Audit Checklist

Item:	**Check One**
1. Possess and Understand Field QAPP Manual	
2. Choose the sample points based on locations in figure 3-1 of QAPP Manual appropriate for the application of copper sulfate, acrolein.	
3. Choose the appropriate number of samples according to the QAPP.	
4. Select the appropriate container for samples according to the QAPP.	
5. Fill out sample label and affix to container.	
6. Fill out Field Data Sheet, make field notes to show any reportable conditions. At discharge point and return canal water to receiving water, note any conditions such as color, smell, dead fish, decaying plant material.	
7. Have appropriate safety gear and follow the WID QAPP Health and Safety Plan.	
8. Individual samples shall be placed in plastic bag with cushioning material kept around sample and placed in an insulated, hard plastic cooler, and sealed with tape and chain of custody seals chilled to 4 Degrees C.	
9. Water temperature shall be recorded with a thermometer and noted on the field data sheet.	
10. Sampler shall fill out the Chain of Custody Form and arrange notification and delivery to lab. Samples shall be kept chilled to 4 Degrees C. until shipment.	
11. Field Coordinator (James Shults) shall review and keep a file of test results and verify whether samples passed or failed MDL acceptance standards.	
12. Field Coordinator will immediately notify California Regional Water Quality Control Board of any failure of any test sample.	

Figure 3.1

Map

Figure 3.1 Study Area, and Sample Sites



Sample Sites:

1. **The West Main Canal sample point #1 discharges into Delta sloughs and water ways at this point.**
2. **The South Main Canal sample point #3 at Calavaras discharges into the Calaveras at this point.**
3. **The Northwest Main Canal sample point #4 discharges into Beaver Slough at this point.**
4. **Main Canal Diversion Headgates**

Appendix C

Risk Management Plan Exemption

COUNTY OF SAN JOAQUIN
OFFICE OF EMERGENCY SERVICES
ROOM 610, COURTHOUSE
222 EAST WEBER AVENUE
STOCKTON, CALIFORNIA 95202
TELEPHONE (209) 468-3962
HAZARDOUS MATERIALS DIVISION (209) 468-3969

RONALD E. BALDWIN
DIRECTOR OF
EMERGENCY OPERATIONS

July 13, 2000

ATTN JAMES SHULTS
WOODBRIDGE IRRIGATION DISTRICT
18777 N LOWER SACRAMENTO RD
WOODBRIDGE, CA 95258-9122

SUBJECT: RISK MANAGEMENT PLAN EXEMPTION

Fixed facilities in San Joaquin County which handle Regulated Substances may be exempt from the requirements of the Risk Management Plan (RMP) if the Administering Agency determines that the likelihood of an accidental release is remote.

Woodbridge Irrigation District, located at 18777 N. Lower Sacramento Rd., is exempt from the requirements of the Federal RMP and CalARP programs under the category indicated below:

___ The facility has eliminated all Regulated Substances.

___ Upon a written finding by this office the facility does not pose a significant likelihood for an accidental release risk.

___ The facility has reduced quantities below the Threshold Quantity.

_X_ The facility does not store quantities at or above the Threshold Quantity. Note: As per inspection on September 9, 1999, the inventory of acrolein was reduced to 370 lbs. which is below the Federal TQ of 5,000 lbs. and CalARP TQ of 500 lbs.

Please be advised that in the future should your inventories exceed the Threshold Quantities, a notification to this office will be required.

If you have any questions or need additional clarification of any of the categories described in this letter, please contact Art Bentley Jr. at (209) 468-3969.

SAN JOAQUIN COUNTY OFFICE OF EMERGENCY SERVICES
RISK MANAGEMENT PROGRAM

Appendix D

Laboratory Analytical Data for Water Samples

DELLAVALLE®
Laboratory, Inc.
Chemists and Consultants

July 7, 2003

Andy Christensen
Woodbridge Irrigation Dist #11203
18777 N Lower Sacramento Rd
Woodbridge, CA 95242

Re: Lab No 67754

Dear Andy:

Attached are the results of water samples submitted for sulfate, copper, Acrolein and Glyphosate.

Analyte	Result
SO_4	2.1 mg/l
Cu	<0.01 mg/l
Glyphosate	ND
Acrolein	<PQL

ND = Non-Detected
PQL = Below Quality Control Limit

Please review and if you should have any questions, please call.

Sincerely,

Hugh A. Rathbun, CCA, CPAg/SS
Consultant Sales Manager

HAR:mc

Enclosures

DELLAVALLE®
Laboratory, Inc.
Chemists and Consultants

July 7, 2003

Andy Christensen
Woodbridge Irrigation Dist #11203
18777 N Lower Sacramento Rd
Woodbridge, CA 95242

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Cu	<0.01 mg/l
Glyphosate	ND
Acrolein	<PQL

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PQL = Below Quality Control Limit

Please review and if you should have any questions, please call.

Sincerely,

Hugh A. Rathbun, CCA, CPAg/SS
Consultant Sales Manager

HAR:mc

Enclosures

Appendix E

Department of Fish and Game Approval Letter for Use of Acrolein

STATE OF CALIFORNIA - THE RESOURCES AGENCY GRAY DAVIS, Governor
DEPARTMENT OF FISH AND GAME
SACRAMENTO VALLEY AND CENTRAL SIERRA REGION
701 NIMBUS ROAD, SUITE A
RANCHO CORDOVA, CALIFORNIA 95670
Telephone (916) 358-2900

February 14, 2003

FEB 20 2003

Mr. Anders Christensen
Woodbridge Irrigation District
18777 N. Lower Sacramento Road
Woodbridge, CA 95258

Dear Mr. Christensen:

We have received your letter of intent to use acrolein (Magnacide) in the Irrigation District during the 2003 irrigation season. The Department of Fish and Game (DFG) does not object to its use in control of aquatic vegetation provided:

1. Acrolein is only applied to those ditches previously approved by the DFG.

2. Acrolein is not applied to natural stream channels.

3. Acrolein is not applied to ditches with direct discharges to natural streams.

4. Treated water, unless sufficiently detoxified, is not discharged into any fish-bearing water of the State.

5. Detoxified water discharged into fish-bearing waters does not cause the dissolved oxygen concentration of the receiving water to drop below 5 mg/L.

6. All fish losses are reported immediately to the DFG, Sacramento and Central Valley Region, at (916) 358-2929.

7. Any fish that die as a result of treatment are removed.

8. A permit is obtained from the County Agricultural Commissioner prior to possession or use. All instructions on the container label must be strictly followed.

9. Acrolein is applied by or under the supervision of a certified commercial applicator.

10. The DFG is notified at least 24 hours prior to each application. Contact the DFG Sacramento Valley and Central Sierra Region at (916) 358-2929.

11. The DFG is notified each year of the district's proposed use of acrolein.

For your information, acrolein is extremely toxic to fish and other aquatic life. A review of the literature on the toxicity of acrolein to fish has shown that concentrations less than 0.1 mg/L may be lethal to sunfish, trout and salmon; we therefore recommend extreme caution when using this material.

Thank you for your cooperation in this matter. We are looking forward to working with you in the future. If you should have any questions, please call Ms. Janna Herren, Staff Environmental Scientist, at (916) 358-2918.

Sincerely,

Larry L. Eng, Ph.D.
Assistant Regional Manager

cc: Ms. Janna Herren
Lt. Eric Vielhauer
Wdn. Brian Moore
Department of Fish and Game
1701 Nimbus Road, Suite A
Rancho Cordova, CA 95670

Attachment 5

Woodbridge Irrigation District's Algae/Aquatic Weed Control Program: Contingency Plan

Woodbridge Irrigation District
Contingency Plan

If Woodbridge Irrigation District ("District") were not granted a categorical exception for the use of acrolein and copper sulfate then the District would continue to operate its Algae/Aquatic Weed Control Program according to the District's best management practices found in its Quality Assurance Project Plan ("QAPP"). The District would apply for the use of acrolein and copper sulfate under the 2004 Statewide General NPDES Permit for the Discharge of Aquatic Pesticides for Aquatic Weed Control in Waters of the United States ("General Permit"). The District would be allowed to continue to operate the Algae/Aquatic Weed Control Program following the guidelines set forth in the QAPP because the District has not contributed to the degradation of receiving waters of the United States. Water samples collected by the District during the application season have consistently indicated that no detectable levels of acrolein or copper sulfate are discharged from the District's system into waters of the United States. Therefore, the District has and it anticipates it will continue to operate under the strict guidelines set forth under the General Permit.

Other Options for Controlling Aquatic Weeds/Algal Blooms
The District's Algae/Aquatic Weed Control Program was developed based on many factors, including the following:

- Effectiveness in controlling the targeted species
- Cost-effectiveness
- Practicality of implementation and use in the irrigation system
- Potential environmental impacts

The District has considered several alternatives to the use of acrolein and copper sulfate for the control of aquatic weeds and algae in the districts canals and ditches. These alternatives include (1) mechanical vegetation removal, such as raking and chaining and (2) dewatering canals. Mechanical vegetation removal is significantly more costly, and often less effective, than the use of chemical herbicides. Additionally, mechanical vegetation removal results in higher levels of turbidity. Further, mechanical removal can result in sedimentation and clogging in irrigation equipment. The District has also in the past dewatered the canals in an attempt to control aquatic weeds. However, the canals must be kept dry for significant periods of time to completely kill the vegetation. During the irrigation season, this dry period is not feasible because of the high demand for irrigation water.