

**Analysis and Reporting of Volatile Non-Target Organic Compounds
in Extremely Impaired Water Sources and Recycled Water by Method 524.2**

- 1) Analysis for volatile organic compounds (VOCs)
 - a) USEPA approved drinking water methods should be used, as applicable, to analyze for the regulated and unregulated drinking water chemical contaminants listed by the USEPA or the California Department of Health Services (DHS).
 - b) When a general VOC analysis is required, USEPA method 542.2 should be used. Method 524.2 is used to determine 84 VOCs in water (Table 1) and four additional California regulated/unregulated VOCs (Table 2), but it may also be used to analyze for non-target VOCs. The additional instructions necessary to perform the non-target analysis are described in this appendix.
- 2) Definitions
 - a) Non-target compounds are compounds detected in a sample that are not method compounds (*i.e.*, target or calibrated compounds), internal standards, system monitoring compounds, or surrogate compounds. See Table 1 for the list of target, internal standard and surrogate compound in method 524.2.
 - b) Target compounds are the method listed compounds that generally have been demonstrated to be applicable to the method and are used to calibrate the system for retention time and detector response.
 - c) Tentatively identified compounds (TICs) are non-target compounds that have been subjected to mass spectral library searches for tentative identifications. Concentration estimates for TICs are determined by the internal standard method.
 - d) Unknown compounds are non-target compounds whose mass spectra do not adequately match the mass spectra from the mass spectral library searches for tentative identifications.
- 3) Reporting Requirements for Non-Target Compounds
 - a) The peak threshold for reporting a non-target compound is a signal to noise ratio of five, or higher. All non-target compounds, which are present in the sample at concentrations sufficient to produce peak signals equal to, or greater than the peak threshold shall be library searched and reported.
 - b) The following conditions do not require reporting:
 - i) Compounds detected below the peak threshold criterion (Section 3.a).

- ii) Compounds eluting 30 seconds prior to the first target compound.
 - iii) Compounds eluting 3 minutes after the last target compound.
 - iv) Non-target compounds detected in the sample that were also detected in the method blank, including column bleed.
- c) All non-target compounds that meet the peak threshold criterion that are suspected to be straight-chain, branched, or cyclic alkanes, alone or part of an alkane series, shall be library searched and reported by class (*e.g.*, series of straight chain, branched, or cyclic alkanes, as applicable).
- 4) Identification of Non-Target Compounds
- a) The tentative identifications shall be performed via a forward search of the NIST/EPA/NIH (May 1992 release, or later) and/or Wiley (1991 release, or later), or equivalent, mass spectral library.
 - b) Computer generated library search routines must not use normalization routines that would misrepresent the library or unknown spectra when compared to each other.
 - c) Guidelines for assigning tentative identifications
 - i) The mass scan range should be set to 35 to 260 m/z , as recommended in section 11.3 of method 524.2.
 - ii) Relative intensities of the major ions in the reference library spectrum (ions greater than 10% of the most abundant ion) should be present in the sample spectrum.
 - iii) The relative intensities of the major ion should agree within an absolute $\pm 20\%$. (Example: For an ion with an abundance of 50% in the reference spectrum, the corresponding sample ion abundance should be between 30-70%).
 - iv) A molecular ion present in the reference library spectrum should be present in the sample spectrum.
 - v) Ions present in the sample spectrum, but not in the reference library spectrum, should be reviewed for possible background contamination, or presence of co-eluting compounds.
 - vi) Ions present in the reference library spectrum, but not in the sample spectrum, should be reviewed for possible background subtraction from the sample spectrum because of background contamination, or co-eluting compounds. Data system library reduction programs can sometimes create these discrepancies.

- d) If, after careful review and in the technical judgment of the mass spectroscopist, no valid identification can be made, the compound should be reported as follows.
- i) If the library search produces a match at or above 85%, report that compound.
 - ii) If the library search produces more than one compound at, or above 85%, report the first compound (highest match).
 - iii) If the library search produces no matches at, or above 85%, the compound should be reported as unknown. The mass spectroscopist should give additional classification of the unknown compound, if possible (*i.e.*, unknown aromatic, unknown hydrocarbon, unknown acid type, unknown chlorinated compound, etc.) The unknown should be reported to the DHS along with the total ion chromatogram and the mass spectrum of the unknown, with and without background subtraction. The DHS will evaluate if further research by the water system will be necessary to identify the compound.

5) Quantification of Non-Target Compounds

- a) Concentration estimates must be determined for all tentatively identified compounds, as well as those identified as unknowns. The estimated concentration shall be determined by the internal standard method. Method 524.2 requires that at least one internal standard (fluorobenzene) be used. Additional internal standards may be used, provided that they are similar in physical and chemical properties as the target analytes. The internal standard(s) is prepared at a final concentration of 1 µg/L in each 25 mL sample. Non-target compounds that meet the criteria for reporting (Section 2) shall be quantified using the nearest internal standard that is free from interferences and reported.
- b) Total area counts (or peak heights) from the total ion chromatograms are to be used for both the compound to be measured and the internal standard. A relative response factor (RRF) of one (1) is to be assumed. The resulting concentration shall be qualified as “estimated”, due to lack of a compound-specific response factor, and "presumptive evidence of presence”, indicating the quantitative and qualitative uncertainties associated with this non-target component.

$$conc. (\mu g / L) = \frac{(A_x)(I_s)(DF)}{(A_{IS})(RRF)(V_0)}$$

Where,

A_x = Area of the total ion current for the compound to be measured

A_{IS} = Area of the total ion current for the specific internal standard

I_s = Amount of internal standard added in ng

RRF = 1

V_0 = Sample volume in mL

DF = Sample dilution factor

6) Confirmation of Non-Target Compounds

- a) The DHS will review the 524.2 analysis results to determine if confirmation will be required for any TIC reported in the non-target analysis.
- b) If confirmation of a TIC is required, analyze a reference standard of the TIC, if available, and compare the retention time and mass spectrum of the reference standard with the TIC, as described in method 524.2 for target compounds.
 - i) If a reference standard is not available or cannot be synthesized, the TIC remains unconfirmed.
 - ii) If a reference standard is available and the TIC is positively identified, perform the following.
 - (1) Determine the method performance by performing a MDL study and an accuracy and precision study, as described in method 524.2.
 - (2) If the method performance is determined to be poor, the sample collection, sample preservation, sample extraction conditions, GC/MS parameters, etc., may be optimized to increase the method performance. If a deuterated reference standard is available, and if it is necessary to improve quantification accuracy, the isotope dilution method may be used, if applicable. Section 6.b.ii.1 should then be repeated using the modified procedure. Modifications made to the method must be documented and validated.
 - (3) Quantify the compound against the reference standard using the internal standard approach, as described in method 524.2, or by the isotope dilution method, if applicable.
 - iii) If the TIC is not positively identified, (*i.e.*, retention time and/or spectrum do not match the retention time and/or spectrum of the reference compound), refer to Section 4.d.

7) References

- a) Method 524.2, Revision 4.1, "Methods for the Determination of Organic Compounds in Drinking Water - Supplement III," EPA/600/R-95/131, USEPA, August 1995.
- b) USEPA Contract Laboratory Program Statement of Work for Low Concentration Organic, OLC03.2, December 2000.

Table 1. Volatile Organic Compound List in Method 524.2, Rev.4.1 (1995)

<u>Target Analyte</u>	<u>CAS No.</u>	<u>Target Analyte</u>	<u>CAS No.</u>
Acetone	67-64-1	<i>cis</i> -1,3-Dichloropropene	10061-01-5
Acrylonitrile	107-13-1	<i>trans</i> -1,3-Dichloropropene	10061-02-6
Allyl chloride	107-05-1	Diethyl ether	60-29-7
Benzene	71-43-2	Ethylbenzene	100-41-4
Bromobenzene	108-86-1	Ethyl methacrylate	97-63-2
Bromochloromethane	74-97-5	Hexachlorobutadiene	87-68-3
Bromodichloromethane	75-27-4	Hexachloroethane	67-72-1
Bromoform	75-25-2	2-Hexanone	591-78-6
Bromomethane	74-83-9	Isopropylbenzene	98-82-8
2-Butanone	78-93-3	4-Isopropyltoluene	99-87-6
<i>n</i> -Butylbenzene	104-51-8	Methacrylonitrile	126-98-7
<i>sec</i> -Butylbenzene	135-98-8	Methylacrylate	96-33-3
<i>tert</i> -Butylbenzene	98-06-6	Methylene chloride	75-09-2
Carbon disulfide	75-15-0	Methyl iodide	74-88-4
Carbon tetrachloride	56-23-5	Methylmethacrylate	80-62-6
Chloroacetonitrile	107-14-2	4-Methyl-2-pentanone	108-10-1
Chlorobenzene	108-90-7	Methyl- <i>tert</i> -butyl ether (MTBE)	1634-04-4
1-Chlorobutane	109-69-3	Naphthalene	91-20-3
Chloroethane	75-00-3	Nitrobenzene	98-95-3
Chloroform	67-66-3	2-Nitropropane	79-46-9
Chloromethane	74-87-3	Pentachloroethane	76-01-7
2-Chlorotoluene	95-49-8	Propionitrile	107-12-0
4-Chlorotoluene	106-43-4	<i>n</i> -Propylbenzene	103-65-1
Dibromochloromethane	124-48-1	Styrene	100-42-5
1,2-Dibromo-3-chloropropane	96-12-8	1,1,1,2-Tetrachloroethane	630-20-6
1,2-Dibromoethane	106-93-4	1,1,2,2-Tetrachloroethane	79-34-5
Dibromomethane	74-95-3	Tetrachloroethene	127-18-4
1,2-Dichlorobenzene	95-50-1	Tetrahydrofuran	109-99-9
1,3-Dichlorobenzene	541-73-1	Toluene	108-88-3
1,4-Dichlorobenzene	106-46-7	1,2,3-Trichlorobenzene	87-61-6
<i>trans</i> -1,4-Dichloro-2-butene	110-57-6	1,2,4-Trichlorobenzene	120-82-1
Dichlorodifluoromethane	75-71-8	1,1,1-Trichloroethane	71-55-6
1,1-Dichloroethane	75-34-3	1,1,2-Trichloroethane	79-00-5
1,2-Dichloroethane	107-06-2	Trichloroethene	79-01-6
1,1-Dichloroethene	75-35-4	Trichlorofluoromethane	75-69-4
<i>cis</i> -1,2-Dichloroethene	156-59-2	1,2,3-Trichloropropane (1,2,3-TCP)	96-18-4
<i>trans</i> -1,2-Dichloroethene	156-60-5	1,2,4-Trimethylbenzene	95-63-6
1,2-Dichloropropane	78-87-5	1,3,5-Trimethylbenzene	108-67-8
1,3-Dichloropropane	142-28-9	Vinyl chloride	75-01-4
2,2-Dichloropropane	590-20-7	<i>o</i> -Xylene	95-47-6
1,1-Dichloropropene	563-58-6	<i>m</i> -Xylene	108-38-3
1,1-Dichloropropanone	513-88-2	<i>p</i> -Xylene	106-42-3

Surrogate Standards

1,2-Dichlorobenzene-D₄
Bromofluorbenzene

Internal Standard

Fluorobenzene

Table 2. Additional California Volatile Organic Compounds for 524.2

<u>Target Analyte</u>	<u>CAS No.</u>
<i>tert</i> -Amyl methyl ether (TAME)	994-05-8
<i>tert</i> -Butyl alcohol (TBA)	75-65-0
Ethyl- <i>tert</i> -butyl ether (ETBE)	637-92-3
1,1,2-Trichlorotrifluoroethane	76-13-1