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"When Quality Counts"

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McCampbell Analytical Inc.

Determination of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

EPA Method 8260B / LUFT

Number: O – 8260 **Rev. No.: 2** **DATE: 11-4-13**

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Disclaimer

The 2003 NELAC Standard, Chapter 5 Quality Systems, Section 5.5.4.1.1, Parts a), b), & f), (pg. 207 of 324) states with regard to laboratory SOPs,

> a) These documents, for example, may be equipment manuals provided by the manufacturer, or internally written documents with adequate detail to allow someone similarly qualified, other than the analyst, to reproduce the procedures used to generate the testresult.
>
> b) The test methods may be copies of published methods as long as any changes or selected options in the methods are documented and included in the methods manual (see 5.5.4.1.2).
>
> f) The documents specified in 5.5.4.1.1 a) and 5.5.4.1.1 b) that contain sufficient information to perform the tests do not need to be supplemented or rewritten as internal procedures, if the documents are written in a way that they can be used as written. Any changes, including the use of a selected option must be documented and included in the laboratory's methods manual.

In accordance with these instructions, this SOP is an internally written document that acts as a supplement to the published method it references. This SOP does not stand alone and is to be used in conjunction with the published method. Instrument specific instructions, quality control summaries, as well as internal MAI policies are referenced in this SOP, including any deviations from the published method, if any such deviations exist. In the absence of a stated deviation, this SOP adheres strictly to all the requirements of the published method, regardless of whether or not those requirements are explicitly stated in this document.

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Standard Operating Procedure:

Determination of Volatile Organics Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

EPA Method 8260B/LUFT

1. Scope and Application

1.1 This method is used to determine the concentration of volatile organic compounds in a variety of solid waste matrices and is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludge's, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments.

1.2 Table 1 lists the compounds and reporting limits, which can be routinely determined by this method. Modifications to the analyte list or procedural changes to reach lower reporting limits are allowed if required by client, project or program. The laboratory manager and the Quality Assurance Officer must approve any changes in the analytical procedures before samples can be analyzed.

1.3 This method is based upon a purge-and-trap, gas chromatographic/mass spectrometric (GC/MS) procedure. It is restricted to use by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatograph/mass spectrometers, and skilled in the interpretation of mass spectra and their use as a quantitative tool.

1.4 Reporting Limits are the lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions. The Reporting Limit is derived from the lowest point on the calibration curve. Sample reporting limits are highly matrix-dependent and may not always be achievable. The reporting limits listed apply to soil/sediment and are based on wet weight. Data that are reported on a dry weight basis will have higher RLs, based on the percent dry weight in each sample. The reporting limits for 25 mL purge waters are two fifth of what is listed in the table.

Examples:

Table 1. Method Analytes with Matrix Specific Reporting Limits

8260 + 9 Oxygenates Analyte List	Water MDL (µg/L)	Water PQL (µg/L)	Soil MDL (mg/Kg)	Soil PQL (mg/Kg)	Oil MDL (mg/L)	Oil PQL (mg/L)	Wipe MDL (µg/wipe)	Wipe PQL (µg/wipe)	ZHE* Soil MDL (mg/L)	ZHE* Soil PQL (mg/L)
Acetone	5	10	0.025	0.05	25	50	0.25	2.5	0.2	0.2
tert-Amyl methyl ether (TAME)	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Benzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Bromobenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Bromochloromethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Bromodichloromethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Bromoform	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Bromomethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
2-Butanone (MEK)	2	2	0.01	0.02	10	20	0.05	0.5	0.5	0.5
t-Butyl alcohol (TBA)	2	2	0.025	0.05	25	50	0.25	2.5	0.05	0.05
n-Butyl benzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
sec-Butyl benzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
tert-Butyl benzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Carbon Disulfide	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Carbon Tetrachloride	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005

Table 1. Method Analytes with Matrix Specific Reporting Limits										
8260 + 9 Oxygenates Analyte List	Water MDL (µg/L)	Water PQL (µg/L)	Soil MDL (mg/Kg)	Soil PQL (mg/Kg)	Oil MDL (mg/L)	Oil PQL (mg/L)	Wipe MDL (µg/wipe)	Wipe PQL (µg/wipe)	ZHE* Soil MDL (mg/L)	ZHE* Soil PQL (mg/L)
Chloroethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Chloroform	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Chloromethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
2-Chlorotoluene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
4-Chlorotoluene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Dibromochloromethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,2-Dibromo-3-chloropropane (DBCP)	0.2	0.2	0.002	0.004	2.5	5	0.025	0.25	0.0005	0.0005
1,2-Dibromoethane (EDB)	0.25	0.5	0.002	0.004	2.5	5	0.025	0.25	0.0005	0.0005
Dibromomethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,2-Dichlorobenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,3-Dichlorobenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,4-Dichlorobenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Dichlorodifluoromethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,1-Dichloroethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,2-Dichloroethane (1,2-DCA)	0.25	0.5	0.002	0.004	2.5	5	0.025	0.25	0.0005	0.0005
1,1-Dichloroethene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
cis-1,2-Dichloroethene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
trans-1,2-Dichloroethene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,2-Dichloropropane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,3-Dichloropropane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
2,2-Dichloropropane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,1-Dichloropropene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
cis-1,3-Dichloropropene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
trans-1,3-Dichloropropene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Diisopropyl ether (DIPE)	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Ethanol	50	50	0.25	0.25	500	500	2.5	25	0.05	0.05
Ethylbenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Ethyl tert-butyl ether (ETBE)	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Freon 113 (1,1,2-Trichloro-1,2,2-trifluoroethane)	5	10	0.05	0.1	50	100	0.5	5	0.01	0.01
Hexachlorobutadiene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Hexachloroethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
2-Hexanone	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.02	0.02
Isopropylbenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
4-Isopropyl toluene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Methanol	500	500	2.5	2.5	5000	5000	25	250	0.5	0.5
Methyl-t-butyl ether (MTBE)	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Methylene chloride	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.005	0.005
4-Methyl-2-pentanone (MIBK)	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.005	0.005
Naphthalene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
n-Propyl benzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Styrene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,1,1,2-Tetrachloroethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,1,2,2-Tetrachloroethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Tetrachloroethene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.005	0.005
Toluene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.005	0.005
1,2,3-Trichlorobenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,2,4-Trichlorobenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,1,1-Trichloroethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,1,2-Trichloroethane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Trichloroethene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.005	0.005

Table 1. Method Analytes with Matrix Specific Reporting Limits										
8260 + 9 Oxygenates Analyte List	**Water MDL (µg/L)**	**Water PQL (µg/L)**	**Soil MDL (mg/Kg)**	**Soil PQL (mg/Kg)**	**Oil MDL (mg/L)**	**Oil PQL (mg/L)**	**Wipe MDL (µg/wipe)**	**Wipe PQL (µg/wipe)**	**ZHE* Soil MDL (mg/L)**	**ZHE* Soil PQL (mg/L)**
1,2,3-Trichloropropane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
1,2,4-Trimethylbenzene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Vinyl Chloride	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Xylenes	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25	0.0005	0.0005
Uncommon Analytes										
Acetonitrile	2.5	5					0.05	0.5		
Acrolein (Propenal)	2.5	5	0.025	0.05	25	50	0.25	2.5	0.005	0.005
Acrylonitrile	1	2	0.01	0.02	10	20	0.1	1	0.002	0.002
Allyl alcohol										
Allyl chloride										
Benzyl chloride (a-Clorotoluene)	0.25	0.5	0.0025	0.005						
Bromoacetone										
n-Butanol										
tert-Butylformate	5	5								
Chloral hydrate										
Chloroacetonitrile	10	10	0.1	0.1						
1-Chlorobutane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
2-Chloroethanol										
1-Chlorohexane	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
2-Chloroethyl Vinyl Ether	0.5	1	0.005	0.01	5	10	0.05	0.5	0.001	0.001
Chloroprene (2-Chloro-1,3-butadiene)										
3-Chloropropionitrile										
Crotonaldehyde										
Cyanogen Chloride										
Dibromofluoromethane										
cis-1,4-Dichloro-2-butene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
trans-1,4-Dichloro-2-butene	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
1,3-Dichloro-2-propanol										
1,1-Dichloro-2-propanone										
1,2-Dichloro-1,1,2,2-tetrafluoroethane	5	10	0.05	0.1	50	100	0.5	5		
Diethyl ether (Ethyl ether)	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
1,2,3,4-Diepoxybutane										
Epichlorohydrin										
Ethyl acetate	2.5	5	0.025	0.05	25	50	0.25	2.5		
Ethylene oxide										
Ethyl Methacrylate	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
2-Hydroxypropionitrile										
Iodomethane (Methyl iodide)	2.5	5	0.025	0.05	25	50	0.25	2.5	0.005	0.005
Isobutyl alcohol										
Limonene	2.5	5	0.025	0.05	25	50	0.25	2.5		
Malononitrile										
Methacrylonitrile	?									
Methacrylate	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
Methyl methacrylate	0.25	0.5	0.0025	0.005	2.5	5	0.025	0.25		
Nitrobenzene	5	10	0.05	0.1	50	100	0.5	5	0.01	0.01
2-Nitropropane	0.5	1	0.005	0.01	5	10	0.05	0.5		
n-Nitroso-di-n-butylamine										
Paraldehyde	10	10	0.1	0.1	100	100	0.5	5		
Pentachloroethane	10	10	0.1	0.1	100	100	0.5	5		
2-Pentanone										
2-Picoline										
1-Propanol										

8260 + 9 Oxygenates Analyte List	Water MDL (µg/L)	Water PQL (µg/L)	Soil MDL (mg/Kg)	Soil PQL (mg/Kg)	Oil MDL (mg/L)	Oil PQL (mg/L)	Wipe MDL (µg/wipe)	Wipe PQL (µg/wipe)	ZHE* Soil MDL (mg/L)	ZHE* Soil PQL (mg/L)
2-Propanol (Isopropyl alcohol)	50	50	0.25	0.25	500	500	2.5	25		
Propargyl alcohol										
b-Propiolactone										
Propionitrile (ethyl cyanide)	2.5	5	0.025	0.05	25	50	0.25	2.5		
n-Propylamine										
Pyridine										
Tetrahydrofuran	0.5	1	0.005	0.01	5	10	0.05	0.5		
o-Toluidine (2-methylaniline)										
Vinyl Acetate	2.5	5	0.025	0.05	25	50	0.25	2.5	0.005	0.005

*STLC, TCLP, SPLP, DISTLC, DITCLP, DISPLP

8260 SIM Analyte List	Water MDL (µg/L)	Water PQL (µg/L)	Soil MDL (mg/Kg)	Soil PQL (mg/Kg)
1,2-Dibromo-3-chloropropane	0.01	0.01	0.0001	0.0001
1,2-Dibromoethane (EDB)	0.02	0.02	0.0002	0.0002
1,4-Dioxane	2	2	0.02	0.02
1,2,3-Trichloropropane	0.005	0.005	0.0002	0.0002
Optional Analytes				
1,2-Dichloroethane (1,2-DCA)	0.02	0.02	0.0002	0.0002

9 Oxygenates Analyte List	Water MDL (µg/L)	Water PQL (µg/L)	Soil MDL (mg/Kg)	Soil PQL (mg/Kg)
tert-Amyl methyl ether (TAME)	0.25	0.5	0.0025	0.005
t-Butyl alcohol (TBA)	2	2	0.025	0.05
1,2-Dibromoethane (EDB)	0.25	0.5	0.002	0.004
1,2-Dichloroethane (1,2-DCA)	0.25	0.5	0.002	0.004
Diisopropyl ether (DIPE)	0.25	0.5	0.0025	0.005
Ethanol	50	50	0.25	0.25
Ethyl tert-butyl ether (ETBE)	0.25	0.5	0.0025	0.005
Methanol	500	500	2.5	2.5
Methyl-t-butyl ether (MTBE)	0.25	0.5	0.0025	0.005

2. Method Summary

2.1 Volatile compounds are introduced into the gas chromatograph by the purge-and-trap method. Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and back flushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large 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.

2.2 Qualitative identifications are confirmed by analyzing standards under the same conditions used for samples and comparing resultant mass spectra and GC retention times. Each identified component is quantitated by relating the MS response for an appropriate selected ion produced by that compound to the MS response for another ion produced by an internal standard.

3. Definitions

3.1. ANALYTICAL BATCH – A group of up to 20 field samples analyzed on the same instrument. An analytical batch is not related to matrix, and may consist of samples from several preparatory batches.

3.2. CALIBRATION STANDARD – Prepared from the primary dilution standard solution or stock standard solutions.

3.3. CONTINUING CALIBRATION BLANK (CCB) – A blank matrix ran at the beginning of a sample sequence (i.e., before after the CCV, degradation check, and before sample analysis), to verify the instrumentation is free from contamination. A CCB is associated with an *analytical batch*, not a *preparatory batch*.

3.4. CONTINUING CALIBRATION VERIFICATION STANDARD (CCV) – A mid-level 10ppb CAL solution analyzed before sample analysis in a sample sequence in order to confirm that the initial calibration is still valid. *At MAI, the term CCV is also used for the initial calibration verification (ICV) standard.*

3.5. INITIAL CALIBRATION STANDARDS – A series of CAL solutions used for initial calibration.

3.6. INITIAL CALIBRATION VERIFICATION STANDARD (ICV) – An individual CAL solution analyzed prior to any sample analysis, at the beginning of the day, which verifies initial/historical calibration curves. *At MAI, the term CCV is also used for the ICV standard.*

3.7. INITIAL DEMONSTRATION OF CAPABILITY (IDOC) – A method is prepared and determined which generates data of acceptable accuracy and precision for a reference sample containing the target analytes in a clean matrix. Establish the ability to generate acceptable accuracy and precision.

3.8. INSTRUMENT BLANK (IB) – A blank matrix ran at the beginning of a sample sequence (i.e., before the CCV, degradation check, and sample analysis), to verify the instrumentation is free from contamination. An IB is associated with an *analytical batch*, not a *preparatory batch* .

3.9. LABORARORY CONTROL SAMPLE (LCS*)* – An aliquot of clean matrix (reagent water, Ottawa sand, wipe, CT, etc.) are spiked with midrange levels of analyte and run like a sample. They are analyzed as samples, and % recoveries (accuracy) calculated in order to determine whether the methodology is in control.

3.10. MATRIX SPIKE AND MATRIX SPIKE DUPLICATE (MS/MSD) – Two aliquots of an environmental sample to which midrange levels of method analytes are added. They are analyzed as samples, and % recoveries (accuracy) and %RPD (precision) calculated with the purpose of determining whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes must be determined in a separate aliquot and subtracted.

3.11. METHOD BLANK (MB) – A blank matrix processed simultaneously with, and under the same conditions as, samples through all steps of the analytical procedure. Each *preparatory batch* requires a Method Blank. For aqueous samples, reagent water is treated exactly as a sample, including exposure to glassware, extraction, etc. For soil and solid samples, no matrix is used. For wipes, charcoal tubes, etc, an unused

sample medium is extracted exactly as a sample. Its purpose is to determine if contamination is present from any of the sample preparation or analytical steps.

3.12. METHOD DETECTION LIMIT (MDL) – The minimum amount of a substance that can be measured with a specified degree of confidence that the amount is greater than zero using a specific measurement system. The MDL is a statistical estimation at a specified confidence interval of the concentration at which the relative uncertainty is +100%. The MDL represents a range where qualitative detection occurs using a specific method. Quantitative results are not produced in this range.

3.13. PREPARATORY BATCH – A group of up to 20 field samples of the same matrix, that is associated with a set of Quality Control samples (for example, a MB, LCS /LCSD, and MS/MSD).

3.14. QUALITY CONTROL SAMPLE (QCS) – A control sample, generated at the laboratory or in the field, or obtained from an independent source, used to monitor a specific element in the sampling and/or testing process.

3.15. REPORTING LIMIT (RL) or *PRACTICAL QUANTITATION LIMIT (PQL)* – The lowest level that can be reliably determined within specified limits of precision and accuracy during routine laboratory operating conditions. The RL cannot be lower than the lowest calibration standard used in the initial calibration of the instrument and must be greater than the MDL.

3.16. DUPLICATE SAMPLE – Prepare by dividing a sample into two or more separate aliquots.

3.17. SPIKE – A known amount of an analyte added to a blank, quality control sample, field sample or sub-sample.

3.18. STANDARD CURVE – A curve that plots the concentrations of known standards of an analyte versus the instrument response to the analyte.

4. Interferences

4.1Major 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 not corrected for blanks result in what the laboratory feels to be a false positive for that sample, a detailed explanation with accompany the uncorrected data.

4.2 Interfering 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. To assure there is no contamination present a blank is analyzed.

4.3Special 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.

4.4 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal into the sample during shipment and storage. A trip blank prepared from organic-free reagent water and carried through the sampling and handling protocol can serve as a check on such contamination. MAI provides trip blanks upon client request.

4.5The main source of contamination is analysis of samples containing high levels of organic compounds. These samples may cause system-wide carryover contamination. Table 3 should be used as a general guideline to identify possible instances of contamination.

4.6 Careful attention must be paid to syringe cleanliness. The following procedure is followed to avoid contamination from syringes.

4.7Gastight micro syringes: Rinse three times with reagent grade water. On the first rinse, the plunger must be brought slightly past the point of previous use. On each successive rinse, the plunger should be brought slightly past the previous point.

4.8 Luer-lok syringes

4.9 Any rinse solvent suspected of being contaminated must be dis posed of immediately and replaced with clean solvent.

4.10 If system-wide contamination is suspected, corrective action must be taken before continuing any runs and a method blank must be run to show the problem is corrected.

4.11 For samples containing large amounts of water-soluble materials, suspended solids, high boiling point 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 they dry the purging device in an oven at 105 ºC.

Table 3. Contamination Guidelines

Compounds	Carryover into next sample (ng)	Carryover into more than one sample(ng)
Light: Up to $CHCl_3$	>5000	---
Medium: CHCL3-isopropylbenzene	>1000	>10,000
Heavy: isopropylbenzene-1,2,3 trichlorobenzene	>500	>10,000

5. Safety

5.1. The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined however, each chemical compound should be treated as a potential health hazard, and exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory maintains a reference file of material safety data sheets for the chemicals specified in this method. Good laboratory technique dictates the use of appropriate dermal protection. A laboratory coat, eye protection, and gloves are the minimum requirements.

6. Equipment & Supplies

6.1. Instrumentation:

Instrument #	VOC Equipment	Manufacturer	Model	Serial/ID No.
GC4	MS	Aglient	5973 (G2577A)	US10441883
	GC	Aglient	6890N (G1530N)	US10146001
	P&T Autosampler	VARIAN	Archon 4552	
	P&T Concentrator	Tekmar	3000	96216004
	Control	Tekmar	TT130ELASR2-1	HH209644 3002
	Computer	DELL	DHM	GD00Z01
GC10	MS	Hewlatt-Packard	5973 (G1098A)	US72010690
	GC	Agilent	G1530A	DE00020257
	P&T Autosampler	VARIAN	Archon 4552	
	P&T Concentrator	Tekmar	3100	US02080011
	Computer	DELL		
GC16	MS	Agilent	5973 (G2577A)	US63810219
	GC	Agilent	6890A (G1530A)	US00034859
	P&T Autosampler	VARIAN	Archon 4552	
	P&T Concentrator	Tekmar	3100	0016T011
	Control	Tekmar	TT130ELASR2-1	HH85998
	Computer	Hewlatt-Packard	KAYAK XA 0503	US93495728
GC18	MS	Agilent	5973 (G2577A)	US03940632
	GC	Agilent	6890A (G1530A)	US00039633
	P&T Autosampler	VARIAN	Archon 4552	
	P&T Concentrator	Tekmar	3100	00287008
	Control	Tekmar	TT130ELASR2-1	HH85998
	Computer	DELL		
GC28	MS	Agilent	5975C (G3170A)	US873317109
	GC	Agilent	7890A (G3440A)	CN10727073
	P&T Autosampler	VARIAN	Archon 4552	
	P&T Concentrator	Tekmar		
	Computer	Hewlatt-Packard	7700	2UA7241301

6.2 Balance—Analytical, capable of accurately weighing 0.0001 g.

6.3 Syringes – variety of volumes.

7. Reagents & Standards

7.1 Reagent water—Reagent water is defined as a water in which an interferent is not observed at the MDL of the parameters of interest.

7.2 Sodium thiosulfate—(ACS) Granular.

7.3 Methanol—Pesticide quality or equivalent.

7.4 Standards - Stock standard solutions for all method analytes are purchased as certified solution kits at a concentration of 2000 ppm. Standards should be replaced before expiration date and stored at -10°C - -20°C in amber bottles with Teflon lined-screw caps.

7.4.1 Intermediate Calibration Standards

Intermediate calibration standards can be prepared by diluting the stock standard as appropriate.

Intermediate Standard Preparation						
	Stock Conc.	**Initial Wt./Vol.**	**Final Volume**	**Final conc.**	**Solvent**	Lab ID
8260B-CAL VO-MCACA-1	2000ppm	90 µL	1.8mL	100ppm	PD + H20 1 ;1	8260 CCV 100ppm
8260B-CA L VO-MCACA-8	2000ppm	90 µL		100ppm		
8260 Surr 8260-SSR-5mL	2000ppm	90µL		100ppm		
8260B Soil Surr VO-MCACA-15-5	1000ppm	180µL		100ppm		
8260B-CAL VO-MCACA-1	2000ppm	9µL	1.8mL	10ppm	PD + H20 1:1	8260 CCV 10ppm
8260B-CAL VO-MCACA-8	2000ppm	9µL		10ppm		
8260 Surr 8260-SSR-5mL	2000ppm	9µL		10ppm		
8260B Soil Surr VO-MCACA-15-5	1000ppm	18µL		10ppm		
8260B-ICV VO-MCACA-14	2000ppm	90µL	1.8mL	100ppm	PD + H20 1:1	8260 ERS
8260B-ICV VO-MCACA-11	2000ppm	90µL		100ppm		

8260B IS 8260-IS-5mL	2000ppm	500µL	40mL	25ppm	PD + H20 1:1	8260 IS/SS 25ppm /2.5ppm
8260B Surr 8260-SSR-5mL	2000ppm	500µL		25ppm		
8260B IS 8260-IS-5mL	2000ppm	50µL	4mL	25ppm	PD + H20 1:1	8260 IS 25ppm

Intermediate standards are stored at -10°C to -20°C and are replaced whenever the instrument is recalibrated

7.4.2 Working Calibration Standards

Calibration standards are prepared at a minimum of five concentrations (preferably seven concentrations). To prepare a calibration standard, add an appropriate volume of a secondary standard solution to an aliquot of organic free reagent water in gas tight syringe. Use a microsyringe and rapidly inject the standard into the tip of the syringe.**Mix by inverting the syringe three times.**

Working Calibration Standard Preparation				
10 ppm Stock Standard (µL)	25ppm IS Only (µL)	25ppm IS/SS Mix (µL)	Final Volume (mL)	Final Conc. (ng)
0.2	10		10	2
0.5	10		10	5
1	10		10	10
2	10		10	20
100 ppm stock Std. (µL)				
0.5	10		10	50
1	10		10	100
2		10	10	200
4		10	10	400

7.4.3 Surrogate standards

The surrogates are toluene-d8, bromofluorobenzene, and dibromofluoromethane,
A stock surrogate solution is purchased as a vendor certified solution at a concentration of 2000/200 ppm.

7.4.3.1 An intermediate surrogate standard spiking solution is prepared from the stock at a concentration of 25/250 ppm in PD.

7.4.3.2 Each calibration standard, blank, LCS and sample undergoing GC/MS analysis should be spiked with 25 ppb of the surrogate spiking solution prior to analysis.

7.4.4 Internal standards

The recommended internal standards are chlorobenzene-d5, 1,4-difluorobenzene and, 1,4-dichlorobenzene-d4.Internal standard and surrogate standard are combined in to two mix in PD, 2000 ppm IS and 200/2000ppm SS

7.4.5 Initial Calibration Verification (ICV)

A second source calibration standard is purchased as a vendor certified solution and is analyzed after each new initial calibration and prior to sample analysis. Currently MEOH based standard mixed in PD & boiled water. Also referred to as external reference standard (ERS).

7.4.6 Tuning Standard: The same as IS/SS mix, BFB is at 25ng at a 10µL aliquot.

7.4.7 LCS and Matrix Spiking Standards

7.4.7.1 The same Mix as the CCV is used.

Great care must be taken to maintain the integrity of all standard solutions. It is recommended all standards in methanol be stored at -10C to -20C in amber bottles with Teflon lined screw- caps. **The instrument used for this analysis has an Archon autosampler. The ng values referred to in this SOP for surrogate, internal, calibration and ccv standards represent the amount actually purged.**

8. Sample Collection, Preservation, Shipment & Storage

8.1. Samples should be collected in contaminant free glass containers. [Aqueous samples can be collected in two 40ml amber glass VOAs and solid samples in glass jars with TLE or metal liners (MAI)].

8.2. Holding time and preservation are as follows:

Matrix	Holding time (days)	Storage temp. (deg. c)
Water (preserved)	14	<6
Water (unpreserved)	7	<6
Soil and sludge*	14	<6

* Soil and sludge samples are analyzed ASAP after receipt, usually the same day.

8.3. For aqueous samples with no residual chlorine present, cool to < 6°C. For aqueous sample with residual chlorine present, collect sample in a 125 mL container which has been pre-preserved with 4 drops of 10% sodium thiosulfate solution, gently swirl to mix sample, transfer to a 40 mL VOA vial and cool to < 6°C. When aromatics are to be determined, adjust pH to less than 2 with H_2SO_4, HCl, or solid $NaHSO_4$

9. Quality Control

9.1. Initial Demonstration or capability: Each analyst for a given method must analyze at least 4 replicates of a mid-level standard extracted from a water matrix using the same procedure as for a water sample. Percent recoveries and RSDs for each analyte may be compared to values published in the method

9.2. An MDL study must be performed using a minimum of 7 extracted replicates for each matrix. To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the

entire analytical method. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows: MDL = t x s

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates]

S = standard deviation of the replicate analyses

9.3 Quality Control Acceptance Criteria for this method, including the frequency and corrective actions are followed per 8260 method criteria. Control limits are generated by the laboratory.

9.4 A Laboratory Control Sample is analyzed for every batch of 20 samples.

9.5 Spiked analyte recoveries are calculated to determine whether the operating method is in compliance.

Surrogate recovery limits are 70-130%.

$$\textbf{Surrogate Percent Recovery} = \frac{Q_d}{Q_a} \times 100\ \%$$

where:
Qd = Quanity of surrogate determined by analysis
Qa = Quanity of surrogate added to sample/blank

9.6 Matrix Spike/Matrix Spike Duplicates are analyzed for every batch of 20 samples. Report the results of both the %R in the MS and MSD samples and the %RPD between the MS and MSD.

$$\textbf{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100$$

where: SSR = Spiked Sample Result
SR = Sample Result
SA = Spike Added

$$\textbf{Relative Percent Difference} = \frac{|MSR - MSDR|}{1/2(MSR + MSDR)} \times 100$$

where:
MSR = Matrix spike recovery
MSRD = Matrix spike duplicate recovery

(The vertical bars in the formula above indicate the absolute value of the difference; therefore, RPD is always expressed as a positive value.)

10. Calibration & Standardization

10.1 Instrument Tuning

10.1.1 For each 12-hour shift and prior to any analysis a GC/MS tuning standard must be analyzed.

10.1.2 Each GC/MS system must be hardware-tuned to meet the criteria in Table 5 for a 25 ng injection of bromofluorobenzene (10 uL injection of the IS/SS mix). Analyses cannot begin until these criteria are met.

Table 5. BFB Mass - Intensity Specifications (Bromofluorobenzene)	
Mass	**Intensity Required (relative abundance)**
50	15 to 40% of mass 95
75	30 to 60% of mass 95
95	base peak, 100% relative abundance
96	5 to 9% of mass 95
173	less than 2% of mass 174
174	greater than 50% of mass 95
175	5 to 9% of mass 174
176	greater than 95% but less than 101% of mass 174
177	5 to 9% of mass 176

10.1.3 The BFB should be evaluated using a minimum of one scan. A scan no more than 20 scans prior to the elution of BFB should be chosen for background subtraction. Background subtraction is required.

10.1.4 All subsequent standards, samples, MS/MSDs and blanks associated with a BFB analysis must use the identical mass spectrometer instrument conditions.

10.2 Initial Calibration

10.2.1 Prepare each calibration standard in a gas tight syringe.

10.2.2 Preparation of calibration standards.

- From a 2000ppm stock solution prepare a 100-ppm dilution by filling a 2ml mininert with 1.8ml PD/reagent free water (1:1).
- With a 1ml syringe remove 450 µL of the pd/water mix then cap the mininert lightly.
- Using the 1ml syringe add 90uL of VO-MCACA-1, 90µL VO-MCACA-8, 90µL of 8260-SSR-5mL and 180µL of VO-MCACA-15-5 stock standards to the mininert through the opening for the syringe, close opening then tighten mininert.
- Invert gently to mix the standard. Prepare 10ppm intermediate standard in the same fashion using the appropriate amounts for the desired concentration, as well as for the ERS.
- Fill eight 40ml Voas with exactly 10ml of HCL acidified water (4L: 4ml).
- Label them 2ng, 5ng, 10ng, 20ng, 50ng, 100ng, 200ng, 400ng.
- To VOAs 2ng-100ng add 10uL of the 25ppm IS only mix, to VOAs 200ng and 400ng add 10uL of IS/SS mix Cap all VOAs lightly (do not shake or invert).
- To the 5ng: using a 10uL syringe pull 0.2uL of the 10 ppm dilution. Wipe the syringe tip, then insert the 10uL syringe tip directly into the assigned VOA. Make sure there are no bubbles present in the 0.2uL transfer, then close the vial with the cap tightly.

- To the 5ng: using a 10uL syringe pull 0.5uL of the 10 ppm dilution. Wipe the syringe tip, then insert the 10uL syringe tip directly into the assigned VOA. Make sure there are no bubbles present in the 0.5uL transfer, then close the vial with the cap tightly.
- For the 10ng VOA do the same except withdraw 1uL from 10ppm standard.
- For 20ng withdrawal 2uL of the 10ppm standard.
- For the 50ng VOA add 0.5uL of the 100pm stock standard with the designated 10uL syringe.
- For the 100ng add 1uL of 100ppm standard with the same 10uL syringe, for the 200ng add 2uL and for the 400ng and 4uL.
- After all the standards have been prepared load each VOA on to the Varian Archon.

10.2.3 Carry out the following purge-and-trap analysis procedure for each standard.

10.3 After loading into the Archon Autosampler the sample will be purged for 11 minutes. When the 11 min purge cycle is complete the purge and trap system will automatically be prompted to a dry purge cycle, then a one min desorb mode, and begin to temperature program the GC. Introduce the trapped materials to the GC column by rapidly heating the trap to 250 ºC while back flushing the trap with an inert gas between 20 and 60 mL/min for one minute. If rapid heating of the trap cannot be achieved, the GC column must be used as a secondary trap by cooling it to 30 ºC (sub ambient temperature, if problems persist) instead of the initial program temperature of 45 ºC.

After desorbing the sample for one minute, the trap is reconditioned by a 10 to 20min bake cycle at 250ºC. When the trap is cool, the next sample will begin the purge and trap cycle.

10.4 Chemstation tabulates the area response of the characteristic ions (see Table 1) against concentration for each compound and each internal standard and calculates relative response factors (RRFs) for each compound relative to one of the internal standards. The internal standard selected for the calculation of the RRF for a compound is the internal standard that has a retention time closest to the compound being measured. The RRF calculation is as follows:

$$RRF = A_x C_{is} / A_{is} C_x$$

where:
RRF = Relative response factor
A_X = Area of the characteristic ion for the compound being measured
A_{IS} = Area of the characteristic ion for the specific internal standard IS
C_X = Concentration of the compound being measured (ng on column)
C_{IS} = Concentration of the specific internal standard (ng on column)

10.5 Chemstation calculates the % RSD for each compound as follows:

$$\%RSD = (SD / RRF_A) \times 100$$

where:
%RSD = Percent Relative Standard Deviation
SD = Standard Deviation
RRF_A = Average Relative Response Factor

10.5.1 If the (%RSD) of the response factor for any target analyte is ≤15% over the working range, linearity through the origin can be assumed, and the average response factor calibration mode can be used in place of a calibration curve for that analyte.

If the average %RSD of all spiked analytes in the initial calibration is >15%, the laboratory has the following options:

10.5.2 Review the results (area counts, response factors) for those analytes which failed the %RSD acceptance criteria to determine if the problem is with just one of the standards. Should this be the case, the analyst has the option to reanalyze and replace the standard in question.

10.5.3 The calibration range may be narrowed by replacing one or more of the standards with standards of different concentrations.

10.5.4 If the high standard is dropped, more dilutions may be required.

10.5.5 If the low standard is dropped, the analyst must verify that changing the low standard concentration will not affect any client DQO's (or that the new quantitation level is at least as low as any required regulatory limits or action levels).

10.5.6 For those analytes with RSD > 15%, the laboratory may use a linear regression or quadratic fit analysis to establish the curve and use for quantitation. The instrument response is treated as the dependent variable (y) and the concentration as the independent variable (x). The regression will produce the slope and intercept terms for a linear equation in the form:

$$y = mx + b$$

where:
y = Instrument response (ratio of standard response to IS response) [Ax/Ais] m = Slope of the line (also called the coefficient of x)(ratio of standard concentration to IS concentration) [Cis/Cx]
x = Concentration of the calibration standard
b = intercept

10.5.7 The line must not be forced through the origin. (Do not include the origin [0,0] as the sixth point!) The regression calculation will generate a correlation coefficient (r) that is a measure of the "goodness of fit" of the regression line to the data. A value of 1.00 indicates a perfect fit. The correlation coefficient must be r(0.990) ($r^2$0.980).

10.5.8 The calculated intercept value must also be evaluated before reporting sample results. A positive value for the intercept indicates that there is some threshold instrument response, which is the limiting factor in establishing linearity. A negative intercept value can be transformed into an x-intercept value that represents a threshold concentration, which is the limitation. If the intercept is positive, then, as a general rule, results where the instrument response is less than three times (3x) the intercept value may be unreliable. This will afford some protection against false positive results. If the intercept is negative, results below the concentration of the lowest concentration calibration standard may be unreliable. These adjustments to the quantitation limits will apply to all samples analyzed using the regression line. In calculating sample concentrations, the regression equation is rearranged to solve for the concentration (x), as shown below.

$$x(yb/m)$$

10.5.9 An acceptable approach is to raise the reporting limit to above the y-intercept (or at least meet the y-intercept) if it would not change required client-reporting limits. The analyst must first check the Project Summary to determine if raising the RL exceeds action levels. This must be approved by the laboratory manager prior to reporting of the data package.

10.6 System Performance Check Compounds (SPCC)

10.6.1 A system performance check must be made before the calibration curve is used. Five system performance check compounds (SPCCs) are evaluated for a minimum average response factor.

Compound	Minimum Mean RRF
Chloromethane	0.10
1,1,-Dichloroethane	0.10
Bromoform	0.10
Chlorobenzene	0.30
1,1,2,2,-Tetrachloroethane	0.30

10.6.2 These compounds are used to check compound instability and to check for degradation caused by contaminated lines or active sites in the system.

10.6.3 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

10.6.4 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 inthe 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 ration relative to m/z 95 may improve bromoform response.

10.6.5 Tetrachloroethane and 1,1-Dichloroethane are degraded by contaminated transfer lines in purge and-trap 9.4.2.3 systems and/or active sites.

10.6.6 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.

10.7 Calibration Check Compounds (CCC)

10.7.1 The purpose of the CCCs a re 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.***

10.7.2 The RSD of the Response Factor for each individual Calibration Check Compound (CCC) must be ≤30%. The CCCs are:

1,1-Dichloroethene	Toluene
Chloroform	Ethylbenzene
1,2-Dichloropropane	Vinyl chloride

10.7.3 If a % 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. The relative retention times of each compound in each calibration standard should agree within 0.06 relative retention time units. ***NOTE:*** *All CCCs must have <30% RSD for the calibration to be considered valid. If the average RF calibration model is used for a CCC, that CCC must have a <15% RSD.*

10.8 Relative Retention Time

10.8.1 The relative retention times (RRT) of each compound in each calibration run should agree to ±0.06 relative retention time units.

10.8.1.1 Internal standard - 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 mid-level standard of the most recent initial calibration, then the chromatographic system must be inspected for malfunctions and corrections must be made, as required. After corrections are made, reanalysis of the affected samples is required.

10.9 Initial Calibration Ve rification (ICV)

10.9.1 The initial calibration curve must be verified after the calibration is performed with a mid-level standard. A Quality Control Standard must be evaluated after calibration. The QCS is from a different source than the CCV and ICV.

10.9.2 The percent drift from the initial calibration must be within ± 20% for CCC compounds. If the ICV standard fails the acceptance criteria the standard should be reanalyzed immediately. If the standard fails again, the analysis is stopped and a new initial calibration is performed.

10.10 Continuing Calibration Verification (CCV)

10.10.1 The calibration curve for each compound of interest must be verified daily or once every 12 hours of analysis time. Each CCC analyte must recover at ± 20%, and SPCC criteria must be met.

10.10.2 The internal standard responses in the CCV must be evaluated immediately after or during data acquisition.

10.10.3 If the retention time for any internal standard changes by more than 30 seconds from the last calibration check, the chromatographic system must be inspected for malfunctions and corrections must be made, as required.

10.10.4 If the EICP area for any of the internal standards changes by a factor of two (-50% to +100%) from the mid-level standard of the initial calibration, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate. After corrections are made, reanalysis of the affected samples is required.

11.0 Procedure

11.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

11. 1.1Analysis of Water Samples

11.1.2 (For 10.0 mL samples purged using a VARIAN ARCHON): Fill the a 10.0 mL syringe barrel passed the 10mL mark with the sample. Bring to 10mL volume onto a pH strip. Record in excel if PH>2. Replace the syringe plunger and slowly compress the plunger, dispensing the sample into assigned 40 mL VOA. Inject 10 uL of 25ppm IS/SS standard solution, which include surrogates, internal standards, by slowly adding the standard solution to the 40 mL VOA vial and place in the appropriate slot on the auto sampler. Ensure that the vial cap is tight so as to avoid leakage.

11.1.3 (For 25.0 mL samples purged using a VARIAN ARCHON): Fill the a 25.0 mL syringe barrel passed the 25mL mark with the sample. Bring to 25mL volume onto a pH strip. Record in excel if PH>2. Replace the syringe plunger and slowly compress the plunger, dispensing the sample into assigned 40 mL VOA. Inject 10 uL of 25ppm IS/SS standard solution, which include surrogates, internal standards, by slowly adding the standard solution to the 40 mL VOA vial and place in the appropriate slot on the auto sampler. Ensure that the vial cap is tight so as to avoid leakage.
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11.1.4 Carry out the purge-and-trap analysis procedure for each sample.

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11.2 Analysis of Sediment/Soil and Waste Samples

- Samples are received in brass or stainless steel tubes with zero headspace at ≤ 6ºC.
- Extractions open the cap and scrapes off a thin layer of soil from the surface, and weighs 10 g of sample into a 20 mL VOA.
- 10 mL extraction solvent is added. Extraction solvent is 20% water and 80% 1,5-pentanediol
- The VOA is vortexed for 5 minutes, then centrifuged for 30 minutes (NOTE: this step is not temperature controlled!).
- The centrifuged VOA is given to the VOC analyst, who withdraws 2 mL of extract with a Luer-lok syringe. The Luer-lok syringe should have 8ml reagent water in the barrel before pulling the 2ml of sample extract. The total 10ml are injected into a 43 mL VOA. IS and SS is then added to the VOA. The VOA is then capped tightly and loaded into the auto sampler.
- Smaller volumes of extract are added if dilution is needed.
- Results are always reported out on a wet-weight basis

11.3 In order to produce acceptable sample results, the response of the analyte must be within the working range established by the initial calibration.

11.4 The extrapolation of the calibration to concentrations above or below those of the actual calibration standards is not permitted.

11.5 A method blank is analyzed once for every 12 hour analytical sequence to determine whether or not the analysis has introduced any contamination to the samples.

11.6 Results from the method blank ***are not*** subtracted from the samples.

11.7 When method or solvent blanks are not used after the analysis of high level samples, the results for at least two of the following samples are carefully reviewed to determine if there was any contamination. If the analytes are not present in the samples following the highly concentrated sample, that data is usable. Otherwise, the samples are reanalyzed.

12. Data Analysis and Calculation

12.1 Identification

12.1.1 The qualitative identification of compounds 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.

12.1.2 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.

12.1.3 The relative retention time (RRT) of the sample component is within ± 0.06 RRT units of the RRT of the standard component.

12.1.4 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%

12.1.5 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 achieve 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.

12.1.6 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.

12.1.7 Examination of extracted ion current profiles of appropriate ions can aid in the selection of spectra, and in qualitative identification of compounds. When analytes co elute (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 co eluting compound.

12.1.8 For samples containing components not associated with the calibration standards, a library search may be made for the purpose of tentative identification. The analyst must review the Project Summary or contact the LPM if there are any questions. Data system library search routines should not use normalization routines that would misrepresent the library or unknown spectra when compared to each other. Use the following guidelines for making tentative identifications:

12.1.8.1 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.

12.1.8.2 The relative intensities of the major ions should agree within +/- 20%. For example, an ion with an abundance of 50% in the standard spectrum, the corresponding sample ion abundance must be between 30 and 70%.

12.1.8.3 Molecular ions present in the reference spectrum should be present in the sample spectrum.

12.1.8.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible background contamination or presence of co eluting compounds.

12.1.8.5 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 co eluting peaks. Data system library reduction programs can sometimes create these discrepancies.

12.2 Quantitative Determination

12.2.1 When 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. Quantitation will take place using the internal standard technique. The internal standard used shall be the one nearest the retention time of the given analyte.

12.2.2 Chemstation calculates the ng of each identified analyte in the sample (water and soil) as follows:

$$C_{samp} = \frac{A_{samp} \cdot C_{is}}{A_{is} \cdot RRF}$$

where:
C_{samp} = Sample concentration in ng
A_{samp} = Area for characteristic ion for compound being measured in the sample
C_{is} = Concentration of the injected internal standard (ng)
A_{is} = Area of characteristic ion for the internal standard
RRF = Average relative response factor of compound being measured from initial calibration

12.2.3 Where applicable, an estimate of concentration for noncalibrated components in the sample should be made. The formulae given above should be used with the following modifications: The areas A_{samp} and A_{is} should be from the total ion chromatograms, and the RRF for the compound should sample is be assumed to be 1. The concentration obtained 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.

12.2.4 The final concentration calculations for water samples in µg/L is:

$$C_{samp(\mu g/L)} = \frac{Raw(ng)}{volumepurged(ml)} \times \frac{1\mu g}{1000ng} \times \frac{1000ml}{1L}$$

12.2.5 The final concentration for soils, solids ect in mg/kg is:

$$C_{samp(mg/kg)} = \frac{Raw(ng)}{volumepurged(ml)} \times \frac{extractionsolvent(ml)}{sampleweight(gr)} \times \frac{1mg}{1000000ng} \times \frac{1000gr}{1kg}$$

13 Method Performance

13.1 This method was tested by 15 laboratories using reagent water, drinking water, surface water, and industrial wastewaters spiked at six concentrations over the range 5-600 µg/L.12 Single operator precision, overall precision, and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix.

14 Pollution Prevention

14.1 This method does not contain any specific modifications that serve to minimize or prevent pollution. The chemicals used in this method pose little threat to the environment when properly managed. All standards and reagents should be prepared in volumes consistent with laboratory use to minimize the volume of disposable waste.

14.2 For further information on pollution prevention 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 NW, Washington D.C. 20036, (202) 872-4477.

15 Data assessment and acceptance criteria for quality control measures.

15.1 See section 9.

16 Corrective Actions for out of control data.

16.1 Refer to SOP MAI02-NC/CAR/PR, Nonconformance/Corrective Action Report (NC/CAR/PR) Procedure.

17 Contingencies for handling out of control data or unacceptable data.

17.1 Contact the laboratory manager or technical manager to assess out of control data.

18 Waste Management

18.1All wastes must be disposed of safely, samples and extracts are disposed of following laboratory SOP.

19 References

19.1 United States Environmental Protection Agency. 1997. Test Methods for Evaluating Solid Waste. Physical/Chemical Methods. EPA SW-846, 3rd Edition, Method 8260B. U.S. EPA, Washington, D.C.