Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites

Volume II: Analytical Method Summaries

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The Canadian Council of Ministers of the Environment (CCME) is the major intergovernmental forum in Canada for discussion and joint action on environmental issues of national, international and global concern. The 13 member governments work as partners in developing nationally consistent environmental standards, practices and legislation.

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Abstract

This manual is one of a series of technical support documents being prepared under the National Contaminated Sites Remediation Program of the Canadian Council of Ministers of the Environment (CCME). Use of this manual will provide a consistent approach to sampling, analysis, and data management for contaminated sites on a national basis. The primary objectives of this manual are

- to provide guidance for sampling and analyzing complex environmental matrices, such that the data obtained will be representative and of known quality

- to reduce selection of the many available methods in use to a few of the best so that future analytical data from multiple participating laboratories will be consistent and comparable

The manual stresses the significance of quality assurance (QA)/quality control (QC) and planning, and emphasizes the interdependence of sampling, analysis, and data management objectives in the planning and execution of tasks within each of these three areas. It focuses on the specific analytes identified in the CCME's Interim Environmental Quality Criteria for Contaminated Sites, which was published in September 1991.

In Volume I, Main Report, Chapter 1 introduces the subject matter covered in this manual. Chapter 2 is devoted to the principles and problems involved with obtaining representative samples from the four matrices: soils, sediments, surface waters, and groundwater. Topics include problems unique to each matrix and considerations in obtaining representative samples, selecting sampling locations and equipment, and preserving samples after they have been collected.

Chapter 3 provides a brief discussion of the criteria that are important in selecting appropriate analytical methods. Chapter 4 describes the criteria for selecting analytical methods. Chapter 5 discusses data management, including such topics as data recording and documentation, data custody and transfer, and data validation, completeness, comparability, compatibility, review, verification, handling, and transmission. A final section addresses data reporting by laboratories and data presentation in final reports.

A glossary of scientific terms used is included at the end.

Volume II, Analytical Method Summaries, provides method summaries for the analytes in a consistent format that identifies all the information needed to decide whether to use that method in preference to another, and if so, what major analytical instrumentation would be required. A method summary includes sample preparation, potential interferences, QC requirements, comments on use, and, where applicable, comparison with other methods. For detailed information, however, users are advised to look up the original references. A list of unpublished analytical methods that are used by various federal, provincial, and commercial laboratories is provided in an appendix. Volume II is available in hard copy format or on a computer diskette.

Résumé

Le présent document fait partie d'une série de guides techniques préparés dans le cadre du Programme national d'assainissement des lieux contaminés du Conseil canadien des ministres de l'environnement. Cet ouvrage permettra d'harmoniser à l'échelle nationale l'échantillonnage, l'analyse des échantillons et la gestion des données. Ses deux principaux objectifs sont les suivants :

- constituer un guide pour l'échantillonnage et l'analyse de matrices environnementales complexes de manière à ce que les données obtenues soient représentatives et de qualité reconnue;

- choisir les meilleures méthodes parmi celles qui existent de manière à ce que les données analytiques fournies par les laboratoires participants soient plus cohérentes et comparables.

Dans tout le document, on insiste sur l'importance de l'assurance de la qualité (AQ) et du contrôle de la qualité (CQ). Par ailleurs, on insiste sur l'interdépendance des objectifs de l'échantillonnage, de l'analyse des échantillons et de la gestion des données en ce qui a trait à la planification et à l'exécution des tâches dans chacun de ces trois domaines. Le document porte particulièrement sur les substances mentionnées dans les Critères provisoires canadiens de qualité environnementale pour les lieux contaminés qui ont été publiés en septembre 1991.

Dans le Volume I, Rapport principal, le Chapitre 1 présente le sujet de manière générale. Le Chapitre 2 est consacré aux principes et aux problèmes relatifs au prélèvement d'échantillons représentatifs à partir de quatre matrices, en l'occurrence des sols, des sédiments, des eaux superficielles et des eaux souterraines. Les thèmes traités sont entre autres les suivants : problèmes particuliers liés à chaque matrice, considérations relatives à l'obtention d'échantillons représentatifs, sélection des points de prélèvement et de l'équipement et conservation des échantillons après le prélèvement.

Le Chapitre 3 expose brièvement les critères qui sont importants dans le choix de méthodes d'analyse appropriées. Dans le Chapitre 4, on décrit les critères de sélection des méthodes d'analyse. Le Chapitre 5 porte sur la gestion des données. On y traite entre autres de la présentation des données et de la documentation, de la garde et du transfert des données, de la validation des données, de l'intégralité des données, de leur compatibilité, de leur révision, de leur vérification, de leur traitement et de leur transmission. Une dernière section porte sur les données fournies par les laboratoires et sur la présentation des données dans les rapports finaux.

Un glossaire des termes scientifiques employés est inclus en appendice à la fin du manuel.

Dans le Volume II, on présente les sommaires des méthodes applicables aux substances spécifiées, de manière à fournir toute l'information nécessaire pour choisir une méthode de préférence à une autre et pour connaître les principaux appareils d'analyse requis. Un sommaire de la méthode comprend la préparation des échantillons, les interférences potentielles, les exigences relatives au contrôle de la qualité, des remarques sur l'utilisation et, le cas échéant, des comparaisons avec d'autres méthodes. On recommande toutefois aux utilisateurs de consulter les références originales pour plus de détails. Une liste des méthodes d'analyse inédites qui sont utilisées par divers laboratoires fédéraux, provinciaux et commerciaux se trouve dans un annexe. Le Volume II existe sous forme imprimée ou sur disquette.

Acknowledgements

This guidance manual was prepared under contract to Radian Canada Inc.; Dr. Lawrence H. Keith acted as group leader. During its preparation, this document was extensively reviewed by members of the CCME's Contaminated Sites Advisory Committee, selected Environment Canada scientific personnel, and a number of commercial laboratories. The reviewers who devoted their valuable time and expertise are gratefully acknowledged. Special thanks are due to Anar S. Baweja and T.W. Foote of Environment Canada; Dr. Baweja acted as scientific authority and Mr. Foote provided general guidance.

Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites

Volume II: Analytical Method Summaries

Recommended Analytical Method Summaries

There are usually multiple analytical methods for most of the analytes of interest to the National Contaminated Sites Remediation Program (Table 1). Criteria for selecting recommended methods and the types of analytes covered by these methods were discussed in Chapter 4 of Volume I. The methods summaries are presented in this volume.

Each method summary contains the following format:

Title - The full title is listed under this heading.

Reference - The literature reference source is provided under this heading.

Method Applicability - A brief description of the applicable matrices is provided. This is especially important when the diskette version is searched for methods by desired matrices.

Sample Preparation - This section describes how the sample must be prepared before it can be analyzed. It includes requirements for extraction, concentration, digestion, etc.

Instrumental Analysis - A description of the overall analytical process, including any special method requirements is provided.

Instrumentation Required - All critical instrumentation, including specific chromatographic columns and non-routine laboratory apparatus, is listed under this heading.

Interferences - Known sources of interferences are documented under this heading. Interferences from common sources of contamination as well as from other analytes likely to be in a sample are covered. These are especially important for keywords to search for in the diskette version of these method summaries so that methods susceptible to interferences which are, or may likely be present, can be avoided and other methods selected in their place.

Table 1. All Analytes Covered by Method, Including Representative Compounds

Method	Analytes Covered
U.S. EPA Method 502.2, Rev. 2	Benzene, Carbon tetrachloride, Chlorobenzene, Chloroform; 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,1-Dichloroethane, 1,2-Dichloroethane, 1,1-Dichloroethene, cis-1,2-Dichloroethene, trans-1,2-Dichloroethene, 1,2-Dichloropropane, cis-1,3-Dichloropropene, trans-1,3-Dichloropropene, Ethylbenzene, Methylene chloride, Naphthalene, Styrene, 1,1,2,2-Tetrachloroethane, Tetrachloroethene, Toluene, 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethene, o-Xylene, m-Xylene, p-Xylene
U.S. EPA Method 505, Rev. 2	Aldrin, Chlordane, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Lindane, Methoxychlor, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260
U.S. EPA Method 507, Rev. 2	Diazinon
U.S. EPA Method 515.1, Rev. 4	2,4-D, Pentachlorophenol
U.S. EPA Method 524.2, Rev. 3	Benzene, Carbon tetrachloride, Chlorobenzene, Chloroform, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,1-Dichloroethane, 1,2-Dichloroethane, 1,1-Dichloroethene, cis-1,2-Dichloroethene, trans-1,2-Dichloroethene, 1,2-Dichloropropane, cis-1,3-Dichloropropene, trans-1,3-Dichloropropene, Ethylbenzene, Methylene chloride, Naphthalene, Styrene, 1,1,2,2-Tetrachloroethane, Tetrachloroethene, Toluene, 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethene, o-Xylene, m-Xylene, p-Xylene
U.S. EPA Method 531.1, Rev. 3	Carbaryl, Carbofuran
SM 6220C	Benzene, Chlorobenzene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, Ethylbenzene, Styrene, Tetrachloroethene, Toluene, 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, Trichloroethene, m-Xylene, o-Xylene, p-Xylene
SM 6410B	Benzo(a)anthracene, Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, bis(2-Ethylhexyl) phthalate, Butyl benzyl phthalate, Chlordane, 4,4'-DDT, Dibenzo(a,h)anthracene, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, Dieldrin, Diethyl phthalate, Dimethyl phthalate, Di-n-octyl phthalate, Heptachlor, Heptachlor epoxide, Hexachlorobenzene, Indeno(1,2,3-cd)pyrene, Naphthalene, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260, Pyrene, 1,2,4-Trichlorobenzene
SM 6420B	2-Chlorophenol, 2,4-Dichlorophenol, 2,4-Dimethylphenol, 2,4-Dinitrophenol, 2-Methyl-4,6-dinitrophenol, Pentachlorophenol, Phenol, 2,4,6-Trichloropheno

Table 1. Continued

Method	Analytes Covered
U.S. EPA Method 8080B, Rev. 2	Aldrin, γ-BHC (Lindane), Chlordane (technical), 4,4'-DDT, Dieldrin, Endrin, Heptachlor, Heptachlor epoxide, Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260
U.S. EPA Method 8240B, Rev. 2	Benzene, Carbon tetrachloride, Chlorobenzene, Chloroform, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,1-Dichloroethane, 1,2-Dichloroethane, 1,1-Dichloroethene, trans-1,2-Dichloroethene, 1,2-Dichloropropane, cis-1,3-Dichloropropene, trans-1,3-Dichloropropene, Ethylbenzene, Styrene, 1,1,2,2-Tetrachloroethane, Tetrachloroethene, Toluene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethene
U.S. EPA Method 8260A, Rev. 1	Benzene, Carbon tetrachloride, Chlorobenzene, Chloroform, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 1,1-Dichloroethane, 1,2-Dichloroethane, 1,1-Dichloroethene, cis-1,2-Dichloroethene, trans-1,2-Dichloroethene, 1,2-Dichloropropane, Ethylbenzene, Methylene chloride, Naphthalene, Styrene, 1,1,2,2-Tetrachloroethane, Tetrachloroethane, Toluene, 1,2,3-Trichlorobenzene, 1,2,4-Trichlorobenzene, 1,1,1-Trichloroethane, 1,1,2-Trichloroethane, Trichloroethene, o-Xylene, m-Xylene, p-Xylene
U.S. EPA Method 8270B, Rev. 2	Aroclor 1242, Aroclor 1248, Aroclor 1254, Aroclor 1260, Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(a)pyrene, γ-BHC (Lindane), bis(2-Ethylhexyl) phthalate, Butyl benzyl phthalate, Carbaryl, Carbofuran, 2-Chlorophenol, 4,4'-DDT, Dibenz(a,h)anthracene, Di-n-butyl phthalate, 1,2-Dichlorobenzene, 1,3-Dichlorobenzene, 1,4-Dichlorobenzene, 2,4-Dichlorophenol, 2,6-Dichlorophenol, Diethyl phthalate, 2,4-Dimethylphenol, Dimethyl phthalate, 4,6-Dinitro-2-methylphenol, 2,4-Dinitrophenol, Di-n-octyl phthalate, Endrin, Heptachlor, Hexachlorobenzene, Indeno(1,2,3-cd)pyrene, Methoxychlor, Naphthalene, Parathion, Pentachlorobenzene, Pentachlorophenol, Phenanthrene, Phenol, Pyrene, 1,2,4,5-Tetrachlorobenzene, 2,3,4,6-Tetrachlorophenol, 1,2,4-Trichlorobenzene, 2,4,5-Trichlorophenol, 2,4,6-Trichlorophenol
Method Environment Canada 1/RM/3 (revised)	2,3,7,8-T_4CDD, 2,3,7,8-T_4CDF, 1,2,3,7,8-P_5CDD, 1,2,3,7,8-P_5CDF, 2,3,4,7,8-P_5CDF, 1,2,3,4,7,8-H_6CDD, 1,2,3,6,7,8-H_6CDD, 1,2,3,7,8,9-H_6CDD, 1,2,3,4,7,8-H_6CDF, 1,2,3,6,7,8-H_6CDF, 1,2,3,7,8,9-H_6CDF, 2,3,4,6,7,8-H_6CDF, 1,2,3,4,6,7,8-H_7CDD, 1,2,3,4,6,7,8-H_7CDF, 1,2,3,4,7,8,9-H_7CDF, OCDD, OCDF
Method Environment Canada 1/RM/19	2,3,7,8-T_4CDD, 2,3,7,8-T_4CDF, 1,2,3,7,8-P_5CDD, 1,2,3,7,8-P_5CDF, 2,3,4,7,8-P_5CDF, 1,2,3,4,7,8-H_6CDD, 1,2,3,6,7,8-H_6CDD, 1,2,3,7,8,9-H_6CDD, 1,2,3,4,7,8-H_6CDF, 1,2,3,6,7,8-H_6CDF, 1,2,3,7,8,9-H_6CDF, 2,3,4,6,7,8-H_6CDF, 1,2,3,4,6,7,8-H_7CDD, 1,2,3,4,6,7,8-H_7CDF, 1,2,3,4,7,8,9-H_7CDF, OCDD, OCDF
U.S. EPA Method 8280, Rev. 0	1,2,3,4,7,8-H_6CDD, 1,2,3,6,7,8-H_6CDD, 1,2,3,4,6,7,8-H_7CDD, OCDD, 2,3,7,8-TCDF, 2,3,7,8-TCDD, 1,2,3,7,8-P_5CDF, 1,2,3,4,7,8-H_6CDF, 1,2,3,7,8-P_5CDD, 1,2,3,4,6,7,8-H_7CDF, OCDF
U.S. EPA Method 8290, Rev. 0	2,3,7,8-T_4CDD, 1,2,3,7,8-P_5CDD, 1,2,3,4,7,8-H_6CDD, 1,2,3,6,7,8-H_6CDD, 1,2,3,7,8,9-H_6CDD, 1,2,3,4,6,7,8-H_7CDD, OCDD, 2,3,7,8-T_4CDF, 1,2,3,7,8-P_5CDF, 2,3,4,7,8-P_5CDF, 1,2,3,4,7,8-H_6CDF, 1,2,3,6,7,8-H_6CDF, 1,2,3,7,8,9-H_6CDF, 2,3,4,6,7,8-H_6CDF, 1,2,3,4,6,7,8-H_7CDF, 1,2,3,4,7,8,9-H_7CDF, OCDF

Table 1. Continued

Method	Analytes Covered
U.S. EPA Method 340.2	Fluoride
SM 3111B	Antimony, Cadmium, Chromium (total), Cobalt, Copper, Lead, Nickel, Silver, Thallium, Tin, Zinc
SM 3111D	Barium, Beryllium, Molybdenum, Vanadium
SM 3112B	Mercury
SM 3113B	Antimony, Arsenic, Barium, Beryllium, Cadmium, Chromium (total), Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Silver, Tin
SM 3114B	Arsenic, Selenium
SM 3120B	Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Chromium (total), Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Silver, Thallium, Vanadium, Zinc
U.S. EPA Method 6010, Rev. 0	Antimony, Arsenic, Barium, Beryllium, Boron, Cadmium, Chromium (total), Cobalt, Copper, Lead, Molybdenum, Nickel, Selenium, Silver, Thallium, Vanadium, Zinc
U.S. EPA Method 7196, Rev. 0	Chromium, Hexavalent
U.S. EPA Method 7470A, Rev. 1	Mercury in Liquid Waste (Manual Cold Vapor Technique)
U.S. EPA Method 7471A, Rev. 1	Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique)
SAR	Sodium Adsorption Ratio
U.S. EPA Method 7870, Rev. 0	Tin
U.S. EPA Method 9012, Rev. 0	Total cyanide and amenable cyanide (which includes free cyanide)
U.S. EPA Method 9040A, Rev. 1	pH
U.S. EPA Method 9050A, Rev. 1	Specific Conductance

Quality Control Requirements - QC requirements vary greatly among the methods and often very specific internal standards, calibration curves, blanks, replicate analyses, and other requirements are necessary to obtain reliable data. These are documented in this section of the method summaries.

Comparison with Other Methods - Because there are often multiple methods for a particular analyte, a brief comparison of the advantages and disadvantages of applicable methods is helpful in selecting one method instead of another. These comparisons are made, where appropriate, in this section.

Analytes Covered by this Method - Many methods cover multiple analytes, not all of which are target compounds for the National Contaminated Sites Remediation Program. All analytes for each method summarized are listed in a table and those analytes targeted by the National Contaminated Sites Remediation Program are flagged with an asterisk after their name.

Comments on Use of this Method - This final section is used to document special problems, notations, requirements and comments about the use or performance of methods which were not covered in the other sections.

Title:

Volatile Organic Compounds in Water by Purge and Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series. U.S. EPA Method 502.2, Revision 2, 1989.

Reference:

Methods for the Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH, 45268, USA.

Method Applicability:

Drinking water and raw source water. The latter should include most surface water and groundwater sources.

Sample Preparation:

Remove the plungers from two 5-mL syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. Add 10 µL of the internal calibration standard to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

Instrumental Analysis:

An inert gas (zero grade nitrogen or helium) is bubbled through a 25 mL or a 5 mL water sample (depending on the expected concentration of the analytes). Purged sample components are trapped in a tube of sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample onto a capillary GC column. The column is temperature programmed to separate the method analytes which are then detected with a photoionization detector (PID) and an electrolytic conductivity (ELCD) placed in series. The PID is selective for aromatic compounds and the ELCD is selective for halogenated compounds.

Instrumentation Required:

Gas Chromatography System: Column #1: VOCOL glass wide-bore capillary column; Column #2: RTX-502.2 mega-bore capillary column; Column #3: DB-62 mega-bore capillary column. A series configuration of a high temperature photoionization detector (PID) equipped with 10.0 eV (nominal) lamp and electroconductivity detector (ELCD) is required. Also required is an all-glass 5 mL purging device, a sorbent trap, and a thermal desorption apparatus which is connected to the GC system.

Interferences:

Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for many contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-plastic coating, non-plastic thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. Method blanks prepared from reagent water and analyzed under the same conditions as the samples can identify these interferences. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of method blanks to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample. Recondition of traps containing combinations of silica gel and coconut charcoal is performed to minimize release of residual water from previous analyses.

Samples also 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 field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination. The laboratory where volatile analysis is performed and also the refrigerated storage area should be completely free of solvents.

Quality Control Requirements:

As an initial demonstration of lab accuracy and precision, analyze 4 to 7 replicates of a lab fortified blank containing analyte at 0.1 - 5 µg/L. Collect all samples in duplicate. Surrogate analytes (similar to those of the analytes of interest), whose concentration is known in every sample, are measured using the same internal standard calibration procedure. Duplicate field reagent water blanks (trip blanks) must be analyzed with each set of samples, laboratory reagent blanks (method blanks) must be analyzed with each batch of samples processed as a group within a work shift. Also, a single laboratory-fortified blank that contains each of the analytes of interest should be analyzed with each batch of samples processed as a group within a work shift. A 3 to 5 point calibration curve is needed depending on the calibration range factor required.

Comparison with Other Methods:

This method uses capillary GC columns which provide excellent chromatographic resolution of 60 volatile organic compounds. It also uses a PID and ELCD in series for detectors. These provide good sensitivity but not as good specificity for analyte detection as mass spectrometry. The purge-and-trap technique requires little in the way of sample preparation and accommodates most water matrices.

Its disadvantage over GC methods that use more selective detectors (such as EPA Methods 524.2 and 8240 which use mass spectrometers as detectors) is that it will usually produce more false positives because of its lesser selectivity. Its advantage over GC/MS methods is lesser capital expense for the instrumentation and a resulting lesser cost of analysis.

Another disadvantage, in comparison to EPA Method 8020, is that the latter may also be used with soil and sediment matrices whereas Method 502.2 is limited to relatively clean water matrices. Its advantage over EPA Method 8020 is that the latter only uses a photoionization detector. Thus, Method 8020 can not be used for halogenated compounds and, lacking a second detector in series, will be more prone to interferences and false positive identifications.

Analytes Covered by this Method:

Method 502.2 covers 60 volatile organic compounds including all of the monocyclic aromatic hydrocarbons, naphthalene and 17 of the chlorinated hydrocarbons that are of interest to the National Contaminated Sites Remediation Program as shown in Tables 2 and 3.

Table 2. Analytes Covered by U.S. EPA Method 502.2, Rev. 2, Using an Electrolytic Conductivity Detector

Analyte Name	CAS No.	Range[a] (µg/L)	Method Det. Limit[b] (µg/L)	Mean Accuracy[c] (Avg % Recovery)	Precision[c] (Rel. Std. Dev. %)
Benzene*	71-43-2	0.02-200	Not listed	Not listed	Not listed
Bromobenzene	108-86-1	0.02-200	0.03	97	2.7
Bromochloromethane	74-97-5	0.02-200	0.01	96	3.0
Bromodichloromethane	75-27-4	0.02-200	0.02	97	2.9
Bromoform	75-25-2	0.02-200	1.6	106	5.2
Bromomethane	74-83-9	0.02-200	1.1	97	3.8
n-Butylbenzene	104-51-8	0.02-200	Not listed	Not listed	Not listed
sec-Butylbenzene	135-98-8	0.02-200	Not listed	Not listed	Not listed
tert-Butylbenzene	98-06-6	0.02-200	Not listed	Not listed	Not listed
Carbon tetrachloride*	56-23-5	0.02-200	0.01	92	3.6
Chlorobenzene*	108-90-7	0.02-200	0.01	103	3.6
Chloroethane	75-00-3	0.02-200	0.1	96	3.9
Chloroform*	67-66-3	0.02-200	0.02	98	2.5
Chloromethane	74-87-3	0.02-200	0.03	96	9.2
2-Chlorotoluene	95-49-8	0.02-200	0.01	97	2.7
4-Chlorotoluene	106-43-4	0.02-200	0.01	97	3.2
Dibromochloromethane	124-48-1	0.02-200	0.3	102	3.3
1,2-Dibromo-3-chloropropane	96-12-8	0.02-200	3.0	86	11.3
1,2-Dibromoethane	106-93-4	0.02-200	0.8	97	2.8
Dibromomethane	74-95-3	0.02-200	2.2	109	6.7
1,2-Dichlorobenzene*	95-50-1	0.02-200	0.02	100	1.5
1,3-Dichlorobenzene*	541-73-1	0.02-200	0.02	106	4.0
1,4-Dichlorobenzene*	106-46-7	0.2-20	0.01	98	2.3
Dichlorodifluoromethane	75-71-8	0.02-200	0.05	89	6.6
1,1-Dichloroethane*	75-34-3	0.02-200	0.07	100	5.7

Table 2. Continued

Analyte Name	CAS No.	Range[a] (µg/L)	~Method Det. Limit[b] (µg/L)	Mean Accuracy[c] (Avg % Recovery)	Precision[c] (Rel. Std. Dev. %)
1,2-Dichloroethane*	107-06-2	0.02-200	0.03	100	3.8
1,1-Dichloroethene*	75-35-4	0.02-200	0.07	103	2.8
cis-1,2-Dichloroethene*	156-59-4	0.02-200	0.01	105	3.3
trans-1,2-Dichloroethene*	156-60-5	0.02-200	0.06	99	3.7
1,2-Dichloropropane*	78-87-5	0.02-200	0.01	103	3.7
1,3-Dichloropropane	142-28-9	0.02-200	0.03	100	3.4
2,2-Dichloropropane	590-20-7	0.02-200	0.05	105	3.4
1,1-Dichloropropene	563-58-6	0.02-200	0.02	103	3.3
cis-1,3-Dichloropropene*	10061-01-5	Not listed	Not listed	Not listed	Not listed
trans-1,3-Dichloropropene*	10061-02-6	Not listed	Not listed	Not listed	Not listed
Ethylbenzene*	100-41-4	0.02-200	Not listed	Not listed	Not listed
Hexachlorobutadiene	87-68-3	0.02-200	0.02	98	8.3
Isopropylbenzene	98-82-8	0.02-200	Not listed	Not listed	Not listed
4-Isopropyltoluene	99-87-6	0.02-200	Not listed	Not listed	Not listed
Methylene chloride*	75-09-2	0.02-200	0.02	97	2.9
Naphthalene*	91-20-3	0.02-2000	Not listed	Not listed	Not listed
n-Propylbenzene	103-65-1	0.02-200	Not listed	Not listed	Not listed
Styrene*	100-42-5	0.02-2000	Not listed	Not listed	Not listed
1,1,1,2-Tetrachloroethane	630-20-6	0.02-200	0.01	99	2.3
1,1,2,2-Tetrachloroethane*	79-34-5	0.02-200	0.01	99	6.8
Tetrachloroethene*	127-18-4	0.02-200	0.04	97	2.5
Toluene*	108-88-3	0.02-200	Not listed	Not listed	Not listed
1,2,3-Trichlorobenzene*	87-61-6	0.02-200	0.03	98	3.1
1,2,4-Trichlorobenzene*	120-82-1	0.02-200	0.03	102	2.1
1,1,1-Trichloroethane*	71-55-6	0.02-200	0.03	104	3.3
1,1,2-Trichloroethane*	79-00-5	0.02-200	ND	109	5.6

Table 2. Continued

Analyte Name	CAS No.	Range[a] (µg/L)	Method Det. Limit[b] (µg/L)	Mean Accuracy[c] (Avg % Recovery)	Precision[c] (Rel. Std. Dev. %)
Trichloroethene*	79-01-6	0.02-200	0.01	96	3.6
Trichlorofluoromethane	75-69-4	0.02-200	0.03	96	3.5
1,2,3-Trichloropropane	96-18-4	0.02-200	0.4	99	2.3
1,2,4-Trimethylbenzene	95-63-6	0.02-200	Not listed	Not listed	Not listed
1,3,5-Trimethylbenzene	108-67-8	0.02-200	Not listed	Not listed	Not listed
Vinyl Chloride	75-01-4	0.02-200	0.04	95	5.9
o-Xylene*	95-47-6	0.02-200	Not listed	Not listed	Not listed
m-Xylene*	108-38-3	0.02-200	Not listed	Not listed	Not listed
p-Xylene*	106-42-3	0.02-200	Not listed	Not listed	Not listed

* Analytes targeted by the National Contaminated Sites Remediation Program.

[a]The applicable concentration range of this method is compound, instrument, and matrix dependent. It is listed as being approximately 0.02 to 200 µg/L but no specific information is provided so caution should be observed.

[b]The method detection limits reports with this method are compound, instrument and matrix dependent. The values reported were calculated using reagent water fortified with the corresponding compounds at 10 µg/L and a GC equipped with a 60 m x 0.75 mm VOLCOL wide bore capillary column with 1.5 µm film thickness and using helium carrier gas.

[c]Recoveries and relative standard deviations were determined from seven samples of reagent water fortified with 10 µg/L of each compound. 2-Bromo-1-chloropropane was used as the internal standard for calculating average recoveries.

Table 3. Analytes Covered by U.S. EPA Method 502.2, Rev. 2, Using a Photoionization Detector

Analyte Name	CAS No.	Range[a] (µg/L)	Method Det. Limit[b] (µg/L)	Mean Accuracy[c] (Avg % Recovery)	Presision[c] (Rel. Std. Dev. %)
Benzene*	71-43-2	0.02-200	0.01	99	1.2
Bromobenzene	108-86-1	0.02-200	0.01	99	1.7
Bromochloromethane	74-97-5	0.02-200	Not listed	Not listed	Not listed
Bromodichloromethane	75-27-4	0.02-200	Not listed	Not listed	Not listed
Bromoform	75-25-2	0.02-200	Not listed	Not listed	Not listed
Bromomethane	74-83-9	0.02-200	Not listed	Not listed	Not listed
n-Butylbenzene	104-51-8	0.02-200	0.02	100	4.4
sec-Butylbenzene	135-98-8	0.02-200	0.02	97	2.7
tert-Butylbenzene	98-06-6	0.02-200	0.06	98	2.3
Carbon tetrachloride*	56-23-5	0.02-200	Not listed	Not listed	Not listed
Chlorobenzene*	108-90-7	0.02-200	0.01	100	1.0
Chloroethane	75-00-3	0.02-200	Not listed	Not listed	Not listed
Chloroform*	67-66-3	0.02-200	Not listed	Not listed	Not listed
Chloromethane	74-87-3	0.02-200	Not listed	Not listed	Not listed
2-Chlorotoluene	95-49-8	0.02-200	ND	ND	ND
4-Chlorotoluene	106-43-4	0.02-200	0.02	101	1.0
Dibromochloromethane	124-48-1	0.02-200	Not listed	Not listed	Not listed
1,2-Dibromo-3-chloropropane	96-12-8	0.02-200	Not listed	Not listed	Not listed
1,2-Dibromoethane	106-93-4	0.02-200	Not listed	Not listed	Not listed
Dibromomethane	74-95-3	0.02-200	Not listed	Not listed	Not listed
1,2-Dichlorobenzene*	95-50-1	0.02-200	0.05	102	2.1
1,3-Dichlorobenzene*	541-73-1	0.02-200	0.02	104	1.6
1,4-Dichlorobenzene*	106-46-7	0.2-20	0.01	103	2.1
Dichlorodifluoromethane	75-71-8	0.02-200	Not listed	Not listed	Not listed
1,1-Dichloroethane*	75-34-3	0.02-200	Not listed	Not listed	Not listed

Table 3. Continued

Analyte Name	CAS No.	Range[a] (µg/L)	Method Det. Limit[b] (µg/L)	Mean Accuracy[c] (Avg % Recovery)	Presision[c] (Rel. Std. Dev. %)
1,2-Dichloroethane*	107-06-2	0.02-200	Not listed	Not listed	Not listed
1,1-Dichloroethene*	75-35-4	0.02-200	ND	100	2.4
cis-1,2-Dichloroethene*	156-59-4	0.02-200	0.02	ND	ND
trans-1,2-Dichloroethene*	156-60-5	0.02-200	0.05	93	4.0
1,2-Dichloropropane*	78-87-5	0.02-200	Not listed	Not listed	Not listed
1,3-Dichloropropane	142-28-9	0.02-200	Not listed	Not listed	Not listed
2,2-Dichloropropane	590-20-7	0.02-200	Not listed	Not listed	Not listed
1,1-Dichloropropene	563-58-6	0.02-200	0.02	103	3.5
cis-1,3-Dichloropropene*	10061-01-5	Not listed	Not listed	Not listed	Not listed
trans-1,3-Dichloropropene*	10061-02-6	Not listed	Not listed	Not listed	Not listed
Ethylbenzene*	100-41-4	0.02-200	0.01	101	1.4
Hexachlorobutadiene	87-68-3	0.02-200	0.06	99	9.5
Isopropylbenzene	98-82-8	0.02-200	0.05	98	0.9
4-Isopropyltoluene	99-87-6	0.02-200	0.01	98	2.4
Methylene chloride*	75-09-2	0.02-200	Not listed	Not listed	Not listed
Naphthalene*	91-20-3	0.02-2000	0.06	102	6.2
n-Propylbenzene	103-65-1	0.02-200	0.01	103	2.0
Styrene*	100-42-5	0.02-2000	0.01	104	1.3
1,1,1,2-Tetrachloroethane	630-20-6	0.02-200	Not listed	Not listed	Not listed
1,1,2,2-Tetrachloroethane*	79-34-5	0.02-200	Not listed	Not listed	Not listed
Tetrachloroethene*	127-18-4	0.02-200	0.05	101	1.8
Toluene*	108-88-3	0.02-200	0.01	99	0.8
1,2,3-Trichlorobenzene*	87-61-6	0.02-200	ND	106	1.8
1,2,4-Trichlorobenzene*	120-82-1	0.02-200	0.02	104	2.2
1,1,1-Trichloroethane*	71-55-6	0.02-200	Not listed	Not listed	Not listed
1,1,2-Trichloroethane*	79-00-5	0.02-200	Not listed	Not listed	Not listed

Table 3. Continued

Analyte Name	CAS No.	Range[a] (µg/L)	Method Det. Limit[b] (µg/L)	Mean Accuracy[c] (Avg % Recovery)	Presision[c] (Rel. Std. Dev. %)
Trichloroethene*	79-01-6	0.02-200	0.02	100	0.78
Trichlorofluoromethane	75-69-4	0.02-200	Not listed	Not listed	Not listed
1,2,3-Trichloropropane	96-18-4	0.02-200	Not listed	Not listed	Not listed
1,2,4-Trimethylbenzene	95-63-6	0.02-200	0.05	99	1.2
1,3,5-Trimethylbenzene	108-67-8	0.02-200	0.01	101	1.4
Vinyl Chloride	75-01-4	0.02-200	0.02	109	5.0
o-Xylene*	95-47-6	0.02-200	0.02	99	0.8
m-Xylene*	108-38-3	0.02-200	0.01	100	1.4
p-Xylene*	106-42-3	0.02-200	0.01	99	0.9

* Analytes targeted by the National Contaminated Sites Remediation Program.

[a]The applicable concentration range of this method is compound, instrument, and matrix dependent. It is listed as being approximately 0.02 to 200 µg/L but no specific information is provided so caution should be observed.

[b]The method detection limits reports with this method are compound, instrument and matrix dependent. The values reported were calculated using reagent water fortified with the corresponding compounds at 10 µg/L and a GC equipped with a 60 m x 0.75 mm VOLCOL wide bore capillary column with 1.5 µm film thickness and using helium carrier gas.

[c]Recoveries and relative standard deviations were determined from seven samples of reagent water fortified with 10 µg/L of each compound. Fluorobenzene was used as the internal standard for calculating average recoveries.

Comments on Use of this Method:

Method detection limits (MDLs) are compound, matrix, and instrument dependent and vary from approximately 0.01 - 3.0 µg/L. The applicable concentration range of this method is also compound matrix, and instrument dependent and is approximately 0.02 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

Two of the three isomeric xylenes may not be resolved on the capillary column, and if not, must be reported as isomeric pairs. Tentative identifications are confirmed by analyzing standards under the same conditions used for sampling and comparing resultant GC retention times. Additional confirmatory information can be gained by comparing the relative response from the two detectors. Each identified component is measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard. For absolute confirmation, a gas chromatography/mass spectrometry (GC/MS) determination according to Method 524.2 is recommended.

Title:

Analysis of Organohalide Pesticides and Commercial Polychlorinated Biphenyl (PCB) Products in Water by Microextraction and Gas Chromatography. U.S. EPA Method 505, Revision 2, 1989.

Reference:

Methods for the Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH 45268, USA.

Method Applicability:

This method is applicable to drinking water and raw source water. The latter should include most surface water and groundwater sources.

Sample Preparation:

Remove the sample from storage and allow it to come to room temperature. Remove a 5 mL volume from each container and weigh the container to the nearest 0.1 g. Add 6 g of sodium chloride and 2.0 mL of hexane to each sample bottle. Recap the sample and shake it vigorously for one minute. Allow the water and hexane phases to separate, remove the cap, and transfer 0.5 mL of hexane into autosampler vial using a disposable glass pipet. Transfer the remaining hexane phase into a second autosampler vial and store at 4°C for reanalysis, if necessary. Discard the remaining sample/hexane mixture and reweigh the empty container to determine net weight of sample.

Instrumental Analysis:

The sample extracts placed in the first vials are transferred to an autosampler set-up to inject 1-2 µL portions into the gas chromatograph (GC) for analysis. Alternatively, 1-2 µL portions of samples, blanks, and standards may be manually injected.

Instrumentation Required:

Gas chromatograph/electron capture detector/data system, with temperature programming and split/splitless injector suitable for use with capillary columns. Column #1: 0.32 mm ID x 30 M fused silica capillary with chemically bond methyl polysiloxane phase (DB-1, 1.0 µm film, or equivalent); Column #2: 0.32 mm ID x 30 M fused silica capillary with 1:1 mixed phase of dimethyl silicone and polyethylene glycol (Durawax-DX3, 0.25 µm film, or equivalent); Column #3: 0.32 mm ID x 25 M fused silica capillary with chemically bonded 50:50 methyl-phenyl silicone (OV-17, 1.5 µm film, or equivalent). Column #1 should be used as the primary analytical column. Columns #2 and #3 are recommended for use as confirmatory columns when GC/MS confirmation is not available.

Interferences:

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus that lead to discrete artifacts or elevated baselines. All reagents and apparatus must be demonstrated to be free from interferences under the conditions of the analysis by running laboratory reagent blanks. All glassware should be washed with detergent, rinsed with reagent water, and dried at 400°C for 1 hour.

Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations of the analytes. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of method blanks to check for cross-contamination. Matrix interferences also may be caused by contaminants that are coextracted from the sample; cleanup of sample extracts may be necessary in these cases.

Caution must be taken in the determination of endrin since the splitless injector may cause endrin degradation. Also, variable amounts of pesticides and commercial PCB products from aqueous solutions adhere to glass surfaces. Sample transfers and contact with glass surfaces should be minimized. Aldrin, hexachlorocyclopentadiene and methoxychlor are rapidly oxidized by chlorine, dechlorination with sodium thiosulfate at time of sample collection should retard further oxidations of these compounds.

Quality Control Requirements:

Minimum quality control requirements are initial demonstration of laboratory capability, analysis of laboratory reagent blanks, fortified blanks, fortified sample matrix, and quality control samples. The laboratory must analyze at least one fortified blank per sample set, or at least one for every 20 samples. The fortifying concentration of each analyte should be 10 times the method detection limit (MDL) or the maximum calibration limit (MCL), whichever is less. Calculate accuracy as percent recovery and develop control limits from the mean percent recovery and standard deviation.

The laboratory must add a known concentration of the analytes to a minimum of 10% of the routine samples, or one laboratory fortified sample matrix per sample set. Calculate the percent recovery for each analyte and compare to the control limits established from the analyses of the fortified blanks.

Comparison with Other Methods:

This is a very sensitive method that is more useful for monitoring than for exploratory analyses. The electron capture detector is easy to use but it is a nonselective detector compared to mass spectrometry and therefore more subject to false positive detections than GC/MS methods. The microextraction technique also eliminates the expensive sample preparation costs of other methods, but it has the disadvantage of being less sensitive than most because the extracts are not concentrated.

Analytes Covered by this Method:

Method 505 covers 25 pesticides and commercial PCB products including 5 of the chlorinated hydrocarbons and 8 of the pesticides that are of interest to the National Contaminated Sites Remediation Program, as shown in Table 4.

Comments on the Use of this Method:

Method detection limits (MDLs) for the organohalides and Aroclors are highly dependent upon the characteristics of the gas chromatographic system used. Analytes that are not separated chromatographically cannot be individually identified and used in the same calibration mixture or water samples unless an alternative technique for identification and quantitation is used, such as mass spectrometry. Note that one of the target analytes (Aldrin) had somewhat low recovery from tap water (Aldrin) and another (Heptachlor) had an abnormally high recovery from tap water. Aroclor 1248 also had a high percent relative standard deviation in reagent water. No explanation is offered in the method protocol for these anomalies.

Table 4. Analytes Covered Using U.S. EPA Method 505, Rev. 2

Analyte Name	CAS No.	Method Det. Limit (µg/L)	Concentration (µg/L)	Reagent Water		Groundwater		Tap Water	
				Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Alachlor	5972-60-8	0.225	0.50	102	13.4	Not listed	Not listed	Not listed	Not listed
Aldrin*	309-00-2	0.075 0.007	0.15 0.05	86 106	9.5 20.0	100 86	11.0 16.3	69 Not listed	9.0 Not listed
Atrazine	1912-24-9	2.4	5.0 20.0	85 95	16.2 5.2	95 86	7.3 9.1	108 91	10.9 3.1
Chlordane*	57-74-9	0.14	0.17 3.4	NA NA	8.0 3.6	Not listed Not listed	Not listed Not listed	105 95	12.4 9.6
α-Chlordane	5103-71-9	0.006	0.06 0.35	95 86	3.5 17.0	83 94	4.4 10.2	85 91	7.1 2.4
γ-Chlordane	5103-74-2	0.12	0.06 0.35	95 86	0.4 18.5	86 95	5.3 14.5	83 91	14.7 6.0
Dieldrin*	60-57-1	0.012	0.10 3.6	87 114	17.1 9.1	67 94	10.1 8.6	92 81	15.7 14.0
Endrin*	72-20-8	0.063	0.10 3.6	119 99	29.8 6.5	94 100	20.2 11.3	106 85	14.0 12.4
Heptachlor*	76-44-8	0.003	0.032 1.2	77 80	10.2 7.4	37 71	6.8 9.8	200 106	22.6 16.8
Heptachlor epoxide*	1024-57-3	0.004	0.04 1.4	100 115	15.6 6.6	90 103	14.2 6.9	112 81	7.5 5.9
Hexachlorobenzene*	118-74-1	0.002	0.003 0.09	104 103	13.5 6.6	91 1.1	10.9 4.4	100 88	15.6 13.4
Hexachlorocy-clopentadiene	77-74-4	0.13	0.15 0.35	73 73	5.1 11.7	87 69	5.1 4.8	191 109	18.5 14.3
Lindane*	58-89-9	0.003	0.03 1.2	91 111	6.5 5.0	88 109	7.7 3.4	103 93	8.1 18.4

Table 4. Continued

Analyte Name	CAS No.	Method Det. Limit (µg/L)	Concentration (µg/L)	Reagent Water		Groundwater		Tap Water	
				Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Methoxychlor*	72-43-5	0.96	2.10 7.03	100 98	21.0 10.9	Not listed Not listed	Not listed Not listed	Not listed Not listed	Not listed Not listed
cis-Nonachlor		0.027	0.06 0.45	110 82	15.2 21.3	101 93	7.2 18.3	93 87	14.3 5.4
trans-Nonachlor	39765-80-5	0.011	0.06 0.35	95 86	9.6 21.8	83 94	7.1 17.2	73 86	4.1 5.1
Simazine	122-34-9	6.8	25 60	99 65	8.3 3.6	97 59	9.2 18.0	102 67	13.4 6.2
Toxaphene	8001-35-2	1.0	10 80	NA NA	12.6 15.3	Not listed Not listed	Not listed Not listed	110 114	9.5 13.5
Aroclor 1016	12674-11-2	0.08	1.0	NA	6.6	Not listed	Not listed	97	7.5
Aroclor 1221	11104-28-2	15.0	180	NA	8.3	Not listed	Not listed	92	9.6
Aroclor 1232	11141-16-5	0.48	3.9	NA	13.5	Not listed	Not listed	86	7.3
Aroclor 1242*	53469-21-9	0.31	4.7	NA	6.0	Not listed	Not listed	96	7.4
Aroclor 1248*	12672-29-6	0.102	3.6 3.4	NA Not listed	115 Not listed	Not listed Not listed	Not listed Not listed	Not listed 84	Not listed 9.9
Aroclor 1254*	11097-69-1	0.102	1.8 1.7	NA Not listed	10.4 Not listed	Not listed Not listed	Not listed Not listed	Not listed 85	Not listed 11.8
Aroclor 1260*	11098-82-5	0.189	2.0 1.8	NA NA	20.7 Not listed	Not listed Not listed	Not listed Not listed	Not listed 88	Not listed 19.8

* Analytes targeted by the National Contaminated Sites Remediation Program.

Title:

Determination of Nitrogen and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector. U.S. EPA Method 507, Revision 2, 1989.

Reference:

Methods for the Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH, 45268, USA.

Method Applicability:

This method is applicable to the determination of certain nitrogen and phosphorus-containing pesticides in finished drinking water and groundwater.

Sample Preparation:

Samples collected for analysis using this method may be extracted using a manual procedure or an automated procedure with a mechanical tumbler. For the manual procedure mark the water meniscus or the sample bottle for later determination of sample volume. Fortify the sample with 50 µL of the surrogate standard solution and pour the sample into a 2 L separatory funnel. Adjust the sample to pH 7 by adding 50 mL of phosphate buffer. Add 100 g NaCl to the sample, seal, and shake to dissolve salt.

Add 60 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse walls. Transfer to the separatory funnel and extract the sample by shaking vigorously for 2 minutes with periodic venting. Allow the organic layer to separate for a minimum of 10 minutes and collect the extract in a 500 mL Erlenmeyer flask. Repeat extraction twice more with 60 mL volumes of methylene chloride. Determine sample volume by refilling sample bottle to the mark and transfer to a 1000 mL graduated cylinder.

For the automated procedure, mark the water meniscus for sample volume determination and fortify the sample with 50 µL of the surrogate standard solution. Pour the sample into mechanical tumbler bottle and adjust it to pH 7 by adding 50 mL of phosphate buffer. Add 100 g NaCl to the sample, seal, and shake it to dissolve salt.

Add 300 mL methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse walls. Transfer the solvent to tumbler, seal, and shake for 10 seconds, venting periodically. Repeat shaking and venting until no pressure release is observed. Reseal and place it in a mixing device and tumble the sample for 1 hour. Remove and pour contents into a 2 L separatory funnel to allow the organic layer to separate for a minimum of 10 minutes. Collect the methylene chloride extract in a 500 mL Erlenmeyer flask.

Dry the extract from either procedure by pouring it through a solvent-rinsed drying column containing about 10 cm of anhydrous sodium sulfate. Collect the extract in a Kuderna-Danish (K-D) concentrator and rinse the column with 20-30 mL methylene chloride.

Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL methylene chloride to the top. Place the K-D apparatus on a hot water bath, 65 to 70°C, so that the concentrator tube is partially immersed in the hot water, and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature as required to complete the concentration in 15 to 20 minutes. When the apparent volume of liquid reaches 2 mL, removed the K-D apparatus and allow it to drain and cool for at least 10 minutes.

Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of methyl t-butyl ether (MTBE). Add 5-10 mL of MTBE and a fresh boiling stone. Attach a micro-Snyder column and prewet with about 0.5 mL of MTBE. Place the micro K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature as required to complete concentration in 5 to 10 minutes. When the apparent volume of liquid reaches 2 mL, remove the micro K-D from the bath and allow it to drain and cool. Add 5-10 mL MTBE to the micro K-D and reconcentrate to 2 mL. Remove the micro K-D from the bath and allow it to drain and cool. Remove the micro Snyder column, and rinse the walls of the concentrator tube while adjusting the volume to 5.0 mL with MTBE. NOTE: If methylene chloride is not completely removed from the final extract, it may cause detector problems. Transfer extract to a screw-cap vial and store at 4°C until analysis.

Instrumental Analysis:

Inject 2 µL of the sample extract into the gas chromatographic system. If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze. Alternative techniques such as an alternate detector or second chromatography column should be used to confirm peak identification when sample components are not resolved adequately.

Instrumentation Required:

Gas Chromatograph System equipped with a nitrogen-phosphorus detector (NPD). Column #1: 30 M x 0.25 mm ID DB-5 bonded fused silica column, 0.25 µm film thickness, or equivalent; Column #2: 30 M x 0.25 mm ID DB-1701 bonded fused silica column, 0.25 µm film thickness, or equivalent.

Interferences:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus. All reagents and apparatus must be routinely demonstrated to be free from interferences by running laboratory reagent blanks.

Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations. One or more injections of MTBE should be made following the analysis of a sample with high concentrations of analytes.

Matrix interferences may be caused by contaminants that are co-extracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the water sampled. Further processing of sample extracts may be necessary.

Quality Control Requirements:

Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. A laboratory reagent blank is analyzed to demonstrate that all glassware and reagent interferences are under control.

Initial demonstration of capability is fulfilled by analyzing four fortified reagent water samples with recovery value for each analyte following with the acceptable range (± 30% average recovery). Surrogate recoveries from samples or method blanks must be 70-130%. The internal standard response for any sample chromatogram should not deviate from the daily calibration check standard's internal standard response by more than 30% or laboratory fortified blanks and sample matrices are used to assess laboratory performance and analyte recovery, respectively.

Comparison with Other Methods:

There are no other methods to which this method is compared. It only serves one of the pesticides of interest and only on aqueous samples.

Analytes Covered by this Method:

Method 507 covers 46 nitrogen- and phosphorus-containing pesticides including one compound, diazinon, which is of interest to the National Contaminated Sites Remediation Program, as shown in Table 5.

Table 5. Analytes Covered Using U.S. EPA Method 507, Rev. 2

Analyte Name	CAS No.	Est. Det. Limit (µg/L)**	Concentration Used (µg/L)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Alachlor	15972-60-8	0.38	3.8	95	11
Ametryn	834-12-8	2	20	91	10
Atraton	1610-17-9	0.6	6	91	11
Atrazine	1912-24-9	0.13	1.3	92	8
Bromocil	314-40-9	2.5	25	91	9
Butachlor	23184-66-9	0.38	3.8	96	4
Butylate	2008-41-5	0.15	1.5	97	21
Carboxin	5234-68-5	0.6	6	102	4
Chlorpropham	101-21-3	0.5	5	93	11
Cycloate	1134-23-2	0.25	2.5	89	9
Diazinon*	333-41-5	0.25	2.5	115	7
Dichloroos	62-73-7	2.5	25	97	6
Diphenamid	957-51-7	0.6	6	93	8
Disulfoton	298-04-4	0.3	3	89	10
Disulfoton sulfone	2497-06-5	3.8	7.5	98	10
Disulfoton sulfoxide	2497-07-6	0.38	3.8	87	11
EPTC	759-94-4	0.25	2.5	85	9
Ethoprop	13194-48-4	0.19	1.9	103	5
Fenamiphos	22224-92-6	1	10	90	8
Fenarimol	60168-88-9	0.38	3.8	99	5
Fluridone	59756-60-4	3.8	38	87	9
Hexazinone	51235-04-2	0.76	7.6	90	7
Merphos	150-50-5	0.25	2.5	96	8
Methyl paraoxon	950-35-6	2.5	25	98	10
Metholachlor	51218-45-2	0.75	7.5	93	4
Metribuzin	21087-64-9	0.15	1.5	101	5
Mevinphos	7786-34-7	5	50	95	11
MGK 264	113-48-4	0.5	5	100	4
Molinate	2212-67-1	0.15	1.5	98	18
Napropamide	15299-99-7	0.25	2.5	101	6

Table 5. Continued

Analyte Name	CAS No.	Est. Det. Limit (µg/L)	Concentration Used (µg/L)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Norflurazon	27314-13-2	0.5	5	94	5
Pebulate	1114-71-2	0.13	1.3	94	9
Prometon	1610-18-0	0.3	3	78	9
Prometryn	7287-19-6	0.19	1.9	93	8
Pronamide	23950-58-5	0.76	7.6	91	10
Propazine	139-40-2	0.13	1.3	92	8
Simazine	122-34-9	0.075	0.75	100	7
Simetryn	1014-70-6	0.25	2.5	99	5
Stirofos	22248-79-9	0.76	7.6	98	6
Tebuthiuron	34014-18-1	1.3	13	84	9
Terbacil	5902-51-2	4.5	45	97	6
Terbufos	13071-79-9	0.5	5	97	4
Terfutryn	886-50-0	0.25	2.5	94	9
Triademefon	43121-43-3	0.65	6.5	93	8
Tricyclozole	41814-78-2	1	10	86	7
Vernolate	1929-77-7	0.13	1.3	93	6

* Analyte targeted by the National Contaminated Sites Remediation Program.

** Estimated detection limit defined as either Method Detection Limit (MDL) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

Comments on Use of this Method:

This method has been validated in a single laboratory and estimated detection limits (EDLs) have been determined for each analyte, as shown in Table 5. Observed detection limits may vary among waters, depending upon the nature of the interferences in the sample matrix and the specific instrumentation used. Analytes that are not separated chromatographically cannot be individually identified and measured unless an alternative technique for identification and quantitation exist.

Title:

Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector. U.S. EPA Method 515.1, Revision 4, 1989.

Reference:

Methods for the Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH, 45268, USA.

Method Applicability:

This method is applicable to the determination of certain chlorinated acids in finished drinking water and groundwater.

Sample Preparation:

For manual hydrolysis, preparation and extraction, mark the water meniscus on the side of the sample bottle for later determination of sample volume. Pour entire contents into a 2 L separatory funnel and fortify sample with 50 µL of the surrogate standard solution. Add 250 g NaCl to the sample, seal, and shake to dissolve the salt. Add 17 mL of 6N NaOH to the sample, seal, and shake. Check pH and continue adding more 6N NaOH until pH $\geq$ 12. Let the sample set at room temperature for 1 hour, shaking contents periodically.

Add 60 mL methylene chloride to the sample bottle, transfer to a separatory funnel and extract the sample by vigorously shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate for a minimum of 10 minutes and discard the methylene chloride phase. Repeat the extraction twice more with 60 mL volumes of methylene chloride, discarding methylene chloride each time. Add 17 mL of 12N H_2SO_4 to the sample seal, and shake to mix it again. Check the pH and continue adding 12N H_2SO_4 until pH $\leq$ 2.

Add 120 mL of ethyl ether to the sample, seal, and extract for 2 minutes. Allow the organic layer to separate for a minimum of 10 minutes. Remove the aqueous phase to a 2 L Erlenmeyer flask and collect the ethyl ether phase in a 500 mL round bottom flask containing about 10 g of acidified anhydrous sodium sulfate. Periodically, vigorously shake the sample and drying agent. Allow the extract to remain in contact with the sodium sulfate for about 2 hours. Return the aqueous phase to the separatory funnel and repeat the extraction twice more with 60 mL volumes of ethyl ether. Determine the original sample volume by refilling the sample bottle to the meniscus mark and transferring to a 1000 mL graduated cylinder.

Pour the dried extract through a funnel plugged with acid-washed glass wool and collect in a Kuderna-Danish (K-D) concentrator. Rinse the round bottom flask and funnel with 20 - 30 mL of ethyl ether.

Add 1 to 2 clean boiling stones to the evaporative flask and attach a macro Snyder column. Prewet the Snyder column by adding about 1 mL of ethyl ether to the top. Place the K-D apparatus on a hot water bath, 60 to 65°C, so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. When the apparent volume of liquid has reached 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 to 2 mL of ethyl ether then add 2 mL of MTBE and a fresh boiling stone. Attach a micro Snyder column and prewet with about 0.5 mL ethyl ether. Concentrate the liquid to 0.5 mL, remove the addition and allow it to cool. Remove the micro Snyder column and add 250 µL methanol. Rinse the walls of the tube while adjusting the volume to either 5.0 mL or 4.5 mL with MTBE, depending on whether the pesticides will be esterified using gaseous diazomethane or diazomethane solution, respectively.

Esterify acids using either gaseous diazomethane or a diazomethane solution. Adjust sample volume to 5.0 mL with MTBE. Transfer the methylated sample to a Florisil column that has been pre-eluted with 5 mL of 5% methanol in MTBE. Collect the sample eluate in K-D tube and add 1 mL of 5% methanol in mtheyl t-butyl ether (MTBE) to sample container to rinse walls, elute and collect it in a K-D tube. Repeat with 1 mL and 3 mL aliquots of 5% methanol in MTBE and collect in K-D tube.

Instrumental Analysis:

Inject 2 µL of the sample extract into gas chromatographic system. If the response for the peak exceeds the working range of the system, dilute the extract and reanalyze. If the internal standard calibration procedure is used, fortify the extract with 25 µL of internal standard solution, thoroughly mix the sample and analyze it.

Instrumentation Required:

Gas Chromatograph System equipped with an electron capture detector (ECD). Column #1: 30 M x 0.25 mm ID DB-5 bonded fused silica column, 0.25 µm film thickness, or equivalent; Column #2: 30 M x 0.25 mm ID DB-1701 bonded fused silica column, 0.25 µm film thickness, or equivalent.

Interferences:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing apparatus. All reagents and apparatus must be routinely demonstrated to be free from interferences by running laboratory reagent blanks. The acid forms of the analytes are strong organic acids which react readily with alkaline substances. Rinse glassware and glass wool with 1N HCl and acidify sodium sulfate with H_2SO_4.

Organic acids and phenols, especially chlorinated compounds, cause the most direct interference with the determination. Interferences by phthalate esters can pose a major problem when using the ECD. Interfering contamination may occur when a sample with low concentrations of analytes is analyzed immediately following a sample with high concentrations. One or more injections of MTBE should be made following the analysis of samples with high concentrations of analytes.

Quality Control Requirements:

Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. A laboratory reagent blank is analyzed to demonstrate that all glassware and reagent interferences are under control.

Initial demonstration of capability is fulfilled by analyzing four fortified reagent water samples with recovery value for each analyte following with the acceptable range (± 30% average recovery). Surrogate recoveries from samples or method blanks must be 70-130%. The internal standard response for any sample chromatogram should not deviate from the daily calibration check standard's internal standard response by more than 30% or laboratory fortified blanks and sample matrices are used to assess laboratory performance and analyte recovery, respectively.

Comparison with Other Methods:

There are no other methods summarized. This and pentachlorophenol are the only compounds on the list of analytes for which this method is applicable and it is limited to aqueous samples.

Analytes Covered by this Method:

Method 515.1 covers 17 chlorinated acids including 2 compounds, 2,4-D and pentachlorophenol, which are of interest to the National Contaminated Sites Remediation Program, as shown in Table 6.

Comments on Use of this Method:

This method has been validated in a single laboratory and estimated detection limits (EDLs) have been determined for each analyte, as shown in Table 6. Observed detection limits may vary among waters, depending upon the nature of the interferences in the sample matrix and the specific instrumentation used. Analytes that are not separated chromatographically cannot be individually identified and measured unless an alternative technique for identification and quantitation exist.

Table 6. Analytes Covered Using U.S. EPA Method 515.1, Rev. 4

Analyte Name	CAS No.	Est. Det. Limit (µg/L)**	Concentration Used (µg/L)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Acifluorfen	50594-66-6	0.096	0.2	121	15.7
Bentazon	25057-89-0	0.2	1	120	16.8
Chloramben	133-90-4	0.093	0.4	111	14.4
2,4-D*	94-75-7	0.2	1	131	27.5
Dalapon	75-99-0	1.3	10	100	20.0
2,4-DB	94-82-6	0.8	4	87	13.1
DCPA acid metabolites		0.02	0.2	74	9.7
Dicamba	1918-40-9	0.081	0.4	135	32.4
3,5-Dichlorobenzoic acid	51-36-5	0.061	0.6	102	16.3
Dichlorprop	120-36-5	0.26	2	107	20.3
Dinoseb	88-85-7	0.14	0.4	42	14.3
5-Hydroxydicamba	7600-50-2	0.04	0.2	103	16.5
4-Nitrophenol	100-02-7	0.13	1	131	23.6
Pentachlorophenol*	87-86-5	0.076	0.04	130	31.2
Picloram	1918-02-1	0.14	0.6	91	15.5
2,4,5-T	93-76-5	0.08	0.4	117	16.4
2,4,5-TP	93-72-1	0.075	0.2	134	30.8

* Analytes targeted by the National Contaminated Sites Remediation Program.

** Estimated detection limit defined as either Method Detection Limit (MDL) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise ratio of approximately 5, whichever value is higher.

Title:

Measurement of Purgeable Organic Compounds in Water by Capillary Column GC/MS. U.S. EPA Method 524.2, Revision 3, 1989.

Reference:

Methods for the Determination of Organic Compounds in Drinking Water. EPA-600/4-88/039. US EPA. 1983. Method 524.2, Revision 3.0 (1989). Environmental Monitoring System Laboratory, Cincinnati, Ohio.

Method Applicability:

Drinking water and raw source water. The latter should include most surface water and groundwater sources.

Sample Preparation:

Remove the plungers from two 25 mL (or 5 mL depending on sample size) syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 25.0 mL (or 5 mL). For samples and blanks, add 5 µL of the fortification solution containing the internal standard and the surrogates to the sample through the syringe valve. For calibration standards and laboratory fortified blanks, add 5 µL of the fortification solution containing the internal standard only. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

Instrumental Analysis:

An inert gas (zero grade nitrogen or helium) is bubbled through a 25 mL or a 5 mL water sample (depending on the expected concentration of the analytes). Purged sample components are trapped in a tube of sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb the trapped sample onto a capillary GC column.

Instrumentation Required:

Gas Chromatography/Mass Spectrometry/Data System. Column #1: VOCOL glass wide bore capillary column; Column #2: DB-624 fused silica capillary column; Column #3: DB-5 fused silica capillary column. Also required is an all-glass 25 mL or 5 mL purging devise, a sorbent trap, and a thermal desorption apparatus which is connected to the GC/MS system.

Interferences:

Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for many contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-PTFE plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. Method blanks prepared from reagent water and analyzed under the same conditions as the samples can identify these interferences. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of method blanks to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample.

Samples also 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 field blank prepared from reagent water and carried through the sampling and handling protocol can serve as a check on such contamination. The laboratory where volatile analysis is performed and also the refrigerated storage area should be completely free of solvents.

Quality Control Requirements:

As an initial demonstration of lab accuracy and precision, analyze 4 to 7 replicates of a lab fortified blank containing analyte at 0.2 - 5 µg/L. Collect all samples in duplicate. Surrogate analytes (similar to those of the analytes of interest), whose concentration is known in every sample, are measured using the same internal standard calibration procedure. Duplicate field reagent water blanks (trip blanks) must be analyzed with each set of samples, laboratory reagent blanks (method blanks) must be analyzed with each batch of samples processed as a group within a work shift. Also, a single laboratory-fortified blank that contains each of the analytes of interest should be analyzed with each batch of samples processed as a group within a work shift. A 3 to 5 point calibration curve is needed depending on the calibration range factor required.

Advantages and Disadvantages with Other Methods:

This method uses capillary GC columns which provide excellent chromatographic resolution of 60 volatile organic compounds. It also uses a mass spectrometer with a data system to provide excellent specificity for analyte identification and good sensitivity. Furthermore, the purge-and-trap technique requires little in the way of sample preparation and accommodates most water matrices.

Its advantage over GC methods with less selective detectors (such as EPA Methods 502.2 and EPA Method 8020 which use photoionization detectors (PIDs)) is that it will usually produce fewer false positives because of its greater selectivity. Its disadvantage over these same methods is greater capital expense for the instrumentation, a higher degree of technical expertise will be required to perform the analyses and a resulting higher cost of analysis.

Its disadvantage, in comparison to EPA Method 8240 is that the latter may also be used with soil and sediment matrices whereas Method 524.2 is limited to relatively clean water matrices.

Analytes Covered by this Method:

Method 524.2 covers 60 volatile organic compounds including all of the monocyclic aromatic hydrocarbons, naphthalene and 17 of the chlorinated hydrocarbons that are of interest to the National Contaminated Sites Remediation Program as shown in Table 7.

Comments on Use of this Method:

Method Detection Limits (MDLs) are compound and instrument dependent, and may vary from approximately 0.02 - 0.35 µg/L. Note in the table above that the "true" concentration range used for accuracy and precision measurements was quite narrow. However, the applicable concentration range of this method is primarily column dependent and is approximately 0.02 to 200 µg/L for the wide-bore thick-film columns. Narrow-bore thin-film columns may have a capacity which limits the range to about 0.02 to 20 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts.

Analytes that are not separated chromatographically, but which have different mass spectra and non-interfering quantitation ions, can be identified and measured in the same calibration mixture or water sample. Analytes which have very similar mass spectra cannot be individually identified and measured in the same calibration mixture or water samples unless they have different retention times. Co-eluting compounds with very similar mass spectra, typically many structural isomers, must be reported as an isomeric group or pair. Two of the three isomeric xylenes and two of the three dichlorobenzenes are examples of structural isomers that may not be resolved on the capillary column, and if not, must be reported as isomeric pairs.

Finally, note that all of the MDLs are determined using reagent water. In addition to being compound and instrument dependent, MDLs may be matrix dependent. Therefore, new MDLs should be determined on the matrix being analyzed if it is anything other than relatively clean surface water or groundwater. Sample matrix effects have been documented to <u>not</u> noticeably affect surface, ground, or drinking water sample analyses.

Table 7. Analytes Covered Using U.S. EPA Method 524.2, Rev. 3

Analyte Name	CAS No.	Range (µg/L)	Method Det. Limit (µg/L)	Mean Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Benzene*	71-43-2	0.1-10	0.04	97	5.7
Bromobenzene	108-86-1	0.1-10	0.03	100	5.5
Bromochloromethane	74-97-5	0.5-10	0.04	90	6.4
Bromodichloromethane	75-27-4	0.1-10	0.08	95	6.1
Bromoform	75-25-2	0.5-10	0.12	101	6.3
Bromomethane	74-83-9	0.5-10	0.11	95	8.2
n-Butylbenzene	104-51-8	0.5-10	0.11	100	7.6
sec-Butylbenzene	135-98-8	0.5-10	0.13	100	7.6
tert-Butylbenzene	98-06-6	0.5-10	0.14	102	7.3
Carbon tetrachloride*	56-23-5	0.5-10	0.21	84	8.8
Chlorobenzene*	108-90-7	0.1-10	0.04	98	5.9
Chloroethane	75-00-3	0.5-10	0.10	89	9.0
Chloroform*	67-66-3	0.5-10	0.03	90	6.1
Chloromethane	74-87-3	0.5-10	0.13	93	8.9
2-Chlorotoluene	95-49-8	0.1-10	0.04	90	6.2
4-Chlorotoluene	106-43-4	0.1-10	0.06	99	8.3
Dibromochloromethane	124-48-1	0.1-10	0.05	92	7.0
1,2-Dibromo-3-chloropropane	96-12-8	0.5-10	0.26	83	19.9
1,2-Dibromoethane	106-93-4	0.5-10	0.06	102	3.9
Dibromomethane	74-95-3	0.5-10	0.24	100	5.6
1,2-Dichlorobenzene*	95-50-1	0.1-10	0.03	93	6.2
1,3-Dichlorobenzene*	541-73-1	0.5-10	0.12	99	6.9
1,4-Dichlorobenzene*	106-46-7	0.2-20	0.03	103	6.4
Dichlorodifluoromethane	75-71-8	0.5-10	0.10	90	7.7
1,1-Dichloroethane*	75-34-3	0.5-10	0.04	96	5.3
1,2-Dichloroethane*	107-06-2	0.1-10	0.06	95	5.4

Table 7. Continued

Analyte Name	CAS No.	Range (µg/L)	Method Det. Limit (µg/L)	Mean Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
,1-Dichloroethene*	75-35-4	0.1-10	0.12	94	6.78 8
cis-1,2-Dichloroethene*	156-59-4	0.5-10	0.12	101	6.7
trans-1,2-Dichloroethene*	156-60-5	0.1-10	0.06	93	5.6
1,2-Dichloropropane*	78-87-5	0.1-10	0.04	97	6.1
1,3-Dichloropropane	142-28-9	0.1-10	0.04	96	6.0
2,2-Dichloropropane	590-20-7	0.5-10	0.35	86	16.9
1,1-Dichloropropene	563-58-6	0.5-10	0.10	98	8.9
cis-1,3-Dichloropropene*	10061-01-5	Not listed	Not listed	Not listed	Not listed
trans-1,3-Dichloropropene*	10061-02-6	Not listed	Not listed	Not listed	Not listed
Ethylbenzene*	100-41-4	0.1-10	0.06	99	8.6
Hexachlorobutadiene	87-68-3	0.5-10	0.11	100	6.8
Isopropylbenzene	98-82-8	0.5-10	0.15	101	7.6
4-Isopropyltoluene	99-87-6	0.1-10	0.12	99	6.7
Methylene chloride*	75-09-2	0.1-10	0.03	95	5.3
Naphthalene*	91-20-3	0.1-100	0.04	104	8.2
n-Propylbenzene	103-65-1	0.1-10	0.04	100	5.8
Styrene*	100-42-5	0.1-100	0.04	102	7.2
1,1,1,2-Tetrachloroethane	630-20-6	0.5-10	0.05	90	6.8
1,1,2,2-Tetrachloroethane*	79-34-5	0.1-10	0.04	91	6.3
Tetrachloroethene*	127-18-4	0.5-10	0.14	89	6.8
Toluene*	108-88-3	0.5-10	0.11	102	8.0
1,2,3-Trichlorobenzene*	87-61-6	0.5-10	0.03	109	8.6
1,2,4-Trichlorobenzene*	120-82-1	0.5-10	0.04	108	8.3
1,1,1-Trichloroethane*	71-55-6	0.5-10	0.08	98	8.1
1,1,2-Trichloroethane*	79-00-5	0.5-10	0.10	104	7.3
Trichloroethene*	79-01-6	0.5-10	0.19	90	7.3

Table 7. Continued

Analyte Name	CAS No.	Range (µg/L)	Method Det. Limit (µg/L)	Mean Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Trichlorofluoromethane	75-69-4	0.5-10	0.08	89	8.1
1,2,3-Trichloropropane	96-18-4	0.5-10	0.32	108	14.4
1,2,4-Trimethylbenzene	95-63-6	0.5-10	0.13	99	8.1
1,3,5-Trimethylbenzene	108-67-8	0.5-10	0.05	92	7.4
Vinyl Chloride	75-01-4	0.5-10	0.17	98	6.7
o-Xylene*	95-47-6	0.1-31	0.11	103	7.2
m-Xylene*	108-38-3	0.1-10	0.05	97	6.5
p-Xylene*	106-42-3	0.5-10	0.13	104	7.7

* Analytes targeted by the National Contaminated Sites Remediation Program.

Note: Data were obtained from 16-31 determinations using a wide-bore capillary column and a jet separator interfaced to a quadrupole mass spectrometer. All analytes were in a reagent water matrix.

Title:

Measurement of N-Methylcarbamoyloximes and N-Methylcarbamates in Water by Direct Aqueous Injection HPLC with Post Column Derivatization. U.S. EPA Method 531.1, Revision 3, 1989.

Reference:

Methods for the Determination of Organic Compounds in Drinking Water, EPA/600/4-88/039. U.S. EPA Environmental Monitoring Systems Laboratory, Cincinnati, OH, 45268, USA.

Method Applicability:

This method is applicable to the determination of certain N-methylcarbanoyloximes and N-methylcarbamates in finished drinking water and groundwater.

Sample Preparation:

Adjust the pH of the sample to pH 3 ± 0.2 by adding 1.5 mL of 2.5 M monochloroacetic acid buffer to each 50 mL of sample, if not previously done during sample collection. Fill a 50 mL volumetric flask to the mark with the sample. Add 5 µL of the internal standard fortification solution.

Affix the three-way valve to a 10 mL syringe and place a clear filter in the filter holder. Affix the filter holder and the 7 to 10 cm syringe needle to the syringe valve. Prewet the filter by passing 5 mL of reagent water through the filter. Draw 10 mL of sample into the syringe, expel through the filter, and collect the last 5 mL for analysis. Rinse the syringe with reagent water and discard the filter.

Instrumental Analysis:

Inject 400 µL of the sample into the high performance liquid chromatograph (HPLC) where separation of analytes is achieved using gradient elution chromatography. If the response for the peak exceed the working range of the system, dilute the sample with pH 3 buffered reagent water and reanalyze.

After elution from the HPLC column, the analytes are hydrolyzed with 0.05N sodium hydroxide at 95°C in the post column reactor. The methyl amine formed during hydrolysis is reacted with o-phthalaldehyde and 2-mercaptoethanol to form a highly fluorescent derivative which is detected by a fluorescence detector.

Instrumentation Required:

High Performance Liquid Chromatograph (HPLC) system capable of performing binary linear gradients at a constant flow rate and equipped with a post column reactor and a fluorescence detector. Column #1: 150 mm x 3.9 mm ID stainless steel packed with 4 µm NovaPak C18; Column #2: 250 mm x 4.6 mm ID stainless steel packed with 5 µm Beckman Ultrasphere ODS; Column #3: 250 mm x 4.6 mm ID stainless steel packed with 5 µm Supelco LC-1.

Interferences:

Method interferences may be caused by contaminants in solvents, reagents, glassware and other sample processing apparatus. All reagents and apparatus must be routinely demonstrated to be free from interferences by running laboratory reagent blanks. Interfering contamination may occur when a sample containing low concentrations of analytes is analyzed immediately following a sample containing relatively high concentrations. One or more laboratory method blanks should be analyzed following the analysis of a sample with high concentration of analytes.

Matrix interference may be caused by contaminants that are present in the sample. The extent of matrix interference will vary considerably from source to source, depending on the water sampled.

Quality Control Requirements:

Minimum quality control (QC) requirements are initial demonstration of laboratory capability, determination of surrogate compound recoveries in each sample and blank, monitoring internal standard peak area or height in each sample and blank, analysis of laboratory reagent blanks, laboratory fortified samples, laboratory fortified blanks, and QC samples. A laboratory reagent blank is analyzed to demonstrate that all glassware and reagent interferences are under control.

Initial demonstration of capability is fulfilled by analyzing four fortified reagent water samples with recovery value for each analyte following with the acceptable range (± 30% average recovery). Surrogate recoveries from samples or method blanks must be 70-130%. The internal standard response for any sample chromatogram should not deviate from the daily calibration check standard's internal standard response by more than 30% or laboratory fortified blanks and sample matrices are used to assess laboratory performance and analyte recovery, respectively.

Comparison with Other Methods:

There are no other methods summarized for carbaryl and carbofuran.

Analytes Covered by this Method:

Method 531.1 covers 10 N-methylcarbamoyloximes and N-methylcarbamate compounds including two compounds, carbaryl and carbofuran, which are of interested to the National Contaminated Sites Remediation Program, as shown in Table 8.

Comments on Use of this Method:

This method has been validated in a single laboratory and estimated detection limits (EDLs) have been determined for each analyte, as shown in Table 8. Observed detection limits may vary among waters, depending upon the nature of the interferences in the sample matrix and the specific instrumentation used. Analytes that are not separated chromatographically cannot be individually identified and measured unless an alternative technique for identification and quantitation exist.

Table 8. Analytes Covered Using U.S. EPA Method 531.1, Rev. 3

Analyte Name	CAS No.	Est. Det. Limit (µg/L)**	Concentration Used (µg/L)	Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Aldicarb	116-06-3	1.0	5	115	3.5
Aldicarb sulfone	1646-88-4	2.0	10	101	4.0
Aldicarb sulfoxide	1646-87-3	2.0	10	97	4.9
Baygon	114-26-1	1.0	5	106	3.2
Carbaryl*	63-25-2	2.0	10	97	5.8
Carbofuran*	1563-66-2	1.5	7.5	102	5.1
3-Hydroxycarbofuran	16655-82-6	2.0	10	102	4.1
Methiocarb	2032-65-7	4.0	20	94	1.9
Methomyl	16752-77-5	0.5	2.5	105	4.2
Oxamyl	23135-22-0	2.0	10	100	4.0

* Analytes targeted by the National Contaminated Sites Remediation Program.

** Estimated detection limit defined as Method Detection Limit (MDL) or a level of compound in a sample yielding a peak in the final extract with signal-to-noise of approximately 5, whichever is higher.

Title:

Purge and Trap Gas Chromatographic Method II, Method 6220C for Purgeable Aromatic and Unsaturated Compounds

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable to the determination of purgeable aromatic and unsaturated compounds in finished drinking water, raw source water, or drinking water in any treatment stage. It is, however, not applicable to styrene in chlorinated drinking water because of its rapid oxidation rate.

Sample Preparation:

Remove the plungers from two 5-mL syringes and attach a closed syringe valve to each. Warm the sample to room temperature, open the sample bottle, and carefully pour the sample into one of the syringe barrels to just short of overflowing. Replace the syringe plunger, invert the syringe, and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5 mL. For samples and blanks, add 10.0 µL of the surrogate addition solution and 10.0 µL of the internal standard addition solution to the sample through the syringe valve. Close the valve. Fill the second syringe in an identical manner from the same sample bottle. Reserve this second syringe for a reanalysis if necessary.

Instrumental Analysis:

An inert gas (zero grade nitrogen or helium) is bubbled through the sample. Attach the syringe-syringe assembly to syringe valve on purging device. Purge sample for 12.0 ± 0.1 min. at ambient temperature. Purged sample components are trapped in a tube of sorbent materials. When purging is complete, the sorbent tube is heated and backflushed to desorb the trapped sample onto a GC column.

Instrumentation Required:

Gas Chromatography System equipped with a photoionization detector (PID). Column #1: 1.5-2.5 m x 2.2 mm ID stainless steel or glass, packed with 5% SP-1000 and 1.75% Bentone-34 on Supelcoport (100/120 mesh); Column #2: 1.5-2.5 m x 2.2 mm ID stainless steel or glass, packed with 5% 1,2,3-tris(2-cyanoethoxy) propane on Chromosorb W-AW (60/80 mesh). Also required is a 5 mL purging device, a sorbent trap, and thermal desorption apparatus.

Interferences:

Impurities in the purge gas and organic compounds outgassing from the plumbing ahead of the trap account for most contamination problems. Demonstrate that the system is free from contamination under operational conditions by analyzing method blanks daily. Avoid using non-PTFE plastic tubing, non-PTFE thread sealants, or flow controllers with rubber components in the purge and trap system.

Samples can be contaminated by diffusion of volatile organics (particularly fluorocarbons and methylene chloride) through the septum seal during shipment and storage. Use a field reagent blank prepared from reagent water and carried through the sampling and handling procedure as a check on such contamination.

Contamination by carryover can occur whenever high-level and low-level concentration samples are analyzed sequentially. To reduce carryover, rinse purging device and sample syringe with reagent water between samples. Follow analysis of an unusually concentrated sample with an analysis of reagent water to check for cross-contamination. For samples containing large amounts of water-soluble materials, suspended solids, high boiling compounds, or high levels of the subject group of compounds, wash purging device with a detergent solution, rinse it with distilled water, and then dry it in an oven at 105°C between analyses. The trap and other parts of the system also are subject to contamination; therefore, frequently bake and purge the entire system. Loss of volatile constituents is also an important source of error.

Quality Control Requirements:

Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Demonstrate through the analysis of quality control check standards that the measurement system is in control. Analyze check standards equivalent to 10% of all samples analyzed. Acceptable recovery is 60% to 140% of the expected value.

Comparison with Other Methods:

The main advantage of this method is the lower cost of equipment. However, disadvantages include the lack of MDL data and less specificity of the PID as compared to mass spectrometric methods.

Analytes Covered by this Method:

Method 6220C covers 28 volatile organic compounds including all 11 of the monocyclic aromatic hydrocarbons and 4 of the chlorinated hydrocarbons that are of interest to the National Contaminated Sites Remediation Program as shown in Table 9.

Table 9. Analytes Covered Using SM 6220C

Analyte Name	CAS No.	Range (µg/L)	Method Det. Limit (µg/L)	Mean Accuracy (Avg %) Recoveries	Precision (Rel Std. Dev. %)
Benzene*	71-43-2	2.2-600	0.01-0.05	100	2.8
Bromobenzene	108-86-1	2.2-600	0.01-0.05	93	6.2
n-Butylbenzene	104-51-8	2.2-600	0.01-0.05	78	15.7
sec-Butylbenzene	135-98-8	2.2-600	0.01-0.05	80	11.0
tert-Butylbenzene	98-06-6	2.2-600	0.01-0.05	88	8.7
Chlorobenzene*	108-90-7	2.2-600	0.01-0.05	96	5.8
2-Chlorotoluene	95-49-8	2.2-600	0.01-0.05	Not listed	Not listed
4-Chlorotoluene	106-43-4	2.2-600	0.01-0.05	91	5.0
1,2-Dichlorobenzene*	95-54-1	2.2-600	0.01-0.05	92	7.1
1,3-Dichlorobenzene*	541-73-1	2.2-600	0.01-0.05	91	8.5
1,4-Dichlorobenzene*	106-46-7	2.2-600	0.01-0.05	95	6.4
Ethylbenzene*	100-41-4	2.2-600	0.01-0.05	93	8.5
Hexchlorobutadiene	87-68-3	2.2-600	0.01-0.05	74	16.8
Isopropylbenzene	98-82-8	2.2-600	0.01-0.05	88	8.7
4-Isopropyltoluene	99-87-6	2.2-600	0.01-0.05	Not listed	Not listed
Naphthalene	91-20-3	2.2-600	0.01-0.05	92	14.8
n-Propylbenzene	103-65-1	2.2-600	0.01-0.05	83	9.3
Styrene*	100-42-5	2.2-600	0.01-0.05	Not listed	Not listed
Tetrachloroethene*	127-18-4	2.2-600	0.01-0.05	97	7.8
Toluene*	108-88-3	2.2-600	0.01-0.05	94	6.6
1,2,3-Trichlorobenzene*	87-61-6	2.2-600	0.01-0.05	85	10.4
1,2,4-Trichlorobenzene*	120-82-1	2.2-600	0.01-0.05	86	10.1
Trichloroethene*	79-01-6	2.2-600	0.01-0.05	97	6.8
1,2,4-Trimethylbenzene	95-63-6	2.2-600	0.01-0.05	75	8.7
1,3,5-Trimethylbenzene	108-67-8	2.2-600	0.01-0.05	92	8.7
m-Xylene*	108-38-3	2.2-600	0.01-0.05	90	7.7
o-Xylene*	95-47-6	2.2-600	0.01-0.05	90	7.2
p-Xylene*	106-42-3	2.2-600	0.01-0.05	85	8.7

* Analytes targeted by the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

In a single laboratory using reagent water and known additions of 0.2 µg/L, observed method detection limits (MDLs) for these compounds were in the range of 0.01 to 0.05 µg/L, depending on the compound. These detection limits depend on instrument sensitivity and matrix effects. Individual aromatic compounds can be measured at concentrations up to 1500 µg/L. Analysis of complex mixtures containing partially resolved compounds may be hampered by concentration difference larger than a factor of 10.

Note that no specific ranges were provided on an individual compounds basis and also that no individual MDLs were available.

Title:

Liquid-Liquid Extraction Gas Chromatographic/Mass Spectrometric Method, Method 6410B, for Organic Compounds in Municipal and Industrial Discharges.

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable to the determination of organic compounds in municipal and industrial discharges that are partitioned into an organic solvent and are amenable to gas chromatography .

Sample Preparation:

Samples are made alkaline to pH >11 with 10 N sodium hydroxide solution and extracted with methylene chloride. The extracts are concentrated using a Kuderna-Danish (K-D) concentrator. The pH of the aqueous phase is then made acidic to pH <2 using sulfuric acid and again extracted with methylene chloride. The extracts are concentrated using a K-D concentrator. Either separatory funnels or continuous liquid-liquid extractors may be used to extract the aqueous phase with methylene chloride.

Instrumental Analysis:

An internal standard is added to the sample extract, mixed thoroughly, and 2 to 5 µL of the sample is immediately injected into the GC/MS system using the solvent-flush technique to minimize losses due to adsorption, chemical reaction, or evaporation. Smaller (1.0 µL) volumes may be injected if automatic samling devices are used.

Instrumentation:

A Gas Chromatography/Mass Spectrometry/Data System (GC/MS/DS) is required. The GC column for base/neutrals is 1.8 m x 2 mm ID glass, packed with 3% SP-2250 on Supelcoport (100/120 mesh or equivalent). Other packed or capillary columns (such as the DB-5 fused silica capillary column) may be used if quality control requirements are met.

Interferences:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. Laboratory reagent blanks should be routinely run to demonstrate that all materials are free from interferences. Clean all glassware thoroughly as soon as possible after use by rinsing with the last solvent used in it, followed by detergent washing with hot water and rinsing with distille d water.

Drain glassware dry and heat in a muffle furnace at 400°C for 15 to 30 minutes. Solvent rinses with acetone and hexane may be substituted for the baking to eliminate thermally stable materials, such as PCBs. After drying and cooling, seal and store glassware in a clean environment.

Quality Control Requirements:

As a quality control check, make known additions to all samples of surrogate standard solutions and calculate percent recovery of each surrogate compound. GC column performance tests and GC/MS calibration are required each day these analyses are performed. Analyze field duplicates to assess precision of environmental measurements.

Comparison with Other Methods:

Although not specified by the method, it should be applicable to both surface water and groundwater matrices. Either packed or capillary GC columns can be used with low resolution mass spectrometers. It is not applicable for analysis of soils or sediments.

Analytes Covered by this Method:

Method 6410B covers 61 base/neutral extractable and 11 acid extractable organic compounds, including all of the polycyclic aromatic hydrocarbons, all of the phthalic acid esters, 7 of the pesticides, 8 of the phenolic compounds, 3 of the monocyclic aromatic hydrocarbon, and 2 of the chlorinated hydrocarbons that are of interest to the National Contaminated Sites Remediation Program. The analytes covered by this method are shown in Table 10 and Table 11.

Comments on the Use of this Method:

Method 6410B is a broad-spectrum gas chromatographic/mass spectrometric (GC/MS) packed or capillary column method for the detection of semivolatile compounds following liquid-liquid extraction. A measured volume of sample is extracted serially with methylene chloride at a pH above 11 and again at a pH below 2. The extract is dried, concentrated, and analyzed by GC/MS. Although this method can be used to determine all of the listed compounds, it is not the most sensitive method for individual classes of compounds, which are detected at lower concentration by GC methods.

Table 10. Analytes Covered Using SM 6410B

Analyte Name	CAS No.	Method Det. Limit (µg/L)	Range (µg/L)	Bias and Recovery, x^* (µg/L)	Overall Precision, s^* (µg/L)
Acenaphthene	83-32-9	1.9	5-1300	0.96C+0.19	$0.21\bar{x}$-0.67
Acenaphthylene	208-96-8	3.5	5-1300	0.89C+0.74	$0.26\bar{x}$-0.54
Aldrin*	309-00-2	1.9	5-1300	0.78C+1.66	$0.43\bar{x}$+1.13
Anthracene	120-12-7	1.9	5-1300	0.80C+0.68	$0.27\bar{x}$-0.64
Benzo(a)anthracene*	56-55-3	7.8	5-1300	0.88C-0.60	$0.26\bar{x}$-0.28
Benzo(b)fluoranthene*	205-99-2	4.8	5-1300	0.93C-1.80	$0.29\bar{x}$+0.96
Benzo(k)fluoranthene*	207-08-9	2.5	5-1300	0.87C-1.56	$0.35\bar{x}$+0.40
Benzo(ghi)perylene	191-24-2	4.1	5-1300	0.98C-0.86	$0.51\bar{x}$-0.44
Benzo(a)pyrene*	50-32-8	2.5	5-1300	0.90C-0.13	$0.32\bar{x}$+1.35
β-BHC	319-85-7	4.2	5-1300	0.87C-0.94	$0.30\bar{x}$-1.94
δ-BHC	319-86-8	3.1	5-1300	0.29C-1.09	$0.93\bar{x}$-0.17
bis(2-Chloroethoxy) methane	111-91-1	5.3	5-1300	1.12C-5.04	$0.26\bar{x}$+2.01
bis(2-Chloroethyl) ether	111-44-4	5.7	5-1300	0.86C-1.54	$0.35\bar{x}$+0.10
bis(2-Chloroisopropyl) ether	108-60-1	5.7	5-1300	1.03C-2.31	$0.25\bar{x}$+1.04
bis(2-Ethylhexyl) phthalate*	117-81-7	2.5	5-1300	0.84C-1.18	$0.36\bar{x}$+0.67
4-Bromophenyl phenyl ether	101-55-3	1.9	5-1300	0.91C-1.34	$0.16\bar{x}$+0.66
Butyl benzyl phthalate*	85-68-7	2.5	5-1300	0.66C-1.68	$0.53\bar{x}$+0.92
Chlordane*	57-74-9	Not listed	5-1300	Not listed	Not listed
2-Chloronaphthalene	91-58-7	1.9	5-1300	0.89C+0.01	$0.13\bar{x}$+0.34
4-Chlorophenyl phenyl ether	7005-72-3	4.2	5-1300	0.91C+0.53	$0.30\bar{x}$-0.46
Chrysene	218-01-9	2.5	5-1300	0.93C-1.00	$0.33\bar{x}$-0.09
4,4'-DDD	72-54-8	2.8	5-1300	0.56C-0.40	$0.66\bar{x}$-0.96
4,4'-DDE	72-55-9	5.6	5-1300	0.70C-0.54	$0.39\bar{x}$-1.04
4,4'-DDT*	50-29-3	4.7	5-1300	0.79C-3.28	$0.65\bar{x}$-0.58
Dibenzo(a,h)anthracene*	53-70-3	2.5	5-1300	0.88C+4.72	$0.59\bar{x}$+0.25

Table 10. Continued

Analyte Name	CAS No.	Method Det. Limit (µg/L)	Range (µg/L)	Bias and Recovery, x* (µg/L)	Overall Precision, s* (µg/L)
Di-n-butyl phthalate	84-74-2	2.5	5-1300	0.59C+0.71	0.39$\bar{x}$+0.60
1,2-Dichlorobenzene*	95-50-1	1.9	5-1300	0.80C+0.28	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene*	541-73-1	1.9	5-1300	0.86C-0.70	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene*	106-46-7	4.4	5-1300	0.73C-1.47	0.29$\bar{x}$+0.36
3,3'-Dichlorobenzidine	91-94-1	16.5	5-1300	1.23C-12.65	0.47$\bar{x}$+3.45
Dieldrin*	60-57-1	2.5	5-1300	0.82C-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate*	84-66-2	1.9	5-1300	0.43C+1.00	0.52$\bar{x}$+0.22
Dimethyl phthalate*	131-11-3	1.6	5-1300	0.20C+1.03	1.05$\bar{x}$-0.92
2,4-Dinitrotoluene	121-14-2	5.7	5-1300	0.92C-4.81	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	606-20-2	1.9	5-1300	1.06C-3.60	0.19$\bar{x}$+0.35
Di-n-octyl phthalate*	117-84-0	2.5	5-1300	0.76C-0.79	0.37$\bar{x}$+1.19
Endosulfan sulfate	1031-07-8	5.6	5-1300	0.39C+0.41	0.63$\bar{x}$-1.03
Endrin aldehyde	7421-93-4	Not listed	5-1300	0.76C-3.86	0.73$\bar{x}$-0.62
Fluoranthene	206-44-0	2.2	5-1300	0.81C+1.10	0.28$\bar{x}$-0.60
Fluorene	86-73-7	1.9	5-1300	0.90C-0.00	0.13$\bar{x}$+0.61
Heptachlor*	76-44-8	1.9	5-1300	0.87C-2.97	0.50$\bar{x}$-0.23
Heptachlor epoxide*	1024-57-3	2.2	5-1300	0.92C-1.87	0.28$\bar{x}$-0.64
Hexachlorobenzene*	118-74-1	1.9	5-1300	0.74C+0.66	0.43$\bar{x}$-0.52
Hexachlorobutadiene	87-68-3	0.9	5-1300	0.71C-1.01	0.26$\bar{x}$+0.49
Hexachloroethane	67-72-1	1.6	5-1300	0.73C-0.83	0.17$\bar{x}$+0.80
Indeno (1,2,3-cd)pyrene*	193-39-5	3.7	5-1300	0.78C-3.10	0.50$\bar{x}$+0.44
Isophorone	78-59-1	2.2	5-1300	1.12C+1.41	0.33$\bar{x}$+0.26
Naphthalene*	91-20-3	1.6	5-1300	0.76C+1.58	0.30$\bar{x}$-0.68
Nitrobenzene	98-95-3	1.9	5-1300	1.09C-3.05	0.27$\bar{x}$+0.21
N-Nitrosodi-n-propylamine	621-64-7	Not listed	5-1300	1.12C-6.22	0.44$\bar{x}$+0.47

Table 10. Continued

Analyte Name	CAS No.	Method Det. Limit (µg/L)	Range (µg/L)	Bias and Recovery, x^* (µg/L)	Overall Precision, s^* (µg/L)
Aroclor 1016	12674-11-2	Not listed	5-1300	Not listed	Not listed
Aroclor 1221	11104-28-2	30	5-1300	Not listed	Not listed
Aroclor 1232	11141-16-5	Not listed	5-1300	Not listed	Not listed
Aroclor 1242*	53469-21-9	Not listed	5-1300	Not listed	Not listed
Aroclor 1248*	12672-29-6	Not listed	5-1300	Not listed	Not listed
Aroclor 1254*	11097-69-1	36	5-1300	Not listed	Not listed
Aroclor 1260*	11096-82-5	Not listed	5-1300	0.81C-10.86	$0.43\bar{x}+1.82$
Phenanthrene	85-01-8	5.4	5-1300	0.87C-0.06	$0.15\bar{x}+0.25$
Pyrene*	129-00-0	1.9	5-1300	0.84C-0.16	$0.15\bar{x}+0.31$
Toxaphene	8001-35-2	Not listed	5-1300	Not listed	Not listed
1,2,4-Trichlorobenzene*	120-82-1	1.9	5-1300	0.94C-0.79	$0.21\bar{x}+0.39$

* Analytes targeted by the National Contaminated Sites Remediation Program.
x^* = Expected recovery for one or more measurements of a sample containing a concentration of C.
s^* = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$.
C = True value for the concentrations
$\bar{x}$ = average recovery found for measurements of samples containing a concentration of C.
Note: Endrin δ-BHC (Lindane) and several other compounds decompose under the alkaline conditions of the initial extraction.

Table 11. Method Performance Criteria for Acid Extractables

Analyte Name	CAS No.	Method Det. Limit (µg/L)	Range (µg/L)	Bias as Recovery, x^*	Overall Precision, s^* (µg/L)
4-Chloro-3-methylphenol	59-50-7	3.0	5-1300	0.84C+0.35	$0.29\bar{x}+1.31$
2-Chlorophenol*	95-57-8	3.3	5-1300	0.78C+0.29	$0.28\bar{x}+0.97$
2,4-Dichlorophenol*	120-83-2	2.7	5-1300	0.87C+0.13	$0.21\bar{x}+1.28$
2,4-Dimethylphenol*	105-67-9	2.7	5-1300	0.71C+4.41	$0.22\bar{x}+1.31$
2,4-Dinitrophenol*	51-28-5	42	5-1300	0.81C-18.04	$0.42\bar{x}+26.29$
2-Methyl-4,6-dinitrophenol*	534-52-1	24	5-1300	1.04C-28.04	$0.26\bar{x}+23.10$
2-Nitrophenol	88-75-5	3.6	5-1300	1.07C-1.15	$0.27\bar{x}+2.60$
4-Nitrophenol	100-02-7	2.4	5-1300	0.61C-1.22	$0.44\bar{x}+3.24$
Pentachlorophenol*	87-86-5	3.6	5-1300	0.93C+1.99	$0.30\bar{x}+4.33$
Phenol*	108-95-2	1.5	5-1300	0.43C+1.26	$0.35\bar{x}+0.58$
2,4,6-Trichlorophenol*	88-06-2	2.7	5-1300	0.91C-0.18	$0.22\bar{x}+1.81$

* Analytes targeted by the National Contaminated Sites Remediation Program.
x^* = Expected recovery for one or more measurements of a sample containing a concentration of C.
s^* = Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$.
C = True value for the concentrations
$\bar{x}$ = average recovery found for measurements of samples containing a concentration of C.
Note: Endrin δ-BHC (Lindane) and several other compounds decompose under the alkaline conditions of the initial extraction.

Table 12. Suggested Internal and Surrogate Standards

Base/Neutral Fraction	Acid Fraction
Aniline-d_5	2-Fluorophenol
Anthracene-d_{10}	Pentafluorophenol
Benzo(a)anthracene-d_{12}	Phenol-d_5
4,4'-Dibromobiphenyl	2-Perfluoromethyl phenol
4,4'-Dibromooctafluorobiphenyl	
Decafluorobiphenyl	
2,2'-Difluorobiphenyl	
4-Fluoroaniline	
1-Fluoronaphthalene	
2-Fluoronaphthalene	
Naphthalene-d_8	
Nitrobenzene-d_5	
2,3,4,5,6-Pentafluorobiphenyl	
Phenanthrene-d_{10}	
Pyridine-d_5	

Title:

Liquid-Liquid Extraction Gas Chromatographic Method, Method 6420B.

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable to the determination of phenol and certain substituted phenols in municipal and industrial discharges.

Sample Preparation:

Mark the water meniscus on side of sample bottle for later determination of volume. Pour the entire sample into a 2-L separatory funnel. For samples high in organic content, solvent wash sample at basic pH as prescribed in next paragraph, to remove potential interferences. During the wash, avoid prolonged or exhaustive contact with solvent which may result in low recovery of some phenols, notably phenol and 2,4-dimethylphenol. For relatively clean samples, omit the wash and extract directly.

To wash, adjust the pH to 12.0 or greater with NaOH solution. Add 60 mL of methylene chloride and shake the funnel for 1 min with periodic venting to release excess pressure and discard the solvent layer. Repeat the wash up to two additional times if significant color is being removed. Before extraction, adjust to a pH of 1 to 2 with H_2SO_4 and extract three times with methylene chloride. Assemble the Kuderna-Danish (K-D) apparatus, concentrate the extract to 1 mL, and remove, drain, and cool the K-D apparatus.

Increase the temperature of a hot water bath to 100°C. Remove the Snyder column and rinse flask and its lower joint into concentrator tube with 1 to 2 mL of 2-propanol. Preferably use a 5-mL syringe for this operation. Attach a two-ball micro-Snyder column to the concentrator tube and prewet the column by adding about 0.5 mL 2-propanol to the top. Place the micro-K-D apparatus on a water bath so that concentrator tube is partially immersed in hot water. Adjust vertical position of the apparatus and water temperature so as to complete the concentration in 5 to 10 minutes. When the apparent volume of liquid reaches 2.5 mL, remove K-D apparatus and let it drain and cool for at least 10 minutes. Add 2 mL 2-propanol through top of micro-Snyder column and resume concentrating as before. When the apparent volume of liquid reaches 0.5 mL, remove the K-D apparatus and let it drain and cool for at least 10 min.

Remove the micro-Snyder column and rinse the lower joint into the concentrator tube with a minimum amount of 2-propanol. Adjust extract volume to 1.0 mL. Stopper the concentrator tube and store it at 4°C if further processing will not be done immediately. If the extract is to be stored longer than 2 days, transfer it to a PTFE-sealed screw-cap vial. If the sample extract requires no further cleanup, proceed with chromatographic analysis. If the sample requires further cleanup, follow the procedure below.

Place 4.0 g of silica gel in a chromatographic column. Tap column to settle silica gel and add about 2 g anhydrous Na_2SO_4 to the top. Pre-elute the column with 6 mL hexane. Discard the eluate and just before exposing Na_2SO_4 layer to air, pipet the sample onto the column. Elute the column with 10.0 mL hexane and discard eluate. Elute column, in order, with 10.0 mL 15% toluene in hexane (Fraction 1), 10.0 mL 40% toluene in hexane (Fraction 2), 10.0 mL 75% toluene in hexane (Fraction 3), and 10.0 mL 15% 2-propanol in toluene (Fraction 4). Prepare all elution mixtures on a volume:volume basis. Fractions may be combined as desired, depending on the specific phenols of interest or level of interferences.

Determine the original sample volume by refilling sample bottle to the mark and transferring liquid to a 1000 mL graduated cylinder. Record sample volume to nearest 5 mL.

Instrumental Analysis:

This method is a gas chromatographic (GC) method using either flame ionization detection (FID) or derivatization and electron capture detection (ECD) to determine phenols. For GC/FID, if the internal standard calibration procedure is used, add internal standard to sample extract and mix it thoroughly immediately before injecting 2 to 5 µL of the sample extract or standard into the GC using the solvent-flush technique. Smaller (1.0 µL) volumes may be injected if automatic devices are used. Record the volume injected to nearest 0.05 µL and the resulting peak size in area or peak height units.

For analysis by GC/ECD, derivatization is required. Pipet 1.0 mL of the 2-propanol solution of standard or sample extract into a glass reaction via. Add 1.0 mL derivatizing reagent; this is sufficient to derivatize a solution having a total phenolic content not exceeding 0.3 mg/mL. Add about 3 mg K_2CO_3 and shake gently. Cap mixture and heat for 4 hours at 80°C in a hot water bath. Remove from hot water bath and let cool. Add 10 mL of hexane and shake vigorously for 1 minute. Add 3.0 mL distilled, deionized water and shake for 2 minutes. Decant a portion of the organic layer into a concentrator tube and cap with a glass stopper. Clean up solution using procedure described in the Sample Preparation section.

Inject 2 to 5 µL column fractions into the gas chromatograph using the solvent-flush technique. Smaller (1.0 µL) volumes can be injected if automatic devices are used. Record the volume injected to nearest 0.05 µL and resulting peak size in area or peak height units. If peak response exceeds the linear range of system, dilute the extract and reanalyze.

Instrumentation Required:

Gas Chromatograph System equipped with either a flame ionization detector (FID) or an electron capture detector (ECD). The system should be temperature programmable and be suitable for on-column injection. Column for underivatized phenols: 1.8 M x 2 mm ID glass, packed with 1% SP1240DA or Supelcoport (80/100 mesh), or equivalent; Column for derivatized phenols: 1.8 M x 2 mm ID glass, packed with 5% OV-17 or Chromosorb W-AW-DMCS (80/100 mesh), or equivalent. Other packed or capillary columns may be used if the quality control requirements are met.

Interferences:

Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. Laboratory reagent blanks should be routinely run to demonstrate that all materials are free from interferences. Clean all glassware thoroughly as soon as possible after use by rinsing with the last solvent used in it, followed by detergent washing with hot water and rinsing with distilled water. Drain dry and heat in a muffle furnace at 400°C for 15 to 30 minutes. Solvent rinses with acetone and hexane may be substituted for the baking to eliminate thermally stable materials, such as PCBs. After drying and cooling, seal and store glassware in a clean environment.

The cleanup procedure can be used to overcome many of the interferences, but unique samples may require additional cleanup to achieve the method detection limits. The basic sample wash may cause low recovery of phenol and 2,4-dimethylphenol.

Quality Control Requirements:

A minimum quality control program consists of an initial demonstration of laboratory capability and an ongoing analysis of samples with known additions. Each day, analyze a reagent water blank to demonstrate that interferences from the analytical system are under control. Make known additions to, and analyze, a minimum of 10% of all samples to monitor and evaluate laboratory data quality. Also, control of the measurement system should be demonstrated through the analysis of quality control check standards.

Quality control check standards should be prepared at a concentration of 100 µg/L in four 1 L portions of reagent water. The check sample should be analyzed in the same manner as samples following sample preparation. If analysis of any compound fails to meet the acceptance criteria for recovery, prepare and analyze a check standard containing the compound that failed.

Comparison with Other Methods:

This method is applicable only for monitoring proposes because of the relative non-selective characteristics of the detectors used. However, it is relatively rapid and inexpensive. It is also limited to aqueous samples.

Analytes Covered by this Method:

Method 6420B covers 11 phenolic compounds including 8 of the phenolic compounds that are of interest to the National Contaminated Sites Remediation Program, as shown in Table 13.

Comments on the Use of this Method:

This method is applicable to the determination of phenolic compounds. When analyzing unfamiliar samples for any or all of these compounds, support the identifications by at least one additional technique. Alternatively, use the derivatization, cleanup and the GC/ECD procedure to confirm measurements made by the GC/FID procedure.

Table 13. Analytes Covered Using SM 6420B

Analyte Name	CAS No.	GC/FID Method Det. Limit (µg/L)	GC/ECD** Method Det. Limit (µg/L)	Range (µg/L)	Bias, as Recovery, x^* (µg/L)	Overall Precision, s^* (µg/L)
4-Chloro-3-methylphenol	59-50-7	0.36	1.8	12-450	0.87C-1.97	$0.16\bar{x}+1.41$
2-Chlorophenol*	95-57-8	0.31	0.58	12-450	0.83C-0.84	$0.21\bar{x}+0.75$
2,4-Dichlorophenol*	120-83-2	0.39	0.68	12-450	0.81C+0.48	$0.18\bar{x}+0.62$
2,4-Dimethylphenol*	105-67-9	0.32	0.63	12-450	0.62C-1.64	$0.25\bar{x}+0.48$
2,4-Dinitrophenol*	51-28-5	13.0	Not listed	12-450	0.80C-1.58	$0.29\bar{x}+4.51$
2-Methyl-4,6-dinitrophenol*	523-52-1	16.0	Not listed	12-450	0.84C-1.01	$0.19\bar{x}+5.85$
2-Nitrophenol	88-75-5	0.45	0.77	12-450	0.81C-0.76	$0.14\bar{x}+3.84$
4-Nitrophenol	100-02-7	2.8	0.70	12-450	0.46C+0.18	$0.19\bar{x}+4.79$
Pentachlorophenol*	87-86-5	7.4	0.59	12-450	0.83C+2.07	$0.23\bar{x}+0.57$
Phenol*	108-95-2	0.14	2.2	12-450	0.43C+0.11	$0.17\bar{x}+0.77$
2,4,6-Trichlorophenol*	88-06-2	0.64	0.58	12-450	0.86C-0.40	$0.13\bar{x}+2.40$

* Analytes targeted by the National Contaminated Sites Remediation Program.
** No bias and precision data available for GC/ECD approach.
x^* Expected recovery for one or more measurements of a sample containing a concentration of C.
s^* Expected interlaboratory standard deviation of measurements at an average concentration found of $\bar{x}$.
C True value for the concentration
$\bar{x}$ Average recovery found for measurements of samples containing a concentration of C.

Title:

Organochlorine Pesticides and Polychlorinated Biphenyls By Gas Chromatography. U.S. EPA Method 8080B, Revision 2, November 1990

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 8080B, Revision 1, November 1990. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is used to determine the concentration of various organochlorine pesticides and polychlorinated biphenyls in extracts prepared from water, ground water, soils, and sediments.

Sample Preparation:

Using a 1 liter graduated cylinder, measure out 1 liter (nominal) of sample and transfer it quantitatively to the continuous extractor. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 liter. Check the pH of the sample with wide-range pH paper and adjust the pH, if necessary, to pH 5-9 using 1:1 (V/V) sulfuric acid or 10 N sodium hydroxide. Pipet 1.0 mL of the surrogate standard spiking solution into each sample in the extractor and mix well.

For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. Add 300 - 500 mL of methylene chloride and several boiling chips to distilling flask. Add sufficient reagent water to the extractor to ensure operation and extract for 18 - 24 hours. Allow to cool; then detach the boiling flask. Perform concentration using the Kuderna-Danish (K-D) technique described below.

Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 mL concentrator tube to a 500 mL evaporation flask. Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in a K-D concentrator. Rinse the flask which contained the solvent extract with 20 - 30 mL of methylene chloride and add it to the column to complete the quantitative transfer.

Add one or two clean boiling chips to the flask and attach a three ball Snyder column. Prewet the Snyder column by adding about 1 mL of methylene chloride to the top of the column. Place the K-D apparatus on a hot bath at 80 - 90°C and concentrate at constant rate in 10 - 20 minutes.

When the apparent volume of liquid reaches 1 mL, remove the K-D apparatus from the water bath and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joints into the concentrator tube with 1-2 mL of extraction solvent. Proceed to hexane solvent exchange.

Soils and Sediments:

The following step should be performed rapidly to avoid loss of the more volatile extractables. Weigh approximately 30 g of sample into a 400 mL beaker. Record the weigh to the nearest 0.1 g. Nonporous or wet samples (gummy or clay type) that do not have a free flowing sandy texture must be mixed with 60 g of anhydrous sodium sulfate, using a spatula. After addition of sodium sulfate, the sample should be free flowing. Add 1 mL of surrogate standards to all samples, spikes, standards, and blanks. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. Immediately add 100 mL of 1:1 methylene chloride:acetone. Extract ultrasonically for 3 minutes, with output control knob set at 10 (full power) and with mode switch on Pulse. Decant and filter extracts through Whatman No. 41 filter paper using vacuum filtration or centrifuge, and decant extraction solvent.

Repeat the extraction two or more times with two additional 100 mL portions of solvent. Decant off the solvent after each ultrasonic extraction. On the final ultrasonic extraction, pour the entire sample into the Buchner funnel and rinse with extraction solvent.

Dry the extract by passing it through a drying column containing about 10 cm of anhydrous sodium sulfate. Collect the dried extract in the K-D concentrator. Wash the extractor flask and sodium sulfate column with 100-125 mL of extraction solvent to complete the quantitative transfer. Perform concentration using the Kuderna-Danish (K-D) technique described above followed by a hexane solvent exchange.

Hexane/Exchange:

Increase the temperature of the hot water bath to about 90°C. Momentarily remove the Snyder column, add 50 mL of hexane, a new boiling chip, and reattach the Snyder column. Concentrate until the apparent volume of liquid reaches 1 mL, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column and rinse the flask and its lower joint into the concentrator tube with 1 - 2 mL of hexane. Adjust the extract volume to 10.0 mL. Stopper the concentration tube and store refrigerated at 4°C, if further processing will not be performed immediately. If the extract will be stored longer than two days, transfer to a vial with Teflon-lined screw-cap or crimp top.

Instrumental Analysis:

A 2 to 5 uL samples is injected into a gas chromatograph (GC) using the solvent flush technique, and compounds in the GC effluent are detected by an electron capture detector (ECD) or an electrolytic conductivity detector (HECD). Both neat and diluted organic liquids may be analyzed by direct injection.

Instrumentation Required:

Gas Chromatographic System capable of on-column injections, an electron capture detector (ECD), an electrolytic conductivity detector (HECD). Column 1: Supelcoport (100/120 mesh) coated with 1.5% SP-2250/1.95% SP-2401 packed in a 1.8 M x 4 mm ID glass column. Column #2: Supelcoport (100/120 mesh) coated with 3% OV-1 in a 1.8 M x 4 mm ID glass column.

Interferences:

Interferences coextracted from the samples will vary considerably from source to source. Interferences by phthalate esters can pose a major problem in pesticide determinations when using the electron capture detector. These compounds generally appear in the chromatogram as large late-eluting peaks, especially in the 15% and 50% fractions from the Florisil cleanup. Common flexible plastics contain varying amounts of phthalates. These phthalates are easily extracted or leached from such materials during laboratory operations. Cross contamination of clean glassware routinely occurs when plastics are handled during extraction steps, especially when solvent-wetted surfaces are handled. Interferences from phthalates can best be minimized by avoiding contact with any plastic materials. Exhaustive cleanup of reagents and glassware may be required to eliminate background phthalate contamination. The contamination from phthalate esters can be completely eliminated with a microcoulometric or electrolytic conductivity detector.

Solvents, reagent, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks.

Quality Control Requirements:

Before processing any samples, the analyst should demonstrate through the analysis of a reagent water blank that all glassware and reagents are interference free. Each time a set of samples are processed, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

A reagent blank, a matrix spike and a duplicate or matrix spike duplicate must be performed for each analytical batch (up to a maximum of 20 samples) analyzed.

For GC analysis, the analytical system performance must be verified by analyzing quality control (QC) check samples. The QC check sample concentration should contain each single-component analyte at the following concentrations in acetone: 4,4'- DDD, 10 µg/mL; 4,4'- DDT, 10 µg/mL; endosulfan II, 10 µg/mL; endosulfan sulfate, 10 µg/mL; and any other single-component pesticide at 2 µg/mL. If the method is only to be used to analyze PCBs, Chlordane, or Toxaphene, the QC check sample concentrate should contain the most representative multi-component parameter at a concentration of 50 µg/mL in acetone.

Comparison with Other Methods:

This method is suitable for monitoring-type analyses. It is not as selective as methods which use a mass spectrometer as a detector but it is relatively inexpensive. This method also has the advantage of covering both aqueous and solid (soils and sediments) matrices.

Analytes Covered by this Method:

This method covers 26 compounds including 13 pesticides and chlorinated hydrocarbons of interest to the National Contaminated Sites Remediation Program, as shown in Table 14.

Comments on Use of this Method:

This method provides gas chromatographic conditions for the detection of ppb concentrations of certain organochlorine pesticides and PCBs. Prior to the use of this method, appropriate sample extraction techniques must be used.

The sensitivity of this method usually depends on the concentration of interferences rather than on instrumental limitations. If interferences prevent detection of the analytes, method 8080 may also be performed on samples that have undergone cleanup.

The method was tested by 20 laboratories using organic-free reagent water, drinking water, surface water, and three industrial wastewaters spiked at six concentrations. Concentrations used in the study ranged from 0.5 to 30 µg/L for single-component pesticides and from 8.5 to 400 µg/L for multi-component parameters. Overall precision and method accuracy were found to be directly related to the concentration of the parameter and essentially independent of the sample matrix.

Table 14. Analytes Covered Using U.S. EPA Method 8080B, Rev. 2

Compound Name	CAS No.[a]	Method Detection Limit (µg/L)	Conc. Range, (µg/L)	Accuracy, as Recovery, x* (µg/L)	Overall Precision, S* (µg/L)
Aldrin*	309-00-2	0.004	0.5-30	0.81C+0.04	0.20x̄-0.01
α-BHC	319-84-6	0.003	0.5-30	0.84C+0.03	0.23x̄-0.00
β-BHC	319-85-7	0.006	0.5-30	0.81C+0.07	0.33x̄-0.95
δ-BHC	319-86-8	0.009	0.5-30	0.81C+0.07	0.25x̄+0.03
γ-BHC (Lindane)*	58-89-9	0.004	0.5-30	0.82C-0.05	0.22x̄+0.04
Chlordane (technical)*	12789-03-6	0.014	8.5-400	0.82C-0.04	0.18x̄+0.18
4,4'-DDD	72-54-8	0.011	0.5-30	0.84C+0.30	0.27x̄-0.14
4,4'-DDE	72-55-9	0.004	0.5-30	0.85C+0.14	0.28x̄-0.09
4,4'-DDT*	50-29-3	0.012	0.5-30	0.93C-0.13	0.31x̄-0.21
Dieldrin*	60-57-1	0.002	0.5-30	0.90C+0.02	0.16x̄+0.16
Endosulfan I	959-98-8	0.014	0.5-30	0.97C+0.04	0.18x̄+0.08
Endosulfan II	33212-65-9	0.004	0.5-30	0.93C+0.34	0.47x̄-0.20
Endosulfan Sulfate	1031-07-8	0.066	0.5-30	0.89C-0.37	0.24x̄+0.35
Endrin*	72-20-8	0.006	0.5-30	0.89C-0.04	0.24x̄+0.25
Endrin aldehyde	7421-93-4	0.023	0.5-30	Not listed	Not listed
Heptachlor*	76-44-8	0.003	0.5-30	0.69C+0.04	0.16x̄+0.08
Heptachlor epoxide*	1024-57-3	0.083	0.5-30	0.89C+0.10	0.25x̄-0.08
4,4'-Methoxychlor	72-43-5	0.176	0.5-30	Not listed	Not listed
Toxaphene	8001-35-2	0.24	8.5-400	0.80C+1.74	0.20x̄+0.22
Aroclor-1016	12674-11-2	nd	8.5-400	0.81C+0.50	0.15x̄+0.45
Aroclor-1221	1104-28-2	nd	8.5-400	0.96C+0.65	0.35x̄-0.62
Aroclor-1232	11141-16-5	nd	8.5-400	0.91C+10.79	0.31x̄+3.50
Aroclor-1242*	53469-21-9	0.065	8.5-400	0.91C+10.79	0.31x̄+3.50
Aroclor-1248*	12672-29-6	nd	8.5-400	0.91C+10.79	0.31x̄+3.50
Aroclor-1254*	11097-69-1	nd	8.5-400	0.91C+10.79	0.31x̄+3.50
Aroclor-1260*	11096-82-5	nd	8.5-400	0.91C+10.79	0.31x̄+3.50

* Analytes targeted by the National Contaminated Sites Remediation Program
x* Expected recovery for one or more measurements of a sample containing concentration C, in µg/L.
S* Expected interlaboratory standard deviation of measurements at an average concentration found of in µg/L.
C True value for the concentration, in µg/L.
x̄ Average recovery found for measurements of samples containing a concentration of C, in µg/L.

Title:

Volatile Organics by Gas Chromatography/Mass Spectrometry (GC/MS): Packed Column Technique. U.S. EPA Method 8240B, Revision 2, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 8240B, Revision 2, November 1990. Office of Solid Wastes, Washington, D.C.

Method Applicability:

Nearly all types of samples, regardless of water content, including groundwater, 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.

Sample Preparation:

Liquid Samples

Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample 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. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one Volatile Organic Analysis (VOA) vial, the analyst should fill a second syringe 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. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

Add 10 µL of surrogate spiking solution and 10 µL of internal standard spiking solution through the valve bore of the syringe; then close the valve. 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 sample is equivalent to a concentration of 50 µg/L of each surrogate standard.

Sediment/Soil and Waste Samples

It is recommended that all samples of this type be screened by GC analysis prior to the purge-and-trap GC/MS analysis. The headspace method (EPA Method 3810) or the hexadecane extraction and screening method (EPA Method 3820) may be used for this purpose. These samples may contain percent quantities of purgeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/kg) or the high-concentration method (>1 mg/kg).

Low-concentration method - This is designed for samples containing individual purgeable compounds of <1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples.

Remove the plunger from a 5-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution and internal standard solution to the syringe through the valve.

Use a 5 g sample if the expected concentration is <0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount of the sample into a tared purge device. Note and record the actual weight. Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

High-concentration method - This method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes that are insoluble in methanol are diluted with reagent tetraglyme or possibly polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing internal standards. This is purged at ambient temperature. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20 mL vial. Note and record the actual weight. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. Quickly add 9.0 mL of appropriate solvent then add 1.0 mL of the surrogate spiking solution to the vial cap and shake for 2 minutes.

Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 µL of internal standard solution. Also add the volume of solvent extract determined in Table 15 below and a volume of extraction or dissolution solvent to total 100 µL (excluding methanol in standards).

Table 15. Quantity of Methanol Extract Required for Analysis of High-Concentration Soils/Sediments with EPA Method 8240B, Rev. 2

Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

Instrumental Analysis:

The volatile compounds are introduced into a gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). For the purge-and-trap method an inert gas (zero grade nitrogen or helium) is bubbled through a 5 mL solution at ambient temperature. Purged sample components are trapped in a tube of sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with inert gas to desorb the trapped components onto a GC column.

Instrumentation Required:

Gas Chromatography/Mass Spectrometry/Data System. Column: 6 ft x 0.1 in I.D. glass, packed with 1% SP-1000 on Carbopack-B (60/80 mesh). Also required is a 5 mL purging device, a sorbent trap, and a thermal desorption apparatus which may be connected to the GC/MS system.

Interferences:

Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for many contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-PTFE plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

Interferences purged or coextracted from the samples will vary considerably from source to source, depending upon the particular sample or extract being tested. Method blanks prepared from reagent water and analyzed under the same conditions as the samples can identify these interferences. Cross-contamination can occur whenever high-level and low-level samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by the analysis of organic-free reagent water to check for cross-contamination. The purge-and-trap system may require extensive bake-out and cleaning after a high-level sample. Reconditioning of traps containing combinations of silica gel and coconut charcoal is performed to minimize release of residual water from previous analyses.

Samples also 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. The laboratory where volatile analysis is performed and also the refrigerated storage area should be completely free of solvents.

Quality Control Requirements:

Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

Comparison with Other Methods:

EPA Method 8240B covers many of the analytes of interest and is applicable to surface water, groundwater, soils, and sediments. It is also a sensitive and highly selective method since it uses mass spectrometry for identification and quantification of pollutants. However, because it uses a packed column it is not capable of the higher chromatographic resolution and somewhat greater sensitivity that EPA Method 8260, EPA Method 524.2, and Standard Methods 6210D provide. However, the latter two methods are not applicable to soils and sediments but they do cover surface and groundwater matrices. This method is also the only one that specifies xylenes as an unspecified mixture for analyses. The other methods all analyze for the three xylene isomers individually.

Analytes Covered by this Method:

Method 8240B covers 80 volatile organic compounds including 6 of the monocyclic aromatic hydrocarbons and 14 of the chlorinated hydrocarbons that are of interest to the National Contaminated Sites Remediation Program as shown in Table 16.

Table 16. Analytes Covered Using U.S. EPA Method 8240B, Rev. 2

Analyte Name	CAS No.	Range[a]	Estimated Quantitation Limits[b]		Accuracy[c] (µg/L)	Precision[d] (µg/L)
			Groundwater (µg/L)	Low Soil/ Sediment (µg/kg)		
Acetone	67-64-1	5-600 µg/L	100	100	Not listed	Not listed
Acetonitrile	75-05-8	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Acrolein	107-02-8	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Acrylonitrile	107-13-1	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Allyl alcohol	107-18-6	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Allyl chloride	107-05-1	5-600 µg/L	5	5	0.93C+2.00	$0.25\bar{x}$-1.13
Benzene*	71-43-2	5-600 µg/L	5	5	Not listed	Not listed
Benzyl chloride	100-44-7	5-600 µg/L	100	100	Not listed	Not listed
Bromoacetone	598-31-2	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Bromodichloromethane	75-27-4	5-600 µg/L	5	5	1.03C-1.58	$0.20\bar{x}$+1.13
Bromoform	75-25-2	5-600 µg/L	5	5	1.18C-2.35	$0.17\bar{x}$+1.38
Bromomethane	74-83-9	5-600 µg/L	10	10	1.00C	$0.58\bar{x}$
2-Butanone	78-93-3	5-600 µg/L	100	100	Not listed	Not listed
Carbon disulfide	75-15-0	5-600 µg/L	100	100	Not listed	Not listed
Carbon tetrachloride*	56-23-5	5-600 µg/L	5	5	1.10C-1.68	$0.11\bar{x}$+0.37
Chlorobenzene*	108-90-7	5-600 µg/L	5	5	0.98C+2.28	$0.26\bar{x}$-1.92
Chlorodibromomethane	124-48-1	5-600 µg/L	5	5	Not listed	Not listed
Chloroethane	75-00-3	5-600 µg/L	10	10	1.18C+0.81	$0.29\bar{x}$+1.75
2-Chloroethanol	107-07-3	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
2-Chloroethyl vinyl ether	110-75-8	5-600 µg/L	10	10	1.00C	$0.84\bar{x}$
Chloroform*	67-66-3	5-600 µg/L	5	5	0.93C+0.33	$0.18\bar{x}$+0.16
Chloromethane	74-87-3	5-600 µg/L	10	10	1.03C-1.81	$0.58\bar{x}$+0.43
Chloroprene	126-99-8	5-600 µg/L	5	5	Not listed	Not listed
3-Chloropropionitrile	542-76-7	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Dibromochloromethane	124-48-1	5-600 µg/L	Not listed	Not listed	1.01C-0.03	$0.17\bar{x}$+0.49
1,2-Dibromo-3-chloropropane	96-12-8	5-600 µg/L	100	100	Not listed	Not listed

Table 16. Continued

Analyte Name	CAS No.	Range[a]	Estimated Quantitation Limits[b]		Accuracy[c] (µg/L)	Precision[d] (µg/L)
			Groundwater (µg/L)	Low Soil/ Sediment (µg/kg)		
1,2-Dibromoethane	106-93-4	5-600 µg/L	5	5	Not listed	Not listed
Dibromomethane	74-95-3	5-600 µg/L	5	5	Not listed	Not listed
1,2-Dichlorobenzene*	95-50-1	5-600 µg/L	Not listed	Not listed	0.94C+4.47	$0.30\bar{x}$-1.20
1,3-Dichlorobenzene*	541-73-1	5-600 µg/L	Not listed	Not listed	1.06C+1.68	$0.18\bar{x}$-0.82
1,4-Dichlorobenzene*	106-46-7	5-600 µg/L	Not listed	Not listed	0.94C+4.47	$0.30\bar{x}$-1.20
1,4-Dichloro-2-butene	764-41-0	5-600 µg/L	100	100	Not listed	Not listed
Dichlorodifluoromethane	75-71-8	5-600 µg/L	5	5	Not listed	Not listed
1,1-Dichloroethane*	75-34-3	5-600 µg/L	5	5	1.05C+.036	$0.16\bar{x}$+0.47
1,2-Dichloroethane*	107-06-2	5-600 µg/L	5	5	1.02C+0.45	$0.21\bar{x}$-0.38
1,1-Dichloroethene*	75-35-4	5-600 µg/L	5	5	1.12C+0.61	$0.43\bar{x}$-0.22
trans-1,2-Dichloroethene*	156-60-5	5-600 µg/L	5	5	1.05C+0.03	$0.19\bar{x}$+0.17
1,2-Dichloropropane*	78-87-5	5-600 µg/L	5	5	1.00C	$0.45\bar{x}$
1,3-Dichloro-2-propanol	96-23-1	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
cis-1,3-Dichloropropene*	10061-01-5	5-600 µg/L	5	5	1.00C	$0.52\bar{x}$
trans-1,3-Dichloropropene*	10061-02-6	5-600 µg/L	5	5	1.00C	$0.34\bar{x}$
1,2:3,4-Diepoxybutane	1464-53-5	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
1,4-Dioxane	123-91-1	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Epichlorohydrin	106-89-8	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Ethanol	64-17-5	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Ethylbenzene*	100-41-4	5-600 µg/L	5	5	0.98C+2.48	$0.26\bar{x}$-1.72
Ethylene oxide	75-21-8	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Ethyl methacrylate	97-63-2	5-600 µg/L	5	5	Not listed	Not listed
2-Hexanone	591-78-6	5-600 µg/L	50	50	Not listed	Not listed
2-Hydroxypropionitrile	78-97-7	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Iodomethane	74-88-4	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Isobutyl alcohol	78-83-1	5-600 µg/L	100	100	Not listed	Not listed
Malononitrile	109-77-3	5-600 µg/L	Not listed	Not listed	Not listed	Not listed

Table 16. Continued

Analyte Name	CAS No.	Range[a]	Estimated Quantitation Limits[b]		Accuracy[c] (µg/L)	Precision[d] (µg/L)
			Groundwater (µg/L)	Low Soil/ Sediment (µg/kg)		
Methacrylonitrile	126-98-7	5-600 µg/L	100	100	Not listed	Not listed
Methylene chloride	75-09-2	5-600 µg/L	5	5	0.87C+1.88	$0.32\bar{x}$+4.00
Methyl iodide	74-88-4	5-600 µg/L	5	5	Not listed	Not listed
Methyl methacrylate	80-62-6	5-600 µg/L	5	50	Not listed	Not listed
4-Methyl-2-pentanone	108-10-1	5-600 µg/L	50	50	Not listed	Not listed
Pentachloroethane	76-01-7	5-600 µg/L	10	10	Not listed	Not listed
2-Picoline	109-06-8	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Propargyl alcohol	107-19-7	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
b-Propiolactone	57-57-8	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Propionitrile	107-12-0	5-600 µg/L	100	100	Not listed	Not listed
n-Propylamine	107-10-8	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Pyridine	110-86-1	5-600 µg/L	Not listed	Not listed	Not listed	Not listed
Styrene*	100-42-5	5-600 µg/L	5	5	Not listed	Not listed
1,1,1,2-Tetrachloroethane	630-20-6	5-600 µg/L	5	5	Not listed	Not listed
1,1,2,2-Tetrachloroethane*	79-34-5	5-600 µg/L	5	5	0.93C+1.76	$0.20\bar{x}$+0.41
Tetrachloroethene*	127-18-4	5-600 µg/L	5	5	1.06C+0.60	$0.16\bar{x}$-0.45
Toluene*	108-88-3	5-600 µg/L	5	5	0.98C+2.03	$0.22\bar{x}$-1.71
1,1,1-Trichloroethane*	71-55-6	5-600 µg/L	5	5	1.06C+0.73	$0.21\bar{x}$-0.39
1,1,2-Trichloroethane*	79-00-5	5-600 µg/L	5	5	0.95C+1.71	$0.18\bar{x}$+0.00
Trichloroethene*	79-01-6	5-600 µg/L	5	5	1.04C+2.27	$0.12\bar{x}$+0.59
Trichlorofluoromethane	75-69-4	5-600 µg/L	Not listed	Not listed	0.99C+0.39	$0.34\bar{x}$-0.39
1,2,3-Trichloropropane	96-18-4	5-600 µg/L	5	5	Not listed	Not listed
Vinyl acetate	108-05-4	5-600 µg/L	50	50	Not listed	Not listed
Vinyl chloride	75-01-4	5-600 µg/L	10	10	1.00C	$0.65\bar{x}$
Xylene (Total)	1330-20-7	5-600 µg/L	5	5	Not listed	Not listed

Table 16. Continued

* Analytes targeted by the National Contaminated Sites Remediation Program.

[a] The method is reported to have been tested by 15 laboratories using organic-free reagent water, drinking water, surface water, and industrial wastewaters (not specified) fortified at six concentrations over the range 5-600 µg/L.

[b] Sample Estimated Quantitation Limits (EQLs) are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable. EQLs listed for soil/sediment are based on wet weight. Normally, data is reported on a dry weight basis; therefore, EQLs will be higher, based on the percent dry weight of each sample. Table 17 provides estimated multiplication factors for additional types of matrices.

[c] Average recovery found for measurements of samples containing a concentration of C, in µg/L.

[d] Overall precision found for measurements of samples with average recovery $\bar{x}$ for samples containing a concentration of C in µg/L.

$\bar{x}$ Average recovery found for measurement of samples containing a concentration C in µg/L.

Table 17. Method 8240B, Rev. 2, Multiplication Factors for Estimated Quantitation Limits for Matrices Other than Water, Soil and Sediments

Other Matrices	Factor[a]
Waste miscible liquid waste	50
High-concentration soil and sludge	125
Non-water miscible waste	500

[a]EQL = [EQL for low soil sediment (Table 17)] X [Factor]. For non-aqueous samples, the factor is on a wet weight basis.

Comments on Use of this Method:

Method 8240B can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

The estimated quantitation limit (EQL) of Method 8240B for an individual compound is approximately 5 µg/kg (wet weight) for soil/sediment samples, 0.5 mg/kg (wet weight) for wastes, and 5 µg/L for groundwater. EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

Title:

Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique. U.S. EPA Method 8260A, Revision 1, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA 1983. Method 8260A, Revision 1, November 1990. Office of Solid Waste, Washington, D.C.

Method Applicability:

This method is applicable to nearly all types of samples, regardless of water content, including ground water, soils, and sediments.

Sample Preparation:

Liquid Samples:

Remove the plunger from a 5 mL syringe and attach a closed syringe valve. If lower detection limits are required, use a 25 mL syringe. Open the sample 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. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe 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. Filling one 20 mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

Add 10.0 µL of surrogate spiking solution and 10 µL of internal standard spiking solution through the valve bore of the syringe; then close the valve. 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 sample is equivalent to a concentration of 50 µg/L of each surrogate standard.

Sediment/Soil and Waste Samples:

It is recommended that all samples of this type be screened by GC analysis prior to the purge-and-trap GC/MS analysis. The headspace method (EPA Method 3810) or the hexadecane extraction and screening method (EPA Method 3820) may be used for this purpose. These samples may contain percent quantities of permeable organics that will contaminate the purge-and-trap system, and require extensive cleanup and instrument downtime. Use the screening data to determine whether to use the low-concentration method (0.005-1 mg/kg) or the high-concentration method (>1 mg/kg).

Low-Concentration Method: This is designed for samples containing individual purgeable compounds of <1 mg/kg. It is limited to sediment/soil samples and waste that is of a similar consistency (granular and porous). The low-concentration method is based on purging a heated sediment/soil sample mixed with organic-free reagent water containing the surrogate and internal standards. Analyze all reagent blanks and standards under the same conditions as the samples.

Remove the plunger from a 5 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 5.0 mL. Add 10 µL each of surrogate spiking solution and internal standard solution to the syringe through the valve.

Use a 5 g sample if the expected concentration is <0.1 mg/kg or a 1 g sample for expected concentrations between 0.1 and 1 mg/kg. Mix the contents of the sample container with a narrow metal spatula. Weigh the amount of the sample into a tared purge device. Note and record the actual weight to the nearest 0.1 g. Add the spiked water to the purge device, which contains the weighed amount of sample, and connect the device to the purge-and-trap system.

High-Concentration Method: The method is based on extracting the sediment/soil with methanol. A waste sample is either extracted or diluted, depending on its solubility in methanol. Wastes that are insoluble in methanol are diluted with reagent tetraglyme or possible polyethylene glycol (PEG). An aliquot of the extract is added to organic-free reagent water containing surrogate and internal standards. This is purged at ambient temperature. All samples with an expected concentration of >1.0 mg/kg should be analyzed by this method.

Mix the contents of the sample container with a narrow metal spatula. For sediment/soil and solid wastes that are insoluble in methanol, weigh 4 g (wet weight) of sample into a tared 20 mL vial. Note and record the actual weight to 0.1 g. For waste that is soluble in methanol, tetraglyme, or PEG, weigh 1 g (wet weight) into a tared scintillation vial or culture tube or a 10 mL volumetric flask. Quickly add 9.0 mL of appropriate solvent then add 1.0 mL of the surrogate spiking solution to the vial cap and shake for 2 minutes.

Remove the plunger from a 5.0 mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10 µL of internal standard solution. Also add the volume of solvent extract determined in Table 18 below and a volume of extraction or dissolution solvent to total 100 µL (excluding solvent in standards).

Table 18. Quantity of Extract Required for Analysis of High-Concentration Soils/Sediments

Approximate Concentration Range	Volume of Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	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.

Instrumental Analysis:

The volatile compounds are introduced into the gas chromatograph by the purge-and-trap method or by direct injection (in limited applications). Purged sample components are trapped in a tube containing suitable sorbent materials. When purging is complete, the sorbent tube is heated and backflushed with helium to desorb trapped sample components. The analytes are desorbed directly to a large bore capillary or cryofocussed on a capillary precolumn before being flash evaporated to a narrow bore capillary for analysis.

Instrumentation Required:

Gas Chromatograph/Mass Spectrometer/Data System. An analytical system complete with a temperature-programmable chromatograph suitable for splitless injection equipped with variable constant differential flow controllers. Also required is a subambient oven controller, a purging device, sorbent trap, a thermal desorption apparatus and a capillary precolumn interface when using cryogenic cooling. Column #1: 60 M x 0.75mm ID capillary column coated with VOCOL, 1.5 µm film thickness. Column #2: 30 M x 0.53mm capillary column coated with DB-624 or VOCOL, 3 µm film thickness. Column #3: 30 M x 0.32mm ID capillary column coated with DB-5 or SE-54, 1 µm film thickness.

Interferences:

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. Subtracting blank values from sample results is not permitted.

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. The preventive technique is rinsing of the purging apparatus and sample syringes with two portions of organic-free reagent water between samples. After analysis of a sample containing high concentrations of volatile organic compounds, one or more calibration blanks should be analyzed to check for cross contamination. 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 whole 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.

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.

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.

Quality Control Requirements:

Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

Matrix spiking standards should be prepared from volatile organic compounds which will be representative of the compounds being investigated. The recommended internal standards are chlorobenzene-d_5, 1,4-difluorobenzene, 1,4-dichlorobenzene-d_4, and pentafluorobenzene. Using stock standard solutions, prepare in methanol, secondary dilution standards 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 for one week only. Surrogates recommended are toluene-d_8, 4-bromofluorobenzene, and dibromofluoromethane. Each sample undergoing GC/MS analysis must be spiked with 10 µL of the surrogate spiking solution prior to analysis.

Comparison with Other Methods:

This is a complex method but it has sufficient QC and a selective detector so that very good results are usually obtained from experienced labs. It has the additional advantage of covering all matrices of interest including soils, sediments, and waters.

Analytes Covered by this Method:

Method 8260A covers 58 volatile organic compounds including all of the monocyclic aromatic hydrocarbons, napthalene and 14 of the chlorinated hydrocarbons that are of interest to the National Contaminated Sites Remediation Program, as shown in Table 19.

Comments on Use of this Method:

Method 8260A can be used to quantitate most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique. However, for the more soluble compounds, quantitation limits are approximately ten times higher because of poor purging efficiency. Such compounds include low-molecular-weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

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.

This method has been tested 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 19. Calculated MDLs are also presented in Table 19.

Table 19. Analytes Covered Using U.S. EPA Method 8260A, Rev. 1

Analyte	CAS No.	MDL** (µg/L)	Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
Benzene*	71-43-2	0.04	0.1 - 10	97	5.7
Bromobenzene	108-86-1	0.03	0.1 - 10	100	5.5
Bromochloromethane	74-97-5	0.04	0.5 - 10	90	6.4
Bromodichloromethane	75-27-4	0.08	0.1 - 10	95	6.1
Bromoform	75-25-2	0.12	0.5 - 10	101	6.3
Bromomethane	74-83-9	0.11	0.5 - 10	95	8.2
n-Butylbenzene	104-51-8	0.11	0.5 - 10	100	7.6
sec-Butylbenzene	135-98-8	0.13	0.5 - 10	100	7.6
tert-Butylbenzene	98-06-6	0.14	0.5 - 10	102	7.3
Carbon tetrachloride*	56-23-5	0.21	0.5 - 10	84	8.8
Chlorobenzene*	108-90-7	0.04	0.1 - 10	98	5.9
Chloroethane	75-00-3	0.10	0.5 - 10	89	9.0
Chloroform*	67-66-3	0.03	0.5 - 10	90	6.1
Chloromethane	74-87-3	0.13	0.5 - 10	93	8.9
2-Chlorotoluene	95-49-8	0.04	0.1 - 10	90	6.2
4-Chlorotoluene	106-43-4	0.06	0.1 - 10	99	8.3
Dibromochloromethane	124-48-1	0.05	0.1 - 10	83	7.0
1,2-Dibromo-3-chloropropane	96-12-8	0.26	0.5 - 10	92	19.9
1,2-Dibromoethane	106-93-4	0.06	0.5 - 10	102	3.9
Dibromomethane	74-95-3	0.24	0.5 - 10	100	5.6
1,2-Dichlorobenzene*	95-50-1	0.03	0.1 - 10	93	6.2
1,3-Dichlorobenzene*	541-73-1	0.12	0.5 - 10	99	6.9
1,4-Dichlorobenzene*	106-46-7	0.03	0.2 - 20	103	6.4
Dichlorodifluoromethane	75-71-8	0.10	0.5 - 10	90	7.7
1,1-Dichloroethane*	75-34-3	0.04	0.5 - 10	96	5.3
1,2-Dichloroethane*	107-06-2	0.06	0.1 - 10	95	5.4
1,1-Dichloroethene*	75-35-4	0.12	0.1 - 10	94	6.7
cis-1,2-Dichloroethene*	156-59-2	0.12	0.5 - 10	101	6.7
trans-1,2-Dichloroethene*	156-60-5	0.06	0.1 - 10	93	5.6
1,2-Dichloropropane*	75-87-5	0.04	0.1 - 10	97	6.1

Table 19. Continued

Analyte	CAS No.	MDL** (µg/L)	Conc. Range (µg/L)	Mean Accuracy (% of True Value)	Precision (Rel. Std. Dev. %)
1,3-Dichloropropane	142-28-9	0.04	0.1 - 10	96	6.0
2,2-Dichloropropane	594-20-7	0.12	0.5 - 10	86	16.9
1,1-Dichloropropene	563-58-6	0.10	0.5 - 10	98	8.9
Ethylbenzene*	100-41-4	0.06	0.1 - 10	99	8.6
Hexachlorobutadiene	87-68-3	0.11	0.5 - 10	100	6.8
Isopropylbenzene	98-82-8	0.15	0.5 - 10	101	7.6
p-Isopropyltoluene	99-87-6	0.12	0.1 - 10	99	6.7
Methylene chloride*	75-09-2	0.03	0.1 - 10	95	5.3
Naphthalene*	91-20-3	0.04	0.1 - 100	104	8.2
n-Propylbenzene	103-65-1	0.04	0.1 - 10	100	5.8
Styrene*	100-42-5	0.04	0.1 - 100	102	7.2
1,1,1,2-Tetrachloroethane	630-20-6	0.05	0.5 - 10	90	6.8
1,1,2,2-Tetrachloroethane*	79-34-5	0.04	0.1 - 10	91	6.3
Tetrachloroethane*	127-18-4	0.14	0.5 - 10	89	6.8
Toluene*	108-88-3	0.11	0.5 - 10	102	8.0
1,2,3-Trichlorobenzene*	87-61-6	0.03	0.5 - 10	109	8.6
1,2,4-Trichlorobenzene*	120-82-1	0.04	0.5 - 10	108	8.3
1,1,1-Trichloroethane*	71-55-6	0.08	0.5 - 10	98	8.1
1,1,2-Trichloroethane*	79-00-5	0.10	0.5 - 10	104	7.3
Trichloroethene*	79-01-6	0.19	0.5 - 10	90	7.3
Trichlorofluoromethane	75-69-4	0.08	0.5 - 10	89	8.1
1,2,3-Trichloropropane	96-18-4	0.32	0.5 - 10	108	14.4
1,2,4-Trimethylbenzene	95-63-6	0.13	0.5 - 10	99	8.1
1,3,5-Trimethylbenzene	108-67-8	0.05	0.5 - 10	92	7.4
Vinyl chloride	75-01-4	0.17	0.5 - 10	98	6.7
o-Xylene*	95-47-6	0.11	0.1 - 31	103	7.2
m-Xylene*	108-38-3	0.05	0.1 - 10	97	6.5
p-Xylene*	106-42-3	0.13	0.5 - 10	104	7.7

*Analytes targeted by the National Contaminated Sites Remediation Program.

**MDL based on a 25-mL sample volume.

Title:

Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique. U.S. EPA Method 8270B, Revision 2, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA 1983. Method 8270B, Revision 2, November 1990. Office of Solid Waste, Washington, D.C.

Method Applicability:

This method is used to determine the concentration of semivolatile organic compounds in extracts prepared from all types of solid waste matrices, soils and groundwater. Although surface waters are not specifically mentioned, this method is also applicable to water samples from rivers, lakes, etc.

Sample Preparation:

Liquid Samples:

Using a 1-L graduated cylinder, measure out 1 L (nominal) of sample and transfer it quantitatively to the continuous extractor. If high concentrations are anticipated, a smaller volume may be used and then diluted with organic-free reagent water to 1 L. Check the pH of the sample and adjust the pH, if necessary, to pH <2 using 1:1 (V/V) sulfuric acid. Pipet 1.0 mL of the surrogate standard spiking solution into each sample. For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount of the surrogates and matrix spiking compounds added to the sample should result in a final concentration of 100 ng/µL of each base/neutral analyte and 200 ng/µL of each acid analyte in the extract to be analyzed (assuming a 1-µL injection).

Add 300-500 mL of methylene chloride and some boiling chips to the distilling flasks and, with sufficient water in the extractor to ensure proper operation, extract for 18-24 hours.

Adjust the pH of the aqueous phase to pH >11 using 10N sodium hydroxide and extract it with methylene chloride again for 18-24 hours.

The extract is dried by passing it through a column containing anhydrous sodium sulfate and then concentrating it to 1 mL using a Kuderna-Danish concentrator.

Soils/Sediments & Sludges:

The following step should be performed rapidly using approximately 30 g of sample to avoid loss of the more volatile extractables. Nonporous or wet samples (gummy or clay type) that do not have a free-flowing sandy texture must be mixed with anhydrous sodium sulfate until the sample is free flowing. Add 1 mL of surrogate standards to all samples, spikes, standards, and blanks.

For the sample in each analytical batch selected for spiking, add 1.0 mL of the matrix spiking standard. For base/neutral-acid analysis, the amount added of the surrogates and matrix spiking compounds should result in a final concentration of 100 ng/µL of each base/neutral analyte and 200 ng/µL of each acid analyte in the extract to be analyzed (assuming a 1 µL injection). Immediately add 100 mL mixture of 1:1 methylene chloride:acetone and extract ultrasonically for 3 minutes and then decant or filter the extracts. Repeat the extraction two or more times.

Dry the extract using a column with anhydrous sodium sulfate and collect the dried extract a Kuderna-Danish concentrator and concentrate to 1 mL.

Instrumental Analysis:

In very limited applications direct injection of the sample into the GC/MS system may be appropriate but this results in very high detection limits (approximately 10 000 µg/L). Typically, a 1-mL extract from the sample preparation is spiked with 10 µL of the internal standard solution just prior to analysis by GC/MS. The volume injected should contain about 100 ng of base/neutral and 200 ng of acid surrogates (for a 1-µL injection).

Instrumentation:

A gas chromatograph with a mass spectrometer (GC/MS) and a data system are required. The GC column used is a 30 m x 0.25 mm ID (or 0.32 mm ID) 1 µm film thickness silicone-coated fused silica capillary column. A continuous liquid-liquid extractor equipped with Teflon or glass connection joints and stopcocks requiring no lubrication, a K-D apparatus, water bath, and an ultrasonic disrupter with a minimum power wattage of 300 watts with pulsing capability are also required.

Interferences:

Raw GC/MS data from all blanks, samples, and spikes must be evaluated for interferences. Contamination by carryover can occur whenever high-concentration and low-concentration samples are sequentially analyzed. To reduce carryover, the sample syringe must be rinsed out between samples with solvent. Whenever an unusually concentrated sample is encountered, it should be followed by the analysis of solvent to check for cross contamination.

Quality Control Requirements:

A methylene chloride solution containing 50 ng/µL of decafluorotriphenylphosphine (DFTPP) is used for tuning the GC/MS system each 12 hour shift. A system performance check also must be made during every 12 hour shift. This check must be effected before analysis begins. A standard containing 50 ng/µL each of 4,4'-DDT, pentachlorophenol, and benzidine is required to verify injection port inertness and GC column performance. A calibration standard at mid-concentration, containing each compound of interest, including all required surrogates, must be performed every 12 hours during analysis.

After the system performance check is met, Calibration Check Compounds (CCCs) (See Table 20) are used to check the validity of the initial calibration. If the difference for any compound is greater than 20%, the laboratory should consider this a warning limit. If the difference for each CCC is less than 30%, the initial calibration is assumed to be valid.

Table 20. Calibration Check Compounds

Base/Neutral Fraction	Acid Fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitrosodiphenylamine	Phenol
Di-n-octyl phthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo(a)pryene	

The internal standard responses and retention times in the calibration check 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 last check calibration (12 hours), the chromatographic system must be inspected for malfunctions and corrections must be made, as required. If the electron ionization current plot (EICP) area for any of the internal standards changes by a factor of two (-50% to +100%) from the last daily calibration standard check, the mass spectrometer must be inspected for malfunctions and corrections must be made, as appropriate.

Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

A quality control (QC) reference sample concentrate containing each analyte at a concentration of 100 mg/L in methanol is required. The QC reference sample concentrate may be prepared from pure standard materials or purchased as certified solutions. If prepared by the laboratory, the QC reference sample concentrate must be made using stock standards prepared independently from those used for calibration.

Prepare QC reference samples at a concentration of 100 µg/L, by addition of the concentrate to organic-free reagent water. Analyze the well-mixed QC reference samples.

Comparison with Other Methods:

This method, although complex and expensive to run, is one of the most comprehensive methods available for analysis of organic pollutants. It has the additional advantages of being applicable to surface water, groundwater, soils and sediments in addition to solid and liquid wastes.

Analytes Covered by this Method:

This method covers 259 semivolatile organic compounds, including 10 of the phenolic compounds, 8 chlorinated hydrocarbons, 12 pesticides, 6 miscellaneous organic parameters and all of the polycyclic aromatic hydrocarbons of interest to the National Contaminated Sites Remediation Program. Method performance criteria are listed in Table 21.

Comments on Use of this Method:

Method 8270B can be used to quantitate most neutral, acidic, and basic organic compounds that are soluble in methylene chloride and capable of being eluted without derivatization as sharp peaks from a gas chromatographic fused-silica capillary column coated with a slightly polar silicone. Such compounds include polynuclear aromatic hydrocarbons, chlorinated hydrocarbons and pesticides, phthalate esters, organophosphate esters, nitrosamines, haloethers, aldehydes, ethers, ketones, anilines, pyridines, quinolines, aromatic nitro compounds, and phenols, including nitrophenols.

The following compounds may require special treatment when being determined by this method. Benzidine can be subject to oxidative losses during solvent concentration. Also, chromatography is poor. Under the alkaline conditions of the extraction step, α-BHC, γ-BHC, endosulfan I and II, and endrin are subject to decomposition. Neutral extraction should be performed if these compounds are expected. Hexachlorocyclopentadiene is subject to thermal and photochemical decomposition. N-nitrosodimethylamine is difficult to separate from the solvent under the chromatographic conditions described. N-nitrosodiphenylamine decomposes in the gas chromatographic inlet and cannot be separated from diphenylamine. Pentachlorophenol, 2,4-dinitrophenol, 4-nitrophenol, 4,6-dinitro-2-methylphenol, 4-chloro-3-methylphenol, benzoic acid, 2-nitroaniline, 3-nitroaniline, 4-chloroaniline, and benzyl alcohol are subject to erratic chromatographic behavior, especially if the GC system is contaminated with high boiling material.

The estimated quantitation limit (EQL) of Method 8270B for determining an individual compound is approximately 1 mg/kg (wet weight) for soil/sediment samples, 1-200 mg/kg for wastes (dependent on matrix and method of preparation), and 10 µg/L for groundwater samples. EQLs will be proportionately higher for sample extracts that require dilution to avoid saturation of the detector.

Table 21. Analytes Covered Using U.S. EPA Method 8270B, Rev. 2

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
Acenaphthene	83-32-9	10	660	0.96C+0.19	0.21$\bar{x}$-0.67
Acenaphthene-d_{10} (I.S.)		Not listed	Not listed	Not listed	Not listed
Acenaphthylene	208-96-8	10	660	0.89C+0.74	0.26$\bar{x}$-0.54
Acetophenone	98-86-2	10	ND	Not listed	Not listed
2-Acetylaminofluorene	53-96-3	20	ND	Not listed	Not listed
1-Acetyl-2-thiourea	591-08-2	1000	ND	Not listed	Not listed
Aldrin*	309-00-2	Not listed	Not listed	0.78C+1.66	0.43$\bar{x}$+1.13
2-Aminoanthraquinone	117-79-3	20	ND	Not listed	Not listed
Aminoazobenzene	60-09-3	10	ND	Not listed	Not listed
4-Aminobiphenyl	92-67-1	20	ND	Not listed	Not listed
3-Amino-9-ethylcarbazole	132-32-1	Not listed	Not listed	Not listed	Not listed
Anilazine	101-05-3	100	ND	Not listed	Not listed
Aniline	62-53-3	Not listed	Not listed	Not listed	Not listed
o-Anisidine	90-04-0	10	ND	Not listed	Not listed
Anthracene	120-12-7	10	660	0.80C+0.68	0.27$\bar{x}$-0.64
Aramite	140-57-8	20	ND	Not listed	Not listed
Aroclor 1016	12674-11-2	Not listed	Not listed	Not listed	Not listed
Aroclor 1221	11104-28-2	Not listed	Not listed	Not listed	Not listed
Aroclor 1232	11141-16-5	Not listed	Not listed	Not listed	Not listed
Aroclor 1242*	53469-21-9	Not listed	Not listed	Not listed	Not listed
Aroclor 1248*	12672-29-6	Not listed	Not listed	Not listed	Not listed
Aroclor 1254*	11097-69-1	Not listed	Not listed	Not listed	Not listed
Aroclor 1260*	11096-82-5	Not listed	Not listed	0.81C-10.86	0.43$\bar{x}$+1.82
Azinphos-methyl	86-50-0	100	ND	Not listed	Not listed
Barban	101-27-9	200	ND	Not listed	Not listed
Benzidine	92-87-5	Not listed	Not listed	Not listed	Not listed
Benzoic acid	65-85-0	50	3300	Not listed	Not listed
Benzo(a)anthracene*	56-55-3	10	660	0.88C-0.60	0.26$\bar{x}$-0.21
Benzo(b)fluoranthene*	205-99-2	10	660	0.93C-1.80	0.29$\bar{x}$+0.96

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
Benzo(k)fluoranthene*	207-08-9	10	660	0.87C-1.56	.035$\bar{x}$+0.40
Benzo(g,h,i)perylene	191-24-2	10	660	0.98C-0.86	0.51$\bar{x}$-0.44
Benzo(a)pyrene*	50-32-8	10	660	0.90C-0.13	0.32$\bar{x}$+1.35
p-Benzoquinone	106-51-4	10	ND	Not listed	Not listed
Benzyl alcohol	100-51-6	20	1300	Not listed	Not listed
α-BHC	319-84-6	Not listed	Not listed	Not listed	Not listed
β-BHC	319-85-7	Not listed	Not listed	0.87C-0.94	0.30$\bar{x}$+1.94
δ-BHC	319-86-8	Not listed	Not listed	0.29C-1.09	0.93$\bar{x}$-0.17
γ-BHC (Lindane)*	58-89-9	Not listed	Not listed	Not listed	Not listed
bis(2-Chloroethoxy) methane	111-91-1	10	660	1.12C-5.04	0.26$\bar{x}$+2.01
bis(2-Chloroethyl) ether	111-44-4	10	660	0.86C-1.54	0.35$\bar{x}$+0.10
bis(2-Chloroisopropyl) ether	108-60-1	10	660	1.03C-2.31	0.25$\bar{x}$+1.04
bis(2-ethylhexyl) phthalate*	117-81-7	Not listed	Not listed	0.84C-1.18	0.36$\bar{x}$+0.67
4-Bromophenyl phenyl ether	101-55-3	10	660	0.91C-1.34	0.16$\bar{x}$+0.66
Bromoxynil	1689-84-5	10	ND	Not listed	Not listed
Butyl benzyl phthalate*	85-68-7	10	660	0.66C-1.68	0.53$\bar{x}$+0.92
2-sec-Butyl-4,6-dinitrophenol	88-85-7	Not listed	Not listed	Not listed	Not listed
Captafol	2425-06-1	20	ND	Not listed	Not listed
Captan	133-06-2	50	ND	Not listed	Not listed
Carbaryl*	63-25-2	10	ND	Not listed	Not listed
Carbofuran*	1563-66-2	10	ND	Not listed	Not listed
Carbophenothion	786-19-6	10	ND	Not listed	Not listed
Chlordane	57-74-9	Not listed	Not listed	Not listed	Not listed
Chlorfenvinphos	470-90-6	20	ND	Not listed	Not listed
4-Chloroaniline	106-47-8	20	1300	Not listed	Not listed
Chlorobenzilate	510-15-6	10	ND	Not listed	Not listed
5-Chloro-2-methylaniline	95-79-4	10	ND	Not listed	Not listed
4-Chloro-3-methylphenol	59-50-7	20	1300	0.84C+0.35	0.29$\bar{x}$+1.31
3-(Chloromethyl)pyridine hydrochloride	6959-48-4	100	ND	Not listed	Not listed

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
1-Chloronaphthalene	90-13-1	Not listed	Not listed	0.89C+0.01	0.13$\bar{x}$+0.34
2-Chloronaphthalene	91-58-7	10	660	Not listed	Not listed
2-Chlorophenol*	95-57-8	10	660	0.78C+0.29	0.28$\bar{x}$+0.97
4-Chloro-1,2-phenylenediamine	95-83-0	Not listed	Not listed	Not listed	Not listed
4-Chloro-1,3-phenylenediamine	5131-60-2	Not listed	Not listed	Not listed	Not listed
4-Chlorophenyl phenyl ether	7005-72-3	10	660	0.91C+0.53	0.30$\bar{x}$-0.46
Chrysene	218-01-9	10	660	0.93C-1.00	0.33$\bar{x}$-0.09
Chrysene-d_{12} (I.S.)		Not listed	Not listed	Not listed	Not listed
Coumaphos	56-72-4	40	ND	Not listed	Not listed
p-Cresidine	120-71-8	10	ND	Not listed	Not listed
Crotoxyphos	7700-17-6	20	ND	Not listed	Not listed
2-Cyclohexyl-4,6-dinitrophenol	131-89-5	100	ND	Not listed	Not listed
4,4'-DDD	72-54-8	Not listed	Not listed	0.56C-0.40	0.66$\bar{x}$-0.96
4,4'-DDE	72-55-9	Not listed	Not listed	0.70C-0.54	0.39$\bar{x}$-1.04
4,4'-DDT*	50-29-3	Not listed	Not listed	0.79C-3.28	0.65$\bar{x}$-0.58
Demeton-o	298-03-3	10	ND	Not listed	Not listed
Demeton-s	126-75-0	10	ND	Not listed	Not listed
Diallate (cis or trans)	2303-16-4	10	ND	Not listed	Not listed
2,4-Diaminotoluene	95-80-7	20	ND	Not listed	Not listed
Dibenz(a,j)acridine	224-42-0	10	ND	Not listed	Not listed
Dibenz(a,h)anthracene*	53-70-3	10	660	0.88C+4.72	0.59$\bar{x}$+0.25
Dibenzofuran	132-64-9	10	660	Not listed	Not listed
Dibenzo(a,e)pyrene	192-65-4	10	ND	Not listed	Not listed
1,2-Dibromo-3-chloropropane	96-12-8	Not listed	Not listed	Not listed	Not listed
Di-n-butyl phthalate*	84-74-2	10	ND	0.59C+0.71	0.39$\bar{x}$+0.60
Dichlone	117-80-6	NA	ND	Not listed	Not listed
1,2-Dichlorobenzene*	95-50-1	10	660	0.80C+0.28	0.24$\bar{x}$+0.39
1,3-Dichlorobenzene*	541-73-1	10	660	0.86C-0.70	0.41$\bar{x}$+0.11
1,4-Dichlorobenzene*	106-46-7	10	660	0.73C-1.47	0.29$\bar{x}$+0.36

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
1,4-Dichlorobenzene-d_4 (I.S.)		Not listed	Not listed	Not listed	Not listed
3,3'-Dichlorobenzidine	91-94-1	20	1300	1.23C-12.65	0.47$\bar{x}$+3.45
2,4-Dichlorophenol*	120-83-2	10	660	0.87C-0.13	0.21$\bar{x}$+1.28
2,6-Dichlorophenol*	87-65-0	10	ND	Not listed	Not listed
Dichlorovos	62-73-7	10	ND	Not listed	Not listed
Dicrotophos	141-66-2	10	ND	Not listed	Not listed
Dieldrin	60-57-1	Not listed	Not listed	0.82C-0.16	0.26$\bar{x}$-0.07
Diethyl phthalate*	84-66-2	10	660	0.43C+1.00	0.52$\bar{x}$+0.22
Diethylstilbestrol	56-53-1	20	ND	Not listed	Not listed
Diethyl sulfate	64-67-5	100	ND	Not listed	Not listed
Dihydrosaffrole	56312-13-1	Not listed	Not listed	Not listed	Not listed
Dimethoate	60-51-5	20	ND	Not listed	Not listed
3,3'-Dimethoxybenzidine	119-90-4	100	ND	Not listed	Not listed
Dimethylaminoazobenzene	60-11-7	10	ND	Not listed	Not listed
7,12-Dimethylbenz(a)-anthracene	57-97-6	10	ND	Not listed	Not listed
3,3'-Dimethylbenzidine	119-93-7	10	ND	Not listed	Not listed
α,α-Dimethylphenethylamine	122-09-8	ND	ND	Not listed	Not listed
2,4-Dimethylphenol*	105-67-9	10	660	0.71C+4.41	0.22$\bar{x}$+1.31
Dimethyl phthalate*	131-11-3	10	660	0.20C+1.03	1.05$\bar{x}$-0.92
1,2-Dinitrobenzene	528-29-0	40	ND	Not listed	Not listed
1,3-Dinitrobenzene	99-65-0	20	ND	Not listed	Not listed
1,4-Dinitrobenzene	100-25-4	40	ND	Not listed	Not listed
4,6-Dinitro-2-methylphenol*	534-52-1	50	3300	Not listed	Not listed
2,4-Dinitrophenol*	51-28-5	50	3300	0.81C-18.04	0.42$\bar{x}$+26.29
2,4-Dinitrotoluene	121-14-2	10	660	0.92C-4.81	0.21$\bar{x}$+1.50
2,6-Dinitrotoluene	606-20-2	10	660	1.06C-3.60	0.19$\bar{x}$+0.35
Dinocap	39300-45-3	100	ND	Not listed	Not listed
Dinoseb	88-85-7	20	ND	Not listed	Not listed
Dioxathion	78-34-2	Not listed	Not listed	Not listed	Not listed

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
Diphenylamine	122-39-4	Not listed	Not listed	Not listed	Not listed
5,5-Diphenylhydantoin	57-41-0	20	ND	Not listed	Not listed
1,2-Diphenylhydrazine	122-66-7	Not listed	Not listed	Not listed	Not listed
Di-n-octyl phthalate*	117-84-0	10	660	0.76C-0.79	0.37$\bar{x}$+1.19
Disulfoton	298-04-4	10	ND	Not listed	Not listed
Endosulfan I	959-98-8	Not listed	Not listed	Not listed	Not listed
Endosulfan II	33213-65-9	Not listed	Not listed	Not listed	Not listed
Endosulfan sulfate	1031-07-8	Not listed	Not listed	0.39C+0.41	0.63$\bar{x}$-1.03
Endrin*	72-20-8	Not listed	Not listed	Not listed	Not listed
Endrin aldehyde	7421-93-4	Not listed	Not listed	0.76C-3.86	0.73$\bar{x}$-0.62
Endrin ketone	53494-70-5	Not listed	Not listed	Not listed	Not listed
EPN	2104-64-5	10	ND	Not listed	Not listed
Ethion	563-12-2	10	ND	Not listed	Not listed
Ethyl carbamate	51-79-6	50	ND	Not listed	Not listed
Ethyl methanesulfonate	62-50-0	20	ND	Not listed	Not listed
Ethyl parathion	56-38-2	Not listed	Not listed	Not listed	Not listed
Famphur	52-85-7	20	ND	Not listed	Not listed
Fensulfothion	115-90-2	40	ND	Not listed	Not listed
Fenthion	55-38-9	10	ND	Not listed	Not listed
Fluchloralin	33245-39-5	20	ND	Not listed	Not listed
Fluoranthene	206-44-0	10	660	0.81C+1.10	0.28$\bar{x}$-0.60
Fluorene	86-73-7	10	660	0.90C-0.00	0.13$\bar{x}$+0.61
2-Fluorobiphenyl (surr.)	321-60-8	Not listed	Not listed	Not listed	Not listed
2-Fluorophenol (surr.)	367-12-4	Not listed	Not listed	Not listed	Not listed
Heptachlor*	76-44-8	Not listed	Not listed	0.87C-2.97	0.50$\bar{x}$-0.23
Heptachlor epoxide	1024-57-3	Not listed	Not listed	0.92C-1.87	0.28$\bar{x}$+0.64
Hexachlorobenzene*	118-74-1	10	660	0.74C+0.66	0.43$\bar{x}$-0.52
Hexachlorobutadiene	87-68-3	10	660	0.71C-1.01	0.26$\bar{x}$+0.49
Hexachlorocyclopentadiene	77-47-4	10	660	Not listed	Not listed

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
Hexachloroethane	67-72-1	10	660	0.73C-0.83	0.17$\bar{x}$+0.80
Hexachlorophene	70-30-4	50	ND	Not listed	Not listed
Hexachloropropene	1888-71-7	10	ND	Not listed	Not listed
Hexamethyl phosphoramide	680-31-9	20	ND	Not listed	Not listed
Hydroquinone	123-31-9	ND	ND	Not listed	Not listed
Indeno(1,2,3-cd)pyrene*	193-39-5	10	660	0.78C-3.10	0.50$\bar{x}$-0.44
Isodrin	465-73-6	20	ND	Not listed	Not listed
Isophorone	78-59-1	10	660	1.12C+1.14	0.33$\bar{x}$+0.26
Isosafrole	120-58-1	10	ND	Not listed	Not listed
Kepone	143-50-0	20	ND	Not listed	Not listed
Leptophos	21609-90-5	10	ND	Not listed	Not listed
Malathion	121-75-5	50	ND	Not listed	Not listed
Maleic anhydride	108-31-6	NA	ND	Not listed	Not listed
Mestranol	72-33-3	20	ND	Not listed	Not listed
Methapyrilene	91-80-5	100	ND	Not listed	Not listed
Methoxychlor*	72-43-5	10	ND	Not listed	Not listed
3-Methylcholanthrene	56-49-5	10	ND	Not listed	Not listed
4,4'-Methylenebis(2-chloraniline)	101-14-4	NA	ND	Not listed	Not listed
4,4'-Methylenebis(N,N-dimethylaniline)	101-61-1	Not listed	Not listed	Not listed	Not listed
Methyl methanesulfonate	66-27-3	10	ND	Not listed	Not listed
2-Methylnaphthalene	91-57-6	10	660	Not listed	Not listed
2-Methyl-5-nitroaniline	99-55-8	Not listed	Not listed	Not listed	Not listed
Methyl parathion	298-00-0	10	ND	Not listed	Not listed
2-Methylphenol	95-48-7	10	660	Not listed	Not listed
3-Methylphenol	108-39-4	10	ND	Not listed	Not listed
4-Methylphenol	106-44-5	10	660	Not listed	Not listed
2-Methylpyridine	109-06-8	Not listed	Not listed	Not listed	Not listed
Mevinphos	7786-34-7	10	ND	Not listed	Not listed
Mexacarbate	315-18-4	20	ND	Not listed	Not listed

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
Mirex	2385-85-5	10	ND	Not listed	Not listed
Monocrotophos	6923-22-4	40	ND	Not listed	Not listed
Naled	300-76-5	20	ND	Not listed	Not listed
Naphthalene*	91-20-3	10	660	0.76C+1.58	0.30$\bar{x}$-0.68
Naphthalene-d_8 (I.S.)		Not listed	Not listed	Not listed	Not listed
1,4-Naphthoquinone	130-15-4	10	ND	Not listed	Not listed
1-Naphthylamine	134-32-7	10	ND	Not listed	Not listed
2-Naphthylamaine	91-59-8	10	ND	Not listed	Not listed
Nicotine	54-11-5	20	ND	Not listed	Not listed
5-Nitroacenaphthene	602-87-9	10	ND	Not listed	Not listed
2-Nitroaniline	88-74-4	50	3300	Not listed	Not listed
3-Nitroaniline	99-09-2	50	3300	Not listed	Not listed
4-Nitroaniline	100-01-6	20	ND	Not listed	Not listed
5-Nitro-o-anisidine	99-59-2	10	ND	Not listed	Not listed
Nitrobenzene	98-95-3	10	660	1.09C-3.05	0.27$\bar{x}$+0.21
Nitrobenzene-d_5 (surr.)		Not listed	Not listed	Not listed	Not listed
4-Nitrobiphenyl	92-93-3	10	ND	Not listed	Not listed
Nitrofen	1836-75-5	20	ND	Not listed	Not listed
2-Nitrophenol	88-75-5	10	660	0.07C-1.15	0.27$\bar{x}$+2.60
4-Nitrophenol	100-02-7	50	3300	0.61C-1.22	0.44$\bar{x}$+3.24
5-Nitro-o-toluidine	99-55-8	10	ND	Not listed	Not listed
Nitroquinoline-1-oxide	56-57-5	40	ND	Not listed	Not listed
N-Nitrosodibutylamine	924-16-3	10	ND	Not listed	Not listed
N-Nitrosodiethylamine	55-18-5	20	ND	Not listed	Not listed
N-Nitrosodimethylamine	62-75-9	Not listed	Not listed	Not listed	Not listed
N-Nitrosomethylethylamine	10595-95-6	Not listed	Not listed	Not listed	Not listed
N-Nitrosodiphenylamine	86-30-6	10	660	Not listed	Not listed
N-Nitrosodi-n-propylamine	621-64-7	10	660	1.12C-6.22	0.44$\bar{x}$+0.47
N-Nitrosomorpholine	59-89-2	Not listed	Not listed	Not listed	Not listed

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
N-Nitrosopiperidine	100-75-4	20	ND	Not listed	Not listed
N-Nitrosopyrrolidine	930-55-2	40	ND	Not listed	Not listed
Octamethyl pyrophosphoramide	152-16-9	200	ND	Not listed	Not listed
4,4'-Oxydianiline	101-80-4	20	ND	Not listed	Not listed
Parathion*	56-38-2	10	ND	Not listed	Not listed
Pentachlorobenzene*	608-93-5	10	ND	Not listed	Not listed
Pentachloronitrobenzene	82-68-8	20	ND	Not listed	Not listed
Pentachlorophenol*	87-86-5	50	3300	0.93C+1.99	$0.30\bar{x}+4.33$
Perylene-d_{12} (I.S.)		Not listed	Not listed	Not listed	Not listed
Phenacetin	62-44-2	20	ND	Not listed	Not listed
Phenanthrene*	85-01-8	10	660	0.87C+0.06	$0.15\bar{x}+0.25$
Phenanthrene-d_{10} (I.S.)		Not listed	Not listed	Not listed	Not listed
Phenobarbital	50-06-6	10	ND	Not listed	Not listed
Phenol*	108-95-2	10	660	0.43C+1.26	$0.35\bar{x}+0.58$
Phenol-d_6 (surr.)		Not listed	Not listed	Not listed	Not listed
1,4-Phenylenediamine	106-50-3	10	ND	Not listed	Not listed
Phorate	298-02-2	10	ND	Not listed	Not listed
Phosalone	2310-17-0	100	ND	Not listed	Not listed
Phosmet	732-11-6	40	ND	Not listed	Not listed
Phosphamidon	13171-21-6	100	ND	Not listed	Not listed
Phthalic anhydride	85-44-9	100	ND	Not listed	Not listed
2-Picoline	109-06-8	ND	ND	Not listed	Not listed
Piperonyl sulfoxide	120-62-7	100	ND	Not listed	Not listed
Pronamide	23950-58-5	10	ND	Not listed	Not listed
Propylthiouracil	51-52-5	100	ND	Not listed	Not listed
Pyrene*	129-00-0	10	660	0.84C-0.16	$0.15\bar{x}+0.31$
Pyridine	110-86-1	ND	ND	Not listed	Not listed
Resorcinol	108-46-3	100	ND	Not listed	Not listed
Safrole	94-59-7	10	ND	Not listed	Not listed

Table 21. Continued

Compounds	CAS No.	Estimated Quantitation Limits[a]		Accuracy (µg/L)	Overall Precision (µg/L)
		Groundwater (µg/L)	Low Soil/ Sediment[b] (µg/kg)		
Strychnine	60-41-3	40	ND	Not listed	Not listed
Sulfallate	95-06-7	10	ND	Not listed	Not listed
Terbufos	13071-79-9	20	ND	Not listed	Not listed
Terphenyl-d_{14}(surr.)		Not listed	Not listed	Not listed	Not listed
1,2,4,5-Tetrachlorobenzene*	95-94-3	10	ND	Not listed	Not listed
2,3,4,6-Tetrachlorophenol*	58-90-2	10	ND	Not listed	Not listed
Tetrachlorvinphos	961-11-5	20	ND	Not listed	Not listed
Tetraethyl dithiopyrophosphate	3689-24-5	Not listed	Not listed	Not listed	Not listed
Tetraethyl pyrophosphate	107-49-3	40	ND	Not listed	Not listed
Thionazine	297-97-2	20	ND	Not listed	Not listed
Thiophenol (Benzenethiol)	108-98-5	20	ND	Not listed	Not listed
Toluene diisocyanate	584-84-9	100	ND	Not listed	Not listed
o-Toluidine	95-53-4	10	ND	Not listed	Not listed
Toxaphene	8001-35-2	Not listed	Not listed	Not listed	Not listed
2,4,6-Tribromophenol (surr.)		Not listed	Not listed	Not listed	Not listed
1,2,4-Trichlorobenzene*	120-82-1	10	660	0.94C-0.79	0.21$\bar{x}$+0.39
2,4,5-Trichlorophenol*	95-95-4	10	660	Not listed	Not listed
2,4,6-Trichlorophenol*	88-06-2	10	660	0.91C-0.18	0.22$\bar{x}$+1.81
Trifluralin	1582-09-8	10	ND	Not listed	Not listed
2,4,5-Trimethylaniline	137-17-7	10	ND	Not listed	Not listed
Trimethyl phosphate	512-56-1	10	ND	Not listed	Not listed
1,3,5-Trinitrobenzene	99-35-4	10	ND	Not listed	Not listed
Tris(2,3-dibromopropyl) phosphate	126-72-7	200	ND	Not listed	Not listed
Tri-p-tolyl phosphate	78-32-0	10	ND	Not listed	Not listed
0,0,0-Triethyl phosphorothioate	126-68-1	NT	ND	Not listed	Not listed

[a]Sample EQLs are highly matrix-dependent. The EQLs listed herein are provided for guidance and may not always be achievable.
[b]EQLs listed for soil/sediment are based on wet weight. Normally data is reported in a dry weight basis, therefore, EQLs will be higher based on the % dry weight of each sample. This is based on a 30 g sample and gel permeation chromatography cleanup.

Table 21. Continued

ND = Not determined
NA = Not applicable
NT = Not tested
C = True value for concentration, in µg/L
$\bar{x}$ = Average recovery found for measurements of samples containing a concentration of C, in µg/L.
* = Analytes targeted by the National Contaminated Sites Remediation Program.

Other Matrices	Factor[1]
High-concentration soil and sludges by sonicator	7.5
Non-water miscible waste	75

[1]EQL = [EQL for Low Soil/Sediment (Table 20)] X [Factor].

Title:

A Method for the Analysis of Polychlorinated Dibenzo-para-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Polychlorinated Biphenyls (PCBs) in Samples from the Incineration of PCB Waste.

Reference:

Reference Method 1/RM/3 (revised). May 1990. Environment Canada, River Road Environmental Technology Centre, Ottawa, Ontario.

Method Applicability:

This method is appropriate for determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), and trichloro- through decachlorobiphenyl isomers in feedstock processes and stack emission samples from incinerators. These include solids (ashes and solid waste feed), liquids (condensate traps, solvent rinses, etc.), and waste oils.

Sample Preparation:

Solid Samples

Solid samples consist of the train filter and filtered particulates from the front-half rinse, the Amberlite XAD-2, material fed into the incinerator and any ash generated during the burn. The Soxhlet extraction portion of the procedures is common to all solid samples.

Ashes and Feed (solid waste)

Accurately weight a representative 2-10 g portion of finely-divided sample into a 250 mL beaker and spike it with a known amount of isotopically-labelled surrogate PCDD/PCDFs and PCBs. Allow the sample to air-dry for 30 minutes, then add 100 mL of 3 M HCl and subject the sample to ultrasonic agitation for 30 minutes, stirring occasionally with a glass rod.

Transfer the filtrate to a 500 mL separatory funnel and serially extract with 100, 50, 50-mL portions of dichloromethane. Dry the extracts by passing them through a bed of dichloromethane-rinsed sodium sulphate. After adding 1 mL isooctane keeper, concentrate the extract to 3 to 5 mL by rotary evaporation at approximately 38°C. The filtrate extract is combined with the Soxhlet extract of the sample before cleanup.

Soxhlet extract a cellulose thimble with toluene to pre-clean it. Allow the pre-extracted thimble to air-dry in a beaker. Quantitatively transfer the filter containing the acid-treated dried sample into the thimble. Place the thimble into the Soxhlet and extract the sample with approximately 350 mL of benzene, refluxing it for 20 hours at a rate of three to four cycles per hour.

Add the filtrate dichloromethane extract to the sample with three dichloromethane flask rinsings and concentrate the combined sample to approximately 5 mL by rotary evaporation at 38°C. Add approximately 100 mL of hexane to the flask and repeat the concentration step. Dry the sample by passing it through hexane-rinsed sodium sulphate, rinse both the flask and sodium sulphate with hexane, and concentrate the combined extract to 3 to 5 mL by rotary evaporation. The concentrate is next subjected to the acid/base silica and the basic alumina column cleanup described below.

Probe Rinse and Train Filter

Suspended or settled particulate matter which may be present in the solvent rinse of the sampling train probe are removed by filtration through a glass fibre filter. The filtered particulates are combined with the train filter for acid treatment and Soxhlet extraction as described above. The filtered probe rinse is processed as a solvent rinse sample as described in the section on Liquid Samples below. The filter extract and the filtrate are combined for the acid/base silica and the basic alumina column cleanup described below.

Amberlite XAD-2

The ends of the adsorbent cartridge are uncapped and the XAD-2 is air-dried in a desiccator. The XAD-2 is emptied into a pre-extracted thimble, spiked with surrogate standards, and extracted in a Soxhlet apparatus as described above. The concentrate of this extract is subjected to the acid/base silica and the basic alumina column cleanup described below.

Liquid Samples

Liquid samples consist of the contents from the condensate trap, glycol impinger, and solvent rinsings of sampling train glassware. All liquid samples, in their original bottles, should be spiked with the surrogate standards before extraction. If the liquid sample (e.g., impinger contents and back-half rinse) is to be combined with the XAD, only the XAD is spiked with surrogates.

Aqueous Samples

Quantitatively transfer the surrogate-spiked aqueous sample into a separatory funnel, rinsing the sample bottle with deionized water followed by dichloromethane and serially extract with 100-, 50-, 50-mL portions of dichloromethane. These volumes apply to sample sizes in the 500- to 1000-mL range. For small sample volumes dichloromethane volumes may be scaled accordingly. Extract portions are dried and combined by passing them through a bed of dichloromethane-rinsed sodium sulphate and 1-mL of isooctane keeper is added prior to concentrating the extract to 3 to 5 mL by rotary evaporation at approximately 38°C. Add 50 mL of hexane to the flask and concentrate again to 3 to 5 mL. The concentrate is next subjected to the acid/base silica and the basic alumina column cleanups described below.

Ethylene Glycol Sample

Transfer a surrogate-spiked sample into a separatory funnel, rinse the sample bottle with two small portions of deionized water followed by two small portions of hexane, and then dilute the sample to approximately 1.5 times its original volume with deionized water.

Add dichloromethane, shake vigorously for two minutes, allow the layers to separate, and dry the dichloromethane extract by passing it through a bed of dichloromethane-rinsed sodium sulphate.

Repeat the extraction with two additional portions of dichloromethane, passing each extract through the sodium sulphate into the flask, and then rinse the sodium sulphate with dichloromethane.

Add 1 mL of isooctane keeper and then concentrate the sample to 3 to 5 mL by rotary evaporation at 38°C. Exchange the solvent to hexane by adding 50 mL of hexane and reconcentrating to 3 to 5 mL. The concentrate is next subjected to the acid/base silica and the basic alumina column cleanup described below.

Solvent Rinse Samples

Quantitatively transfer a sample into a 500-mL round bottom flask following with three hexane rinses of the bottle. Add a 1-mL isooctane keeper and concentrate the sample to 3 to 5 mL by rotary evaporation at 38°C. Exchange the solvent to hexane as described above. Dry the sample by passing it through a bed of hexane-rinsed sodium sulphate, complete the transfer with hexane rinses and combine the back-half rinse with the ethylene glycol extract. Combine the backholder and condenser rinse with the XAD extract.

Acid/Base Silica and Basic Alumina Column Cleanup

Two columns are used for sample cleanup: an acid/base silica column and an alumina column.

The acid/base silica column is layered from the bottom up with : glass wool, 1.5 g of silver nitrate/silica, (bottom layer), 1 g of silica, 2 g of 33% 1 M sodium hydroxide/silica, 1 g of silica, 4 g of 44% sulfuric acid/silica, 2 g of silica and approximately 1 g of sodium sulphate to top off the column. The column is pre-washed with 30 mL of 2% dichloromethane in hexane (v/v) before use. The concentrated sample extract is transferred onto the top of this column, followed by three, 5-mL 2% dichloromethane/hexane (v/v) rinsings of the sample flask, also transferred using the same pipet. When the third rinse has drained to the top of the sodium sulphate layer, pour an additional 50 mL of 2% dichloromethane/hexane (v/v) through the column. Concentrate the column effluent to a volume of approximately 2 mL by rotary evaporation at 38°C. Add approximately 50 mL of hexane to the flask and repeat the concentration to exchange the solvent to hexane.

The above concentrate is then quantitatively transferred with hexane to a second cleanup column. It consists of 2.5 g of freshly prepared basic alumina topped off with 0.5 cm of sodium sulphate and is first pre-washed with hexane before the sample concentrate is added to it.

Via pasteur pipet, transfer the concentrated extract from the acid/base column onto the alumina column, followed by hexane rinsings of the sample flask, transferred through the same pipet. Add 30 mL of hexane and allow the hexane in the column to drain just to the top of the alumina bed. Add 20 mL of freshly prepared 2% dichloromethane in hexane (v/v) to the column. This fraction (Fraction 1) will contain the PCBs. When the solvent level in the column again just reaches the top of the alumina column add 30 mL of 50% dichloromethane in hexane (v/v) to the column and allow the column to drain completely. This fraction (Fraction 2) contains PCDD/PCDFs. Concentrate Fraction 1 to approximately 3 mL and Fraction 2 to approximately 1 mL by rotary evaporation at 38°C.

Via Pasteur pipet, transfer Fraction 1 (PCBs) to a pre-calibrated centrifuge tube and concentrate further under a gentle stream of pre-purified nitrogen. With the same pipets used above, complete the transfer of the sample from the flask to the centrifuge tube via three, 0.5-mL isooctane rinsings of each flask.

After concentrating the PCB fraction to just under 450 µL, add 50 µL of 4 ng/µL $^{-13}C_{12}$-3,3'4,4'-tetrachlorobiphenyl solution and bring the sample volume to 500 µL with isooctane. Transfer the sample to a 1.5 mL amber glass, screw-capped vial. Store the sample at 4°C until analysis.

The PCDD/PCDF sample (Fraction 2) is transferred via Pasteur pipet to a Reacti-vial and concentrated under a gentle stream of pre-purified nitrogen. Complete the sample transfer using the same pipet to take up three, 0.5-mL hexane rinses of the flask, transferring them into the Reacti-vial. Concentrate the extract to a small, known volume (typically 100 µL) and screen for PCDD/PCDF analytes by using a gas chromatography equipped with a DB-5 capillary column and electron capture detector. An extract which shows a chromatogram of high interfering background may require additional cleanup procedures such as: shaking the extract with strong acid and strong bases, passing the extract through a carbon column, or separating the PCDD/PCDFs from the interferents by HPLC. Just prior to GC/MS analysis the sample is blown dry under a gentle stream of pre-purified nitrogen. A volume (typically 100 µL) of performance standard containing 100 pg/µL $^{13}C_{12}$-1,2,3,4-TCDD is toluene is added to the Reacti-vial and the capped vial is allowed to sit for one hour prior to analysis.

Waste Oil Samples: Cleanup of waste oils for PCB and PCDD/PCDF analysis incorporates the use of the columns described above, plus an additional alumina column for PCDD/PCDF cleanup.

PCDD/PCDFs: One gram of oil is placed in a flask and spiked with a known amount of PCDD/PCDF surrogates. Add 45 mL of hexane and cleanup the sample using both columns as described above. Removal of the oil matrix from the alumina column is enhanced when 40 mL of hexane is used. The fraction containing PCDD/PCDFs (Fraction 2) is concentrated and exchanged to hexane, giving a final volume of 3 to 5 mL. The extract is put through another freshly-prepared alumina column, repeating the solvent elutions as above. Fraction 1 may be discarded while Fraction 2 is transferred to a Reacti-vial.

PCBs: Weight 0.100 g of oil into a flask and spike it with a known amount of the PCB surrogates. Add 3 to 5 mL hexane and put the sample through an acid/base column and concentrate as described above. The sample is then transferred to a freshly prepared alumina column and eluted with 40 mL of hexane which is discarded. Place a flask beneath the alumina column just when hexane reaches the bed level and add 20 mL of 5% dichloromethane in hexane (v/v) to the column to elute the PCBs. When the column has drained, add 3 mL of isooctane to the extract and rotovap to 3 to 5 mL. Transfer the extract to a centrifuge tube (which has been pre-calibrated to 2.0 mL) using three, 0.5-mL isooctane rinses. Concentrate the sample under a gentle stream of nitrogen to just under 2.0 mL. Add a known amount of the performance standard ($^{13}C_{12}$-3,3'4,4'-tetrachlorobiphenyl) and make the volume of the sample up to exactly 2.0 mL with isooctane. Transfer the sample to a 3 mL amber vial with a Teflon-lined cap and store it at 4°C until analysis.

Instrumental Analysis:

Analytes may be present in the sample as single isomers or complex mixtures. The maximum number of target congeners for PCBs (3Cl-10Cl), PCDDs (4Cl-8Cl) and PCDFs (4Cl-8Cl) are 194, 49 and 87 respectively.

Optimum settings for GC parameters and the appropriate retention time windows for time-sequenced SIM mode analysis of PCDDs/PCDFs on a DB-5 column is such that five retention windows can be defined, corresponding to the five levels of chlorine substitution (4Cl-8Cl) without any overlap. Polychlorinated biphenyl congeners, however, overlap up to three levels of chlorine substitution (e.g., 3Cl/4Cl/5Cl,4Cl/5Cl/6Cl...etc.) on a DB-5 column.

Instrumentation Required:

A GC/MS system equipped with a capillary, non-polar column directly coupled to a low resolution quadruple mass spectrometer with a dedicated data system should be used for the analysis. The data system is operator-programmed for time-sequenced acquisition of selected MS data for each analyte.

The GC column for analysis of PCBs is a DB-5, 30 m x 0.25 mm ID fused silica, 0.25 µm film or equivalent.

Selection of a 30-m column for PCB analysis is considered to represent the most appropriate compromise between the competing ideals of maximum resolving power and short analysis time for homologue analysis. For dioxin analysis, however, a 60-m DB-5 column is required in order to adequately separate, 2,3,7,8-TCDD from neighboring isomers as well as for homologue separation (congener 1,2,8,9-TCDD and 1,3,4,6,8-P_5CDF may elute very closely).

Mass spectrometers are operated in the Electron Impact (EI) and Selected Ion Monitoring (SIM) modes. The selected ion masses for PCDD/PCDF and PCB analysis are listed in the method.

Interferences:

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

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.

Interferents co-extracted from the sample will vary considerably from source to source, depending upon the sample. PCDDs and PCDFs are often associated with other interfering chlorinated compounds such as PCBs and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit.

Quality Control Requirements:

Glassware: All reusable glassware must be scrupulously cleaned as soon as possible after use. Glassware is either air-dried, or dried in an oven at temperatures less than 100°C. Prior to the start of a project each piece of glassware including flasks, vials, and rotary evaporators are rinsed with hexane and dichloromethane. The combined rinses are put through the cleanup procedure to yield one solvent sample which is analyzed for PCDDs/PCDFs. If any amount is positively identified, all of the glassware must be recleaned. Before a project starts the Soxhlet apparatus must also be proofed. (This is in addition to the routine blanking procedure). The Soxhlet apparatus containing a cellulose thimble, condensers and flasks are blanked overnight in toluene. The entire apparatus is rinsed three times with toluene and the extract plus the toluene rinses are discarded. A proofing sample is generated by re-extracting the apparatus with fresh toluene. The extracts of all the Soxhlets are then combined into one sample and analyzed by GC/MS to ensure there is no contamination.

Amberlite XAD-2: The resin must be cleaned and proofed to be free of contamination prior to field sampling. Rinse the resin with three column volumes of deionized water followed by Soxhlet extraction sequentially with methanol, dichloromethane and cyclohexane for 20 hours each. After the last extraction, rinse the resin (while still in the Soxhlet) for five cycles with hexane. Spread the clean resin onto a tray lined with pre-rinsed (methanol and hexane) aluminum foil to a depth not exceeding 0.5 cm, air-dry in a fume hood to remove excess solvent, and then dry in a vacuum oven for three to four hours at 50°C. Before sampling, an aliquot (~30g) of the resin is subjected to proofing analysis for target analytes with other train proofing samples.

Glass Wool: Glass wool is compressed into a large glass column and washed sequentially with hexane and dichloromethane. The volume of solvent used for each wash should be twice the estimated volume of glass wool in the column. Loosely cover the mouth of the beaker with hexane and dichloromethane-rinsed aluminum foil, allow the glass wool to air-dry in a fume hood and then condition overnight at 225°C in a vented oven.

Sodium Sulphate: Sequentially wash the sodium sulphate twice with hexane and twice with dichloromethane. The volume of solvent used for each wash should be twice the estimated volume of sodium sulphate. Transfer to a large beaker, cover the mouth loosely with solvent-rinsed aluminum foil, and oven dry at 50°C for at least one hour before conditioning overnight at 225°C.

Silica: Sequentially wash with hexane and dichloromethane as described above. Oven dry the silica at 50°C for a minimum of one hour in a foil-covered beaker, then condition at 225°C for at least four hours.

44% Sulphuric Acid on Silica: Add 78.6 g of concentrated sulfuric acid in a stepwise manner (5 mL at a time) to 100 g of silica (prepared as described above) in a 500 mL glass-stoppered Erlenmeyer flask. After each addition, shake the flask vigorously until no clumps are observed. Store in the stoppered flask. This amount of material is enough for 40 cleanup columns. Larger batches are not recommended.

33% 1 M Sodium Hydroxide on Silica: Add 24.6 g of a 1 M sodium hydrozide solution in a stepwise manner to 50 g of freshly-conditioned silica in a glass-stoppered Erlenmeyer flask. After each addition, shake the flask until no clumps are observed. Store in a screw-capped bottle with a Teflon cap liner.

10% Silver Nitrate on Silica: Dissolve 5.6 g of silver nitrate in 21.5 mL of deionized water. This solution is added in a stepwise fashion to 50 g of freshly-conditioned silica in a glass-stoppered Erlenmeyer flask. Between additions, the flask is shaken until a uniformly-coated, free-flowing powder is produced. After the silver nitrate is added, allow the material to stand for approximately 30 minutes, cover the mouth of the flask with solvent-rinsed aluminum foil, and place in an oven at 30°C. Over a five-hour period, gradually raise the oven temperature to 180°C, and continue to condition overnight at this temperature. Cool to room temperature and immediately transfer to an amber glass, screw-capped bottle which has a Teflon cap liner. Minimize exposure of this material to light. Store in a desiccator until use.

Basic Alumina: Weigh two to three grams more alumina than is necessary (2.5g/sample) for the number of samples to be batch-processed at one time. Add the alumina to a glass conditioning column and wash sequentially with dichloromethane and hexane (two portions each). The volume of solvent used for each wash should bet two to three times the estimated volume of alumina in the conditioning column. After draining, insert a glass wool plug into the column to immobilize the alumina. Drain as much solvent as possible from the wet alumina by suction on the valved end of the column, then place the column in a tube furnace. Connect the glass-jointed end of the column to a cylinder of prepurified nitrogen. With the furnace off, purge the alumina with nitrogen at 200-400 mL per minute for approximately 30 minutes. While maintaining the nitrogen purge, condition the alumina at 350°C for a minimum of two hours. Conditioned alumina must be used immediately after removal from the tube furnace. Do not store for later use.

Comparison with Other Methods:

This method uses a high resolution capillary GC column with low resolution mass spectrometry. It is less expensive then EPA-8290 and Environment Canada 1/RM/19 which both use high resolution mass spectrometry. Its cleanup procedures are different from the U.S. EPA methods in that acid/base silica gel followed by basic alumina columns are used rather than neutral alumina followed by activated carbon columns (EPA-8280 and EPA 8290). Additional details are provided in this method for XAD-2 solid samples, ethylene glycol samples, waste oil samples, etc. It is a newer method and has taken advantage of several years of experience to improve the U.S. EPA methods.

Analytes Covered by this Method:

This method covers 17 PCDDs and PCDFs, all of which are of interest to the National Contaminated Sites Remediation Program as shown in Table 22. It also covers the PCBs as homologs rather than as the specific Aroclor mixtures in Table 1 of Volume I.

Comments on Use of this Method

The sensitivity of this method is dependent on the level of interferents within a given matrix and how well the cleanup procedures remove them. Isotopically-labelled surrogates are added to each sample before extraction and cleanup so that recovery of the analytes can be estimated based on recoveries of the surrogates. Both an internal standard method of quantitation and an external method of quantitation are described. Example data reports are also provided.

One disadvantage of this method is that the DB-5 GC column cannot resolve 2,3,7,8-TCDF from some other isomers. A 30 M DB-225 GC column is recommended if the presence and amounts of 2,3,7,8-TCDF need to be measured.

Table 22. Analytes Covered Using Method Environment Canada 1/RM/3 (revised)

2,3,7,8-T_4CDD*
2,3,7,8-T_4CDF*
1,2,3,7,8-P_5CDD*
1,2,3,7,8-P_5CDF*
2,3,4,7,8-P_5CDF*
1,2,3,4,7,8-H_6CDD*
1,2,3,6,7,8-H_6CDD*
1,2,3,7,8,9-H_6CDD*
1,2,3,4,7,8-H_6CDF*
1,2,3,6,7,8-H_6CDF*
1,2,3,7,8,9-H_6CDF*
2,3,4,6,7,8-H_6CDF*
1,2,3,4,6,7,8-H_7CDD*
1,2,3,4,6,7,8-H_7CDF*
1,2,3,4,7,8,9-H_7CDF*
OCDD*
OCDF*
PCB Homologs 3Cl-10Cl

* Analytes targeted by the National Contaminated Sites Remediation Program.

Title:

Reference Method for the Determination of Polychlorinated Dibenzo-para-dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) in Pulp and Paper Mill Effluents.

Reference:

Environment Canada. EPS 1/RM/19. February 1992. River Road Environmental Technology Centre, Ottawa, Ontario.

Method Applicability:

This method is applicable to the solid and liquid phases of pulp mill effluents.

Sample Preparation:

Spike a 1 kg sample in its sampling bottle with a freshly prepared stable labeled surrogate solution and, after mixing it well for an hour, suction filter it to separate the solid pulp from the aqueous sample. Rinse the pulp with analyte-free deionized water and dry it in a desiccator. The dried pulp and the combined liquid filtrates are extracted separately.

Filtrate Extraction

Quantitatively transfer the filtrate from the flask to a separatory funnel and extract it with dichloromethane. Persistent emulsions may be drained off into a clean, large beaker and broken using mechanical means, such as passage through loosely packed glass wool. Repeat these extractions two more times. If any water or emulsion is observed in the collection flask, the extract must be passed through a bed of dichloromethane-rinsed sodium sulphate to dry it. Concentrate the combined extracts and rinses to 3 to 5 mL by rotary evaporation at 30°C before combining with the extract from the particulate (pulp) fraction of the sample.

Pulp Extraction

Extract the dried pulp and particulates with toluene using a pre-extracted thimble and a Soxhlet apparatus. Reflux the sample at a rate of 3 to 4 cycles per hour for at least 16 hours. Add the concentrate from the filtrate extraction above to this extract and concentrate the combined extracts to 1 to 2 mL using a rotary evaporator and a water bath temperature of 72°C or lower. Exchange the toluene solvent to hexane by adding 100 mL of hexane and repeating the solvent concentration. Dry the sample by passing it through hexane-rinsed sodium sulphate, then rinsing first the extraction flask, then the sodium sulphate, with three 5-mL portions of hexane. Concentrate the sample to 3 to 5 mL by rotary evaporation at 30°C.

Acid/Base Silica and Basic Column Cleanup

Two columns are used for sample cleanup: an acid/base silica column and an alumina column.

The acid/base silica column is layered from the bottom up with: glass wool, 1.5 g of silver nitrate/silica, (bottom layer), 1 g of silica, 2 g of 33% 1 M sodium hydroxide/silica, 1 g of silica, 4 g of 44% sulfuric acid/silica, 2 g of silica and approximately 1 g of sodium sulphate to top off the column. The column is pre-washed (v/v) before use with 30 mL of 2% dichloromethane in hexane.

The concentrated sample extract is transferred onto the top of this column, followed by three, 5-mL 2% dichloromethane/hexane (v/v) rinsings of the sample flask, also transferred using the same pipet. When the third rinse has drained to the top of the sodium sulphate layer, pour an additional 50 mL of 2% dichloromethane/hexane (v/v) through the column. When the solvent has drained, assess the column for saturation of the acid/silica layer and the silver nitrate/silica layer. This is indicated by an appearance of colour throughout the reagent layer.

Saturation of the acid/silica layer suggests that the sample extract (in hexane) should be washed with concentrated sulphuric acid in a separatory funnel, repeating the washes (maximum of four washings) with fresh acid until no colour is observed in the acid layer. Then wash the extract sequentially with deionized water, 1 M sodium hydroxide and a final wash with deionized water. Dry the extract by passing it through sodium sulphate.

Saturation of the silver nitrate/silica layer requires passage of the concentrated sample extract through an additional column containing 2.5g of 10% silver nitrate/silica. Elute the sample extract through the pre-washed column with 30 mL of 2% dichloromethane in hexane. Add hexane to the column eluate and concentrate to 1 to 2 mL by rotary evaporation at 30°C.

The above concentrate is then quantitatively transferred with hexane to a second cleanup column. It consists of 2.5 g of freshly prepared basic alumina topped off with 0.5 cm of sodium sulfate and is first pre-washed with hexane before the sample concentrate is added to it.

Transfer the concentrated extract from the acid/base/silver nitrate/silica column onto the alumina column, followed by three 5-mL hexane rinsings of the sample flask and then add an additional 30 mL of hexane to the column followed by 20 mL of freshly prepared 1.5% dichloromethane in hexane. This combined fraction (Fraction 1) is archived.

Add 30 mL of 50% dichloromethane in hexane (v/v) to the column and allow the column to drain completely. This solution (Fraction 2) contains the PCDDs/PCDFs. Concentrate it to 1 to 2 mL and exchange the solvent to hexane and repeat the concentration step.

An optional step is to prepare another alumina column as just described. Then following the same procedure, apply the PCDD/PCDF sample (Fraction 2) to the column and collect Fraction 1 in the flask containing that eluate from the first column. Fraction 2 is also collected in its original flask. Concentrate both fractions to approximately 1 mL by rotary evaporation at 30°C. Fraction 1 is archived and may be assessed for PCDDs/PCDFs if poor surrogate recovery is observed in Fraction 2.

Fraction 2, containing the PCDDs/PCDFs, is quantitatively transferred to a 1-mL conical sample vial and concentrated under a gentle stream of pre-purified nitrogen to a small volume (approximately 100 µL) for analysis.

Immediately before GC/MS analysis, blow down the sample just to dryness under a gentle stream of pre-purified nitrogen. Add 20 µL of the recovery standard solution, containing 50 pg/µL each of $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-H_6CDD in toluene, to the sample vial. Sonicate the capped vial for one minute or allow to sit for a minimum of one hour before analysis.

An additional optional cleanup step is to pass the sample through another column that contains 1 g of activated carbon/silica. The sample, in 1 mL of hexane is placed on this pre-rinsed column using 1:1 cyclohexane and dichloromethane to rinse the sample flask. Elution of the column is performed using 1:1 cyclohexane and dichloromethane followed by a 75:20:5 mixture of dichloromethane, methanol, and toluene. The final elution is made with toluene; this fraction contains the PCDDs/PCDFs and is concentrated for analysis to a small volume in a rotary evaporator. The first two elution fractions are discarded.

Instrumental Analysis:

Analysis for PCDD/PCDF is performed with a high-resolution gas chromatograph/high-resolution mass spectrometer/computerized data system (HRGC/HRMS/DS). Two characteristic ions are selectively monitored for each PCDD/PCDF congener group. Analyte identification is confirmed when target ions are detected in the correct abundance ratio with established retention time windows. Quantification is based on the use of surrogates (isotopically-labelled compounds added before sample workup) as internal standards. Two other isotopically-labelled standards, added to sample extracts immediately before analysis, serve as recovery standards for the quantification of surrogate recovery.

Optimum settings for GC parameters and appropriate retention time windows for time-sequenced SIM mode analysis of PCDDs/PCDFs on a 60 metre DB-5 column are established from the analysis of Window Defining Mixtures containing the first and last eluting congeners within each homologue group of analytes. The order of elution is such that five retention windows can be defined, corresponding to the five levels of chlorine substitution (4 Cl to 8 Cl), without any overlap. Under optimum conditions, the interval between the latest eluting TCDD and TCDF congeners and the earliest eluting P_5CDF congeners is no more than 0.1 minute. Parameter settings that produce a 2,3,7,8-TCDD retention time of 25 minutes or more will normally represent conditions under which the 4 Cl/5 Cl gap is optimized and the chromatographic performance criterion described in the following subsection can be satisfied. An internal standard method is used to quantify PCDDs/PCDFs. It relies upon consistent linearity of MS response over time and over the calibration range.

Instrumentation Required:

The gas chromatograph (GC) must exhibit isothermal temperature stability of $\pm$ 0.2°C, or better, over its specified range of operation and also have capability to accommodate a minimum of three temperature ramps. A 60 m DB-5 capillary column is directly coupled to a high-resolution, double-focussing mass spectrometer (MS) of any geometry. The MS is operator-programmed for time-sequenced acquisition of selected MS data for each congener group and is operated in the electron impact (EI) and selected ion monitoring (SIM) modes.

Interferences:

Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or elevated baselines that could lead to elevated detection limits and/or loss of ability to detect PCDDs/PCDFs that may be present. Proper cleaning of glassware is extremely important. Glassware should be rinsed with solvent and washed with a detergent solution as soon after use as is practical. Sonication of glassware filled with a detergent solution can also be performed as an aid to cleaning.

Interferences co-extracted from samples will vary considerably from source to source depending upon the exact nature of the sample matrix. Interfering compounds may be present at concentrations several orders of magnitude higher than any PCDDs/PCDFs that may be present. Interfering co-extractants must therefore be eliminated or reduced to the maximum extent practicable in order to ensure reliable quantification of trace amounts of PCDDs/PCDFs. The cleanup procedures described can effectively remove many potential interferents.

Despite rigorous cleanup procedures, matrix interference will still be a possibility. If detection limits are seriously affected by excessive background (non-discrete interference), the sample extract will have to be re-processed using alternative cleanup techniques.

Quality Control Requirements:

Before any effluent samples are processed, all pre-cleaned glassware, including Soxhlet apparatus, concentrators, columns, flasks, and vials, are rinsed with dichloromethane and hexane. Rinses are combined and processed in the same manner as test samples. Contamination levels of individual 2,3,7,8-substituted tetra-, penta-, hexa-, hepta- and octa-CDD/CDF congeners in glassware proof rinses must not exceed 5, 10, 10, 15 and 50 pg per sample, respectively.

Before any effluent samples are processed, laboratory capability must be demonstrated by conducting triplicate analyses of matrix blanks (purified water) spiked with native and labelled PCDD/PCDF standards. Criteria for accuracy and surrogate recoveries described in the method must be met.

Before extraction, each sample is spiked with a mixture of isotopically-labelled surrogates to assess the degree of analyte loss during sample workup. If the recovery of any surrogate is outside the range of 40 to 130% for TCDD and TCDF, and 30 to 130% for penta-, hexa-, hepta-, and octa-CDDs/CDFs, the sample must be re-processed and re-analyzed.

Known concentrations of $^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-H_6CDD must be added to each sample extract immediately before GC/MS analysis. These two compounds serve as retention time references for labelled surrogates and as the basis for calculation of surrogate recoveries.

A method blank sample, consisting of 1 L of high purity water spiked with surrogates, is processed with each batch of up to 10 test samples. Acceptance limits for 2,3,7,8-substituted dioxin and furan congener presence in method blank samples are: 5 pg to TCDD and TCDF; 10 pg for penta- and hexa-CDD/CDF; 15 pg for hepta-CDD/CDF; 50 pg for OCDD/OCDF. A compliance sample result for a 2,3,7,8-substituted congener must be flagged with a "C" if the same congener was present in the corresponding method blank at a level exceeding the applicable acceptance limit.

Hard copied verification of MS resolution at 10,000 or better is required before and after each series of injections related to the application of this method.

A Window Defining Mixture containing the first and last eluting isomer within each homologous group of PCDDs/PCDFs must be used to correctly define retention time windows for selected ion monitoring of individual homologues. This analysis must be repeated daily.

Acceptable chromatographic separation between 2,3,7,8-TCDD and its closest neighbouring isomers must be confirmed daily. If analysis for 2,3,7,8-TCDF on a second column is required, acceptable chromatographic separation between this isomer and its closest neighbouring isomers must also be demonstrated.

Before sample analysis, calibration curves are constructed to verify linearity of MS response for all homologues over the concentration range of 0.25 to 100 pg/µL for native PCDDs/PCDFs.

The established calibration must be verified by analyzing a calibration verification standard at least once during every 12-hour period in which sample analysis occurs. Using four-point average RRFs obtained from initial calibration runs, the calculated concentrations of both 2,3,7,8-TCDD and 2,3,7,8-TCDF must be within 15% of their actual values. The calculated concentrations of all other native analytes must be within 20% of their respective true concentrations. The calculated recovery of each surrogate compound must be within the range of 75 to 125%. Remedial action is required whenever any native or surrogate compound fails this verification test.

Gas chromatograph/mass spectrometer (GC/MS) detection limits must be assessed by analyzing the lowest concentration standard solution. This analysis must be repeated daily.

As a check on accuracy, NIST Reference Material 1614 (2,3,7,8-TCDD in solution) is periodically analyzed as a sample. Reported sample results must be fully documented. All QA/QC documentation and raw GC/MS data must be available for auditing.

Comparison with Other Methods:

This method is very complex and requires expensive instrumentation. It is also applicable to pulp mill effluent solid and liquid samples, neither of which are listed matrices of interest to the National Contaminated Sites Remediation Program. However, the method may, with proper verification, be modified for use with surface and groundwaters or soils and sediments.

Analytes Covered by this Method:

This method covers 17 PCDDs and PCDFs, all of which are of interest to the National Contaminated Sites Remediation Program as shown in Table 23. It also covers the PCBs as homologs rather than as the specific Aroclor mixtures in Table 1 of Volume I.

Table 23. Analytes Covered Using Method Environment Canada 1/RM/19

2,3,7,8-T_4CDD*	
2,3,7,8-T_4CDF*	1,2,3,6,7,8-H_6CDF*
1,2,3,7,8-P_5CDD*	1,2,3,7,8,9-H_6CDF*
1,2,3,7,8-P_5CDF*	2,3,4,6,7,8-H_6CDF*
2,3,4,7,8-P_5CDF*	1,2,3,4,6,7,8-H_7CDD*
1,2,3,4,7,8-H_6CDD*	1,2,3,4,6,7,8-H_7CDF*
1,2,3,6,7,8-H_6CDD*	1,2,3,4,7,8,9-H_7CDF*
1,2,3,7,8,9-H_6CDD*	OCDD*
1,2,3,4,7,8-H_6CDF*	OCDF*

* Analytes targeted by the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

The sensitivity of this method is dependent on the level of interferents within a given matrix and how well the cleanup procedures remove them. Isotopically-labelled surrogates are added to each sample before extraction and cleanup so that recovery of the analytes can be estimated based on recoveries of the surrogates. Example data reports are also provided.

On a DB-5 column, 2,3,7,8-TCDF cannot be resolved from its neighbouring isomers (i.e., 1,2,4,9-, 2,3,4,8- and 2,3,4,6-). In order to accurately quantify any 2,3,7,8-TCDF that may be present in a sample, analysis of a second column is required. Use of a second column is only mandatory when results from the DB-5 run indicate that the concentration of 2,3,7,8-TCDF may equal or exceed the regulatory level. On a 30 metre DB-225 column, 2,3,7,8-TCDF can be resolved from its neighbouring 2,3,4,7- and 1,2,3,9-isomers.

A 60 metre DB-Dioxin column can also be used as an alternative for 2,3,7,8-TCDD and 2,3,7,8-TCDF analysis because this column is capable of separating 2,3,7,8-TCDD from neighbouring isomers 1,2,4,6-/1,2,4,9- and 1,2,3,7-/1,2,6,8-TCDD, and 2,3,7,8-TCDF from neighbouring isomers 2,3,4,7- and 2,3,4,8-TCDF. However, it cannot be used effectively for homologue analysis.

It is important to recognize that most of the 2,3,7,8-substituted congeners cannot be uniquely identified on a DB-5 column, even under optimum conditions.

Title:

The Analysis of Polychlorinated Dibenzo-P-Dioxins and Polychlorinated Dibenzofurans. U.S. EPA Method 8280, Revision 0, September 1986.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA, 1986. Method 8280, Revision 0, September 1986. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is appropriate for the determination of tetra-, penta-, hexa-, hepta-, and octachlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in chemical wastes including still bottoms, fuel oils, sludges, fly ash, reactor residues, soil and water.

Sample Preparation:

Soil Samples

Extract soil samples by placing about 10 g and an equivalent amount of anhydrous sodium sulfate in a 500-mL Erlenmeyer flask fitted with a Teflon stopper. Add 20 mL of methanol and 80 mL of petroleum ether, in that order, to the flask. Shake on a wrist-action shaker for two hours. The solid portion of sample should mix freely. If a small soil aliquot is used, scale down the amount of methanol proportionally.

Filter the extract through a glass funnel fitted with a glass fiber filter and filled with anhydrous sodium sulfate into a 500-mL Kuderna-Danish (K-D) concentrator fitted with a 10-mL concentrator tube. Add petroleum ether to the Erlenmeyer flask, restopper the flask and swirl the sample gently, remove the stopper carefully and decant the solvent through the funnel as above. Repeat this procedure with two additional aliquots of petroleum ether. Wash the sodium sulfate in the funnel with two additional portions of petroleum ether.

Add Teflon or PFTE boiling chip and a three-ball Snyder column to the K-D flask. Concentrate in a 70°C water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow it to cool for 5 minutes.

Add hexane and a new boiling chip to the K-D flask. Concentrate in a water bath to an apparent volume of 10 mL. Remove the apparatus from the water bath and allow to cool for 5 minutes.

Remove and invert the snyder column and rinse it into the K-D with two 1-mL portions of hexane. Decant the contents of the K-D and concentrator tube into a 125-mL separatory funnel. Rinse the K-D with two additional 5-mL portions of hexane and combine them with other hexane rinses. Proceed to clean up.

Aqueous Samples

Mark the water meniscus on the side of a 1-L sample bottle for later determination of the exact sample volume. Pour the entire sample (approximately 1-L) into a 2-L separatory funnel.

Add methylene chloride to the sample bottle, seal and shake 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. If the emulsion interface between layers is more than one-third the volume of the solvent layer, mechanical techniques must be used to complete the phase separation. Collect the methylene chloride (3 x 60 mL) directly into a 500-mL Kuderna-Danish concentrator (mounted with a 10-mL concentrator tube) by passing the sample extracts through a filter funnel packed with a glass wool plug and anhydrous sodium sulfate. After the third extraction, rinse the sodium sulfate with additional methylene chloride to ensure quantitative transfer.

Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid reaches 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, add hexane, re-attach the Snyder column and concentrate to approximately 5 mL. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step.

Rinse the flask and the lower joint twice with 5 mL of hexane and combine rinses with extract to give a final volume of about 15 mL. Determine the original sample volume by refilling the sample bottle to the mark and transferring the liquid to a 1,000-mL graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed with clean-up.

NOTE: A continuous liquid-liquid extractor may be used in place of a separatory funnel to avoid emulsions. Add methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the extractor and repeat the sample bottle rinse with additional methylene chloride. Add 200 to 500 mL of methylene chloride to the distilling flask; add sufficient reagent water to ensure proper operation, and extract for 24 hours. Allow the sample to cool, then detach the distilling flask, dry and concentrate the extract and then proceed with volume determination and clean-up.

Clean-up Procedure

In a 250-mL separatory funnel, partition the solvent (15 mL hexane) against 40 mL of 20 percent (w/v) potassium hydroxide. Shake for 2 minutes. Remove and discard the bottom aqueous layer. Repeat the washing with potassium hydroxide solution until no color is visible in the bottom layer but no more than four times because strong base is known to degrade certain PCDDs/PCDFs, so contact time must be minimized.

Partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 minutes. Remove and discard the bottom aqueous layer. Next, partition the solvent (15 mL hexane) against 40 mL of concentrated sulfuric acid. Shake for 2 minutes. Remove and discard the bottom aqueous layer. Repeat the acid washings until no color is visible in the acid layer (but no more than four times).

Finally, partition the solvent (15 mL hexane) against 40 mL of 5 percent (w/v) sodium chloride. Shake for 2 minutes. Remove and discard the bottom aqueous layer. Dry the organic layer by pouring it through a funnel containing anhydrous sodium sulfate into a 50-mL round bottom flask. Wash the separatory funnel twice with hexane and pour it through the funnel with sodium sulfate and combine all the hexane extracts. Concentrate the hexane solution to near dryness with a rotary evaporator (using a 35°C water bath), making sure all traces of toluene are removed. (Use of an inert gas, such as nitrogen, to concentrate the extract by gently blowing the gas over it is also permitted).

For the second phase of the clean-up, pack a gravity column (glass 300-mm x 10.5-mm), fitted with a Teflon stopcock, in the following manner. Insert a glass-wool plug into the bottom of the column. Add a 4 g layer of sodium sulfate. Add a 4 g layer of Woelm super 1 neutral alumina. Tap the top of the column gently. Woelm super 1 neutral alumina need not be activated or cleaned prior to use but it should be stored in a sealed desiccator. Add a 4 g layer of sodium sulfate to cover the alumina. Elute with 10 mL of hexane and close the stopcock just prior to the exposure of the sodium sulfate layer to air. Discard the eluant. Check the column for channeling. If channeling is present, discard the column. Do not tap a wetted column.

Dissolve the hexane residue from the first phase of the clean-up in 2 mL of hexane and apply it carefully to the top of the column. Elute with enough hexane (3-4 mL) to complete the transfer of the sample quantitatively to the surface of the alumina. Discard the eluant. Elute the column with 10 mL of 8 percent (v/v) methylene chloride in hexane. Check by GC/MS analysis that no PCDDs of PCDFs are elute in this fraction before discarding it. Elute the PCDDs and PCDFs from the column with 15 mL of 60 percent (v/v) methylene chloride in hexane and collect this second fraction in a conical shaped (15-mL) concentrator tube.

Carbon Column Clean-up

Using a carefully regulated stream of nitrogen, concentrate the first 8 percent fraction from the alumina column to about 1 mL. Wash the sides of the tube with a small volume of hexane (1 to 2 mL) and reconcentrate to about 1 mL. Save this 8 percent concentrate for GC/MS analysis to check for breakthrough of PCDDs and PCDFs. Concentrate the second 60 percent fraction to about 2 to 3 mL. Prepare a carbon column and rinse the carbon with 5 mL cyclohexane/methylene chloride (50:50 v/v) in the forward direction of flow and then in the reverse direction of flow. While still in the reverse direction of flow, transfer the sample concentrate to the column and elute with 10 mL of methylene chloride/methanol/benzene (75:20:5, v/v). Save all above eluates and combine them (this fraction may be used as a check on column efficiency). Next, turn the column over and, in the direction of forward flow, elute the PCDD/PCDF fraction with 20 mL toluene.

Evaporate the toluene fraction to about 1 mL on a rotary evaporator and transfer it to a 2.0-mL Reacti-vial using a toluene rinse. Concentrate the sample using a stream of nitrogen gas. The final volume will depend on the relative concentration of target analytes but it is typically 100 µL for soil samples and 500 uL for sludge, still bottom, and fly ash samples. Extracts which are determined to be outside the calibration range for individual analytes must be diluted or a smaller portion of the sample must be re-extracted.

An alternate carbon column clean-up also may be used. Proceed as in above paragraph to obtain the 60 percent fraction re-concentrated to 400 uL which is transferred to a 1 mL HPLC injector loop. The injector loop is connected to the optional HPLC column. Rinse the centrifuge tube with 500 uL of hexane and add this rinsate to the injector loop. Load the combined concentrate and rinsate onto the column and elute the column at 2 mL/min, ambient temperature, with 30 mL of cyclohexane/methylene chloride 1:1 (v/v). Discard the eluant and backflush the column with 40 mL toluene to elute and collect the entire fraction for PCDDs and PCDFs. The column is then discarded and 30 mL of cyclohexane/methylene chloride 1:1 (v/v) is pumped through a new column to prepare it for the next sample.

Approximately 1 hour before HRGC/LRMS analysis, transfer aliquot of the extract to a micro-vial. Add sufficient recovery standard ($^{13}C_{12}$1,2,3,4-TCDD) to it to give a concentration 500 ng/mL.

Instrumental Analysis:

When toluene is employed as the final solvent, use of a bonded phase column is recommended. Solvent exchange into tridecane is required for other liquid phases or nonbonded columns such as CP-Sil-88. Chromatographic conditions must be adjusted to account for solvent boiling points.

Calculate response factors for standards relative to the internal standards, $^{13}C_{12}$-2,3,7,8-TCDD and $^{13}C_{12}$-OCDD. Add the recovery standard $^{13}C_{12}$-1,2,3,4-TCDD) to the samples prior to injection. The concentration of the recovery standard in the sample extract must be the same as that in the calibration standards used to measure the response factors.

Analyze samples with selected ion monitoring, using five sets of ions that are detailed in the method.

Instrumentation Required:

Gas Chromatograph/Mass Spectrometer/Data System: Column #1: 50-m CP-Sil-88 fused silica capillary column. Column #2: DB-5 (30 M x 0.25 mm I.D., 0.25-um film thickness) fused silica capillary column. Column #3: 30 M SP-2250 fused silica capillary column. Mass Spectrometer: A low resolution instrument is specified, utilizing 70 volts (nominal) electron energy in the electron impact ionization mode. The system must be capable of selected ion monitoring (SIM) for at least 11 ions simultaneously, with a cycle time of 1 second or less. Minimum integration time for SIM is 50 ms per m/z. Also required is a GC-to-MS interface constructed of all glass or glass-lined materials.

Interferences:

Solvents, reagents, glassware, and other sample processing hardware may yield discrete artifacts and/or elevated baselines which may cause misinterpretation of chromatographic data. All of these materials must be demonstrated to be free from interferents under the conditions of analysis by running laboratory method blanks.

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.

Interferents co-extracted from the sample will vary considerably from source to source, depending upon the sample. PCDDs and PCDFs are often associated with other interfering chlorinated compounds such as PCBs and polychlorinated diphenyl ethers which may be found at concentrations several orders of magnitude higher than that of the analytes of interest. Retention times of target analytes must be verified using reference standards. These values must correspond to the retention time windows established. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup techniques to achieve the method detection limit.

Quality Control Requirements:

Before processing any samples, it must be demonstrated through the analysis of a method blank that all glassware and reagents are interferent-free at the method detection limit of the matrix of interest. Each time a set of samples is extracted, or there is a change in reagents, a method blank must be processed as a safeguard against laboratory contamination.

A laboratory "method blank" must be run along with each analytical batch (20 or fewer samples). A method blank is performed by executing all of the specified extraction and cleanup steps, except for the introduction of a sample. The method blank is also dosed with the internal standards. For water samples, one liter of deionized and/or distilled water should be used as the method blank. Mineral oil may be used as the method blank for other matrices.

The laboratory will be expected to analyze performance evaluation samples on a periodic basis throughout the course of a given project. Additional sample analyses will not be permitted if the performance criteria are not achieved. Corrective action must be taken and acceptable performance must be demonstrated before sample analyses can resume.

Field duplicates (individual samples taken from the same location at the same time) should be analyzed periodically to determine the total precision (field and lab). Where appropriate, field blanks should be provided to monitor for possible cross-contamination of samples in the field. GC column performance must be demonstrated initially and verified prior to analyzing any sample in a 12-hr period. The GC column performance check solution must be analyzed under the same chromatographic and mass spectrometric conditions used for other samples and standards.

Before using any cleanup procedure, series of calibration standards must be processed through the procedure to validate elution patterns and the absence of interferents from reagents. Both alumina column and carbon column performance must be checked. Routinely check the 8 percent CH_2Cl_2/hexane eluate of environmental extracts from the alumina column for presence of target analytes. This fraction is intended to contain a high level of interferents and analysis near the method detection limit may not be possible.

Comparison with Other Methods:

This method uses a high resolution capillary GC column with low resolution mass spectrometry. It is usually less expensive than EPA-8290 which uses high resolution mass spectrometry. However, it also does not cover all the PCDD/PCDF isomers of interest and, furthermore is not mentioned as being applicable for analysis of sediments whereas EPA method 8290 covers all liquid and solid matrices including sediments. However, simple modifications of the sample preparation should allow the method to be also used for analysis of sediments.

Analytes Covered by this Method:

This method covers 22 compounds, 11 of which are interest to the National Contaminated Sites Remediation Program, as shown in Table 24.

Table 24. Analytes Covered Using U.S. EPA Method 8280, Rev. 0

1,2,3,4 - T_4CDD	1,2,3,4,7,8 - H_6CDD*
1,3,6,8 - T_4CDD	1,2,3,6,7,8 - H_6CDD*
1,3,7,9 - T_4CDD	1,2,3,4,6,7,8 - H_7CDD*
1,3,7,8 - T_4CDD	OCDD*
1,2,7,8 - T_4CDD	1,2,7,8 - T_4CDF
1,2,8,9 - T_4CDD	2,3,7,8 - T_4CDF*
2,3,7,8 - T_4CDD*	1,2,3,7,8 - P_5CDF*
1,2,3,4,7 - P_5CDD	1,2,3,4,7,8 - H_6CDF*
1,2,3,7,8 - P_5CDD*	1,2,3,4,6,7,8 - H_7CDF*
	OCDF*

* Analytes targeted by the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

The sensitivity of this method is dependent upon the level of interferents within a given matrix. Proposal quantification levels for target analytes were 2 ppb in soil samples, up to 10 ppb in other solid wastes and 10 ppt in water. Actual values have been shown to vary by homologous series and, to a lesser degree, by individual isomer. The total detection limit for each CDD/CDF homologous series is determined by multiplying the detection limit of a given isomer within that series by the number of peaks which can be resolved under the gas chromatographic conditions.

Certain 2,3,7,8- substituted congeners are used to provide calibration and method recovery information. Proper column selection and access to reference isomer standards, may in certain cases, provide isomer specific data. Precision, bias and concentration ranges for the compounds covered by this method have not been determined yet.

Title:

Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS). U.S. EPA Method 8290, Revision 0, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 8290, Revision 0, November 1990. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is applicable with a variety of environmental matrices including: water, soil, sediment, paper pulp, fly ash, fish tissue, human adipose tissue, sludges, fuel oil, chemical reactor residue, and still bottom.

Sample Preparation:

Sludge/Wet Fuel Oil

Extract aqueous sludge or wet fuel oil samples by refluxing a sample with 50 mL toluene in a 125 mL flask fitted with a Dean-Stark water separator. Continue refluxing the sample until all the water is removed. Cool the sample, filter the toluene extract through a glass fiber filter, or equivalent, into a 100 mL round bottom flask. Rinse the filter with 10 mL toluene and combine the extract with the rinse. Concentrate the combined solutions to near dryness either on a rotary evaporator at 50°C or using an inert gas. Transfer the concentrate to a 125 mL separatory funnel using 15 mL hexane. Rinse the flask with two 5 mL portions of hexane and add the rinses to the funnel. Shake the combined solutions in the separatory funnel for 2 minutes with 50 mL of 5% sodium chloride solution, discard the aqueous layer. Proceed to clean up.

Soil/Sediment

If the sample is wet, add anhydrous powdered sodium sulfate to it and mix thoroughly with a stainless steel spatula until a free flowing mixture is obtained. After breaking up any lumps, place the soil/sodium sulfate mixture in the Soxhlet apparatus on top of a glass wool plug. Add toluene to the Soxhlet apparatus and reflux for 16 hours. The solvent must cycle completely through the system five times per hour. Cool and filter the extract through a glass fiber filter into a 500 mL round bottom flask for evaporation of the toluene. Rinse the filter with toluene, and concentrate the combined fractions to near dryness on a rotary evaporator at 50°C. Remove the flask from the water bath and allow to cool for 5 minutes. Transfer the residue to a 125 mL separatory funnel, using hexane. Rinse the flask with two additional portions of hexane, and add the rinses to the funnel. Proceed to clean up.

Aqueous Samples

Allow the sample to come to ambient temperature, then mark the water meniscus on the side of the 1-L sample bottle for later determination of the exact sample volume. Add the required acetone diluted sample fortification solution (see Table 25). When the sample is judged to contain 1% or more solids, the sample must be filtered through a 0.45 µm glass fiber filter that has been rinsed with toluene. If the suspended solids content is too great to filter, centrifuge the sample, decant, and then filter the aqueous phase. Combine the solids from the centrifuge bottle(s) with the particulates on the filter and with the filter itself and proceed with Soxhlet extraction for soil/sediment.

Pour the aqueous filtrate into a 2-L separatory funnel. Add methylene chloride to the sample bottle, seal, and shake for 30 seconds to rinse the inner surface. Transfer the solvent to the separatory funnel and extract the sample by shaking the funnel for 2 minutes with periodic venting. Allow the organic layer to separate from the water phase for a minimum of 10 minutes. Collect the methylene chloride in a K-D apparatus, mounted with a 10-mL concentrator tube, by passing the sample extracts through a filter funnel packed with a glass wool plug and 5 g of anhydrous sodium sulfate. A rotary evaporator may be used in place of the K-D apparatus. Repeat the extraction twice with fresh portions of methylene chloride. After the third extraction, rinse the sodium sulfate with additional methylene chloride to ensure quantitative transfer. Combine all extracts and the rinse in the K-D apparatus.

Attach a Snyder column and concentrate the extract on a water bath until the apparent volume of the liquid is 5 mL. Remove the K-D apparatus and allow it to drain and cool for at least 10 minutes. Remove the Snyder column, add hexane, add the concentrate obtained from the Soxhlet extraction of the suspended solids, if applicable, re-attach the Snyder column, and concentrate to approximately 5 mL. Add a new boiling chip to the K-D apparatus before proceeding with the second concentration step. Rinse the flask and the lower joint with two 5 mL portions of hexane and combine the rinses with the extract to give a final volume of about 15 mL. Determine the original sample volume by filling the sample bottle to the mark with water and pouring water into a 1-L graduated cylinder. Record the sample volume to the nearest 5 mL. Proceed to clean up.

Cleanup

The sample extract is cleaned up utilizing a number of different techniques. Partition cleanup is where the sample extract is partitioned with concentrated sulfuric acid, 5% aqueous sodium chloride, and 20% aqueous potassium hydroxide. Silica/alumina column cleanup involves packing gravity columns with silica gel and alumina and sequentially eluting the residue from the partition cleanup. Carbon column cleanup involves packing a column with a mixture of AX-21 and Celite 545 and sequentially eluting the sample concentrate from the silica/alumina cleanup with hexane, cyclohexane/ methylene chloride (50:50), and methylene chloride/methanol/ toluene (75:20:5). Then the column is turned upside down and the PCDD/PCDF fraction is eluted with toluene. The toluene fraction is concentrated and stored in the dark at room temperature until analysis.

Instrumental Analysis:

Remove the sample extract or blank from storage. With a stream of dry, purified nitrogen, reduce the extract volume to 10 µL - 50 µL. Inject a 2 µL aliquot of the extract into a GC, operated under the conditions that have been established to produce acceptable results with the performance check solutions.

Instrumentation Required:

High-Resolution Gas Chromatograph/High-Resolution Mass Spectrometer/ Data System (HRGC/HRMS/DS) equipped with a GC injection port designed so that the separation of 2,3,7,8-TCDD from the other TCDD isomers achieved in the gas chromatographic column is not appreciably degraded. Column #1: 60 m DB-5 fused silica capillary column; Column #2: 30 m DB-225 fused silica capillary column, or equivalent.

Interferences:

Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts of elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferants under the conditions of analysis by analyzing laboratory method blanks. Analysts should avoid using PVC gloves. Interferants coextracted from the sample will vary considerably from matrix to matrix. PCDDs and PCDFs are often associated with other interfering chlorinated substances such as polychlorinated biphenyls (PCBs), polychlorinated diphenyl ethers (PCDEs), polychlorinated naphthalenes, and polychlorinated alkyldibenzofurans that may be found at concentrations several orders of magnitude higher than the PCDDs or PCDFs. While certain cleanup techniques are provided as part of this method, unique samples may require additional cleanup steps to achieve lower detection limits.

A high-resolution capillary column is used in this method. However, no single column is known to resolve all isomers. The 60 m DB-5 GC column is capable of 2,3,7,8-TCDD isomer specificity. In order to determine the concentration of the 2,3,7,8-TCDD (if detected on the DB-5 column), the sample extract must be reanalyzed on a column capable of 2,3,7,8-TCDF isomer specificity (e.g., DB-225, SP-2330, SP-2331, or equivalent). When a column becomes available that resolves all isomers, then a single analysis on this column can be used instead of analyses on more than one column.

Quality Control Requirements:

Before processing any samples, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system, glassware, and reagents are under control. Each time a set of samples is extracted or there is a change in reagents, a reagent water blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement steps.

For each analytical batch (up to 20 samples), a reagent blank, matrix spike and matrix spike duplicate/duplicate must be analyzed (the frequency of the spikes may be different for different monitoring programs). The blank and spiked samples must be carried through all stages of the sample preparation and measurement steps.

It must be documented that all applicable system performance criteria were met before analysis of any sample is performed. A GC column performance check is only required at the beginning of each 12-hour period during which samples are analyzed. An HRGC/HRMS method blank run is required between a calibration run and the first sample run. The same method blank extract may thus be analyzed more than once if the number of samples within a batch requires more than 12 hours of analyses.

At the beginning of each 12-hour period during which samples are to be analyzed, an aliquot of the 1) GC column performance check solution and 2) high-resolution concentration calibration solution No. 3 (HRCC-3; see Table 27) must be analyzed to demonstrate adequate GC resolution and sensitivity, response factor reproducibility, and mass range calibration, and to establish the PCDD/PCDF retention time windows. A mass resolution check must also be performed to demonstrate adequate mass resolution using an appropriate reference compound (perfluorokerosene (PFK) is recommended). If the required criteria are not met, remedial action must be taken before any samples are analyzed.

To validate positive sample data, the routine or continuing calibration (using the high resolution calibration solution Number 3 in Table 27) and the mass resolution check must be performed also at the end of each 12 hour period during which samples are analyzed. Furthermore, a HRGC/HRMS method blank analysis must be recorded following a calibration analysis and the first sample analysis.

To evaluate the performance of the analytical method, the QC check samples must be handled in exactly the same manner as actual samples. Therefore, 1.0 mL of the QC check sample concentrate is spiked into each of four 1 L aliquots of reagent water (which becomes the QC check sample), extracted, and then analyzed by GC. The variety of semivolatile analytes which may be analyzed by GC is such that the concentration of the QC check sample concentrate is different for the different analytical techniques presented in the full method.

The analyst must demonstrate also that the compounds of interest are being quantitatively recovered by the cleanup technique before the cleanup is applied to actual samples. For sample extracts that are cleaned up, the associated quality control samples (e.g., spikes, blanks, and duplicates) must also be processed through the same cleanup procedure. The analysis using each determinative method (GC, GC/MS, HPLC) specifies instrument calibration procedures using stock standards. It is recommended that cleanup also be performed on a series of the same type of standards to validate chromatographic elution patterns for the compounds of interest and to verify the absence of interferences from reagents.

Comparison with Other Methods:

This method is very complex and requires expensive instrumentation and experienced analysts. However, it has the advantage of covering all of the solid and liquid environmental matrices and, when all of the quality control protocols are followed, will produce good quality data for all of the PCDDs and PCDFs of interest.

Analytes Covered by this Method:

Method 8290 covers all 17 PCDD/PCDF compounds all of which are of interest to the National Contaminated Sites Remediation Program as shown in Table 25.

Comments on Use of this Method:

This method provides procedures for the detection and quantitative measurement of polychlorinated dibenzo-p-dioxins (tetra- through octachlorinated homologues; PCDDs), and polychlorinated dibenzofurans (tetra- through octachlorinated homologues; PCDFs) in a variety of environmental matrices and at part-per-trillion (ppt) to part-per-quadrillion (ppq) concentrations. The analytical method calls for the use of high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) on purified sample extracts.

The sensitivity of Method 8290 is dependent upon the level of interferences within a given matrix. Samples containing concentrations of specific congeneric analytes of PCDDs and PCDFs that are greater than ten times the upper method calibration limits (MCLs) must be analyzed by a protocol designed for such concentration levels, e.g., Method 8280.

Precision, bias and concentration ranges for the compounds covered by this method have not been determined yet.

Table 25. Analytes Covered Using U.S. EPA Method 8290, Rev. 0

2,3,7,8-T_4CDD*	2,3,7,8-T_4CDF*
1,2,3,7,8-P_5CDD*	1,2,3,7,8-P_5CDF*
1,2,3,4,7,8-H_6CDD	2,3,4,7,8-P_5CDF*
1,2,3,6,7,8-H_6CDD*	1,2,3,4,7,8-H_6CDF*
1,2,3,7,8,9-H_6CDD*	1,2,3,6,7,8-H_6CDF*
1,2,3,4,6,7,8-H_7CDD*	1,2,3,7,8,9-H_6CDF*
OCDD*	2,3,4,6,7,8-H_6CDF*
	1,2,3,4,6,7,8-H_7CDF*
	1,2,3,4,7,8,9-H_7CDF*
	OCDF*

* Analytes targeted by the National Contaminated Sites Remediation Program.

Table 26. Composition of Method 8290 Sample Fortification and Recovery Standard Solutions[a]

Analyte	Sample Fortification Solution Concentration (pg/µL; Solvent: Nonane)	Recovery Standard Solution Concentration (pg/µL; Solvent: Nonane)
$^{13}C_{12}$-2,3,7,8-TCDD	10	--
$^{13}C_{12}$-2,3,7,8-TCDF	10	--
$^{13}C_{12}$-1,2,3,4-TCDD	--	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	10	--
$^{13}C_{12}$-1,2,3,7,8-PeCDF	10	--
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	--
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	--
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	--	50
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	25	--
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	25	--
$^{13}C_{12}$-OCDD	50	--

[a]These solutions should be made freshly every day because of the possibility of adsorptive losses to glassware. If these solutions are to be kept for more than one day, then the sample fortification solution concentrations should be increased ten-fold, and the recovery standard solution concentrations should be doubled. Corresponding adjustments of the spiking volumes must then be made.

Table 27. Method 8290 High-Resolution Concentration Calibration Solutions

Compound	Concentration (pg/µL, in Nonane)				
	No. 5	No. 4	No. 3	No. 2	No. 1
Unlabeled Analytes					
2,3,7,8-TCDD	200	50	10	2.5	1
2,3,7,8-TCDF	200	50	10	2.5	1
1,2,3,7,8-PeCDD	500	125	25	6.25	2.5
1,2,3,7,8-PeCDF	500	125	25	6.25	2.5
2,3,4,7,8-PeCDF	500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDD	500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDD	500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDD	500	125	25	6.25	2.5
1,2,3,4,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,6,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,7,8,9-HxCDF	500	125	25	6.25	2.5
2,3,4,6,7,8-HxCDF	500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDD	500	125	25	6.25	2.5
1,2,3,4,6,7,8-HpCDF	500	125	25	6.25	2.5
1,2,3,4,7,8,9-HpCDF	500	125	25	6.25	2.5
OCDD	1,000	250	50	12.5	5
OCDF	1,000	250	50	12.5	5
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	50	50	50	50	50
$^{13}C_{12}$-2,3,7,8-TCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDD	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8-PeCDF	50	50	50	50	50
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	125	125	125	125	125
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	125	125	125	125	125
$^{13}C_{12}$-OCDD	250	250	250	250	250

Table 27. Continued

Compound	Concentration (pg/μL, in Nonane)				
	No. 5	No. 4	No. 3	No. 2	No. 1
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD [a]	50	50	50	50	50
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD[b]	125	125	125	125	125

[a]Used for recovery determinations of TCDD, TCDF, PeCDD and PeCDF internal standards.
[b]Used for recovery determinations of HxCDD, HxCDF, HpCDD, HpCDF and OCDD internal standards.

Title:

Fluoride (Potentiometric, Ion Selective Electrode). U.S. EPA Method 340.2.

Reference:

Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020, Method 340.2 (Potentiometric, Ion Selective Electrode), March 1983.

Method Applicability:

This method is applicable to the measurement of total and dissolved fluoride in drinking, surface and saline waters, domestic and industrial wastes.

Sample Preparation:

Place 50.0 mL of sample and 50.0 mL of buffer in a 150 mL beaker on a magnetic stirrer and mix at medium speed. Immerse the electrodes in the solution and observe the meter reading while mixing. The electrodes must remain in the solution for at least three minutes or until the reading has stabilized. At concentrations under 0.5 mg/L, it may require as long as five minutes to reach a stable meter reading; high concentrations stabilize more quickly. If a pH meter is used, record the potential measurements for each unknown sample and convert the potential reading to the fluoride ion concentration of the unknown using the standard curve. If a selective ion meter is used, read the fluoride level in the unknown sample directly in mg/L on the fluoride scale.

NOTE: For industrial waste samples, this amount of buffer may not be adequate. Check the pH first and if it is highly basic (>9), add 1N hydrochloric acid to adjust the pH to 8.3.

Instrumental Analysis:

The fluoride is determined potentiometrically using a fluoride electrode in conjunction with a standard single junction sleeve-type reference electrode and a pH meter with an expanded millivolt scale or a selective ion meter with a direct concentration scale for fluoride.

Instrumentation Required:

Electrometer (pH meter) with an expanded mv scale or a selective ion meter; fluoride ion activity electrode; and a single junction, sleeve-type reference electrode.

Interferences:

Extremes of pH interfere so the sample pH should be between 5 and 9. Polyvalent cations of silicon (Si^{+4}), iron (Fe^{+3}), and aluminum (Al^{+3}) interfere by forming complexes with fluoride. The degree of interference depends upon the concentration of the complexing cations, the concentration of fluoride and the pH of the sample. The addition of a pH 5.0 buffer containing a strong chelating agent preferentially complexes aluminum (the most common interference), silicon, and iron and eliminates the pH problem.

Quality Control Requirements:

A calibration standard curve as well as instrument calibration are required.

Comparison with Other Methods:

This is the only method summarized for fluoride because it is the most commonly used and it provides a sensitive and selective method.

Analytes Covered by this Method:

Method 340.2 covers the determination of fluoride which is an inorganic variable that is of interest to the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

When a synthetic sample containing 0.85 mg/L fluoride and no interferences was analyzed by 111 analysts, a mean of 0.84 mg/L with a standard deviation of ± 0.03 was obtained.

On the same study, a synthetic sample containing 0.75 mg/L fluoride, 2.5 mg/L polyphosphate and 300 mg/L alkalinity, was analyzed by the same 111 analysts and a mean of 0.75 mg/L fluoride* with a standard deviation of ± 0.036 was obtained.

Concentrations of fluoride from 0.1 up to 1000 mg/L may be measured using this method.

* A targeted compound of the National Contaminated Sites Remediation Program.

Title:

Direct Air-Acetylene Flame Method, Method 3111B, for the Determination of Metals.

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable to the determination of 27 elements in water and wastewater samples.

Sample Preparation:

The required sample preparation depends on the need to measure dissolved metals only or total metals. If dissolved metals are to be determined, the sample should be filtered at time of collection. If acid-extractable metals are to be determined, acidify the entire sample at collection with 5 mL conc. HNO_3/L to prepare sample, mix well, transfer 100 mL to a beaker or flask, and add 5 mL (1 + 1) high purity HCl. Heat for 15 minutes in a steam bath. Filter through a membrane filter, adjust filtrate volume to 100 mL with water and analyze. If total metals are to be determined, use the least rigorous digestion method required and make certain that the concentrations of acid and matrix modifiers are the same in both samples and standards. Nitric acid will digest most samples adequately. Some samples may require addition of perchloric, hydrochloric, or sulfuric acid for complete digestion. As a general rule, HNO_3 alone is adequate for clean samples or easily oxidized materials; HNO_3-H_2SO_4 or HNO_3-HCl digestion is adequate for readily oxidizable organic matter; HNO_3-$HClO_4$ or HNO_3-$HClO_4$-HF digestion is necessary for difficult to oxidize organic matter or minerals. Dry ashing is helpful if large amounts of organic matter are present. The HNO_3 digestion method is described below.

Mix sample and transfer 50 to 100 mL to a 125 mL conical flask or beaker. Add 5 mL concentrated HNO_3 and a few boiling chips. Bring to a slow boil and evaporate on a hot plate to about 10 to 20 mL before precipitation occurs. Continue heating and adding concentrated HNO_3 as necessary until digestion is complete. Do not let sample dry during digestion. Wash down with water and then filter if necessary. Transfer filtrate to a 100 mL volumetric flask with two 5 mL portions of water, adding these rinsings to the flask. Cool, dilute to mark, and mix thoroughly.

When determining Ca or Mg dilute and mix 100 mL sample with 10 mL lanthanum solution before atomization. When determining Fe or Mn, mix 100 mL with 25 mL of Ca solution before aspirating. When determining Cr, mix 1 mL 30% H_2O_2 with each 100 mL before aspirating. No special preparations are required when analyzing for the other metals covered by this method.

Instrumental Analysis:

The sample is introduced into an atomic absorption spectrometer by aspiration. Rinse nebulizer by aspirating water containing 1.5 mL concentrated HNO_3/L. Atomize blank and zero instrument. Atomize sample and determine absorbance.

Instrumentation Required:

Atomic absorption spectrophotometer, consisting of a light source limiting the line spectrum of an element, a device for vaporizing the sample (usually a flame), a monochromator or filter and adjustable slit, and a photoelectric detector. Also required is a suitable burner head typically with a premix which introduces the spray into a condensing chamber for removal of large droplets.

Interferences:

The most troublesome type of interference is termed chemical and results from lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is not hot enough to dissociate the molecules or when the dissociated atoms are oxidized immediately to a compound that will not dissociate further at the flame temperature. Such interferences may be reduced or eliminated by adding specific elements or compounds to the sample solution.

Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors. When such phenomenon occur, use background correction to obtain accurate values. Use any one of these types of background correction: continuous-source, Zeeman, or Smith-Hieftge correction.

Quality Control Requirements:

Select at least three concentrations of each standard metal solution to bracket the expected metal concentration of a sample. Aspirate blank and zero the instrument. Then aspirate each standard in turn into flame and record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbance of standards versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instruments it may be necessary to convert percent absorption to absorbance by using a table generally provided by the manufacturer. Plot calibration curves for Ca and Mg based on original concentration of standards before dilution with Ca solution. Plot calibration curve for Cr based on original concentration of standard before addition of hydrogen peroxide (H_2O_2).

Rinse nebulizer by aspirating water containing 1.5 mL concentrated HNO_3/L. Atomize blank and zero instrument. Atomize sample and determine its absorbance. Analyze a blank between sample or standard reading to verify baseline stability. Re-zero the instrument when necessary.

To one sample out of every ten (or one sample from each group of samples if less than ten are being analyzed), add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If little metal is present add an amount close to the middle of the linear range of the test. Recovery of added metal should be between 85 and 115%. Analyze an additional standard solution after every ten samples or with each batch of samples, whichever is less to confirm that the test is in control.

Comparison with Other Methods:

This method can be used to analyze for thallium and zinc whereas the electrothermal AA method (SM-3113B) cannot be used for these two elements. However, SM-3113B can be used for arsenic, barium, beryllium, molybdenum and selenium, but this method cannot. This method also is not usually as sensitive as either the electrothermal AA method (SM-3113B) or plasma emission methods (SM-3120B and EPA-6010A). This method also is not applicable for use with soils and sediments or water samples with high solids content.

Analytes Covered by this Method:

Method 3111B covers 27 elements including 11 of the inorganic variables that are of interest to the National Contaminated Sites Remediation Program as shown in Table 28.

Comments on Use of this Method:

The sensitivity of flame absorption spectrometry is defined as the metal concentration that produces an absorption of 1%. The instrument detection limit is defined as the concentration that produces absorption equivalent to twice the magnitude of the background fluctuation. Sensitivity and detection limits vary with the instrument, the element determined, the complexity of the matrix, and the technique selected. The optimum concentration range usually starts from the concentration of several times the sensitivity and extends to the concentration at which the calibration curve starts to flatten.

Table 28. Analytes Covered Using SM 3111B

Element	CAS No.	Optimum Conc. Range (mg/L)	Inst. Det. Limit (mg/L)	Concentration Used (mg/L)	Relative Standard Deviation (%)	Relative Error (%)
Antimony*	7440-36-0	1-40	0.07	Not listed	Not listed	Not listed
Bismuth	7440-69-9	1-50	0.06	Not listed	Not listed	Not listed
Cadmium*	7440-43-9	0.05-2	0.002	0.05 1.60	21.6 6.9	8.2 5.1
Calcium	7440-70-2	0.2-20	0.003	5.00	4.2	0.4
Cesium	7440-46-2	0.5-15	0.02	Not listed	Not listed	Not listed
Chromium (total)*	7440-47-3	0.2-10	0.02	3.00	10.0	3.7
Cobalt*	7440-48-4	0.5-10	0.03	4.00	6.1	0.5
Copper*	7440-50-8	0.2-10	0.01	1.00 4.00	11.2 8.3	3.4 2.8
Gold	7440-57-5	0.5-20	0.01	Not listed	Not listed	Not listed
Iridium	7439-88-5	Not listed	0.6	Not listed	Not listed	Not listed
Iron	7439-89-6	0.3-10	0.02	4.40 0.30	5.8 16.5	2.3 0.6
Lead*	7439-92-1	1-20	0.05	6.00	4.7	0.2
Lithium	7439-93-2	0.1-2	0.002	Not listed	Not listed	Not listed
Magnesium	7439-95-4	0.02-2	0.0005	0.20 1.10	10.5 10.5	6.3 10.0
Manganese	7439-96-5	0.1-10	0.01	4.05 0.05	7.8 13.5	1.3 6.0
Nickel*	7440-02-0	0.3-10	0.02	3.93	9.8	2.0
Palladium	7440-05-3	Not listed	Not listed	Not listed	Not listed	Not listed
Platinum	7440-06-4	5-75	0.1	Not listed	Not listed	Not listed
Potassium	7440-09-7	0.1-2	0.005	Not listed	Not listed	Not listed
Rhodium	7440-16-6	Not listed	0.5	Not listed	Not listed	Not listed
Ruthenium	7440-18-8	Not listed	0.07	Not listed	Not listed	Not listed
Silver*	7440-22-4	0.1-4	0.01	0.05 2.00	17.5 3.5	10.6 1.0
Sodium	7440-23-5	0.03-1	0.002	2.70	4.5	4.1
Strontium	7440-24-6	0.3-5	0.03	1.00	5.0	0.2
Thallium*	7440-28-0	Not listed	Not listed	Not listed	Not listed	Not listed
Tin*	7440-31-5	10-200	0.8	Not listed	Not listed	Not listed
Zinc*	7440-66-6	0.05-2	0.005	0.50	8.2	0.4

*Analytes targeted by the National Contaminated Sites Remediation Program.

Title:

Direct Nitrous Oxide-Acetylene Flame Method, Method 3111D, for the Determination of Metals.

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable to the determination of 10 elements in water and wastewater samples.

Sample Preparation:

The required sample preparation depends on the need to measure dissolved metals only or total metals. If dissolved metals are to be determined, the sample should be filtered at time of collection. If acid-extractable metals are to be determined, acidify the entire sample at collection with 5 mL HNO_3/L to prepare sample, mix well, transfer 100 mL to a beaker or flask, and add 5 mL 1 + 1 high purity HCl. Heat for 15 minutes in a steam bath. Filter through a membrane filter, adjust filtrate volume to 100 mL with water and analyze. If total metals are to be determined, use the least rigorous digestion method required and make certain that the concentrations of acid and matrix modifiers are the same in both samples and standards. Nitric acid will digest most samples adequately. Some samples may require addition of perchloric, hydrochloric, or sulfuric acid for complete digestion. As a general rule, HNO_3 alone is adequate for clean samples or easily oxidized materials; HNO_3-H_2SO_4 or HNO_3-HCl digestion is adequate for readily oxidizable organic matter; HNO_3-$HClO_4$ or HNO_3-$HClO_4$-HF digestion is necessary for difficult to oxidize organic matter or minerals. Dry ashing is helpful if large amounts of organic matter are present. The HNO_3 digestion method is described below.

Mix sample and transfer 50 to 100 mL to a 125 mL conical flask or beaker. Add 5 mL concentrated HNO_3 and a few boiling chips. Bring to a slow boil and evaporate on a hot plate to about 10 to 20 mL before precipitation occurs. Continue heating and adding concentrated HNO_3 as necessary until digestion is complete. Do not let sample dry during digestion. Wash down with water and then filter if necessary. Transfer filtrate to a 100 mL volumetric flask with two 5 mL portions of water, adding these rinsings to the flask. Cool, dilute to mark, and mix thoroughly.

When determining Ca or Mg dilute and mix 100 mL sample with 10 mL lanthanum solution before atomization. When determining Fe or Mn, mix 100 mL with 25 mL of Ca solution before aspirating. When determining Cr, mix 1 mL 30% H_2O_2 with each 100 mL before aspirating. No special preparations are required when analyzing for the other metals covered by this method.

Instrumental Analysis:

The sample is introduced into an atomic absorption spectrometer by aspiration. Rinse atomizer by aspirating water containing 1.5 mL concentrated HNO_3/L and zero instrument. Atomize sample and determine its absorbance. When determining Al, Ba, and titanium, add 2 mL KCl solution to 100 mL sample before atomization. For Mo and V, add 2 mL $Al(NO_3)_3.9H_2O$ solution to 100 mL sample before atomization.

Instrumentation Required:

Atomic absorption spectrophotometer, consisting of a light source emitting the line spectrum of an element, a device for vaporizing the sample (usually a flame), a monochromator or filter and adjustment slit, and a photoelectric detector. Also required is a special burner head for use with nitrous oxide and a T-junction valve or some other switching valve for rapidly changing from nitrous oxide to air, so that flame can be turned on or off to prevent flashbacks when air is the oxidant.

Interferences:

The most troublesome type of interference is chemical in nature and results from lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is not hot enough to dissociate the molecules or when the dissociated atoms are oxidized immediately to a compound that will not dissociate further at the flame temperature. Such interferences may be reduced or eliminated by adding specific elements or compounds to the sample solution.

Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors. When such phenomena occur, use background correction to obtain accurate values. Use any one of these types of background correction: continuous-source, Zeeman, or Smith-Hieftge correction.

Quality Control Requirements:

Select at least three concentrations of standard metal solutions to bracket the expected metal concentration of a sample. Aspirate each in turn into the flame. Record absorbances. For Al, Ba, and Ti, add 2 mL KCl solution to 100 mL standard before aspiration. For Mo and V, add 2 mL $Al(NO_3)_3$ solution to 100 mL standard before aspiration.

Most modern instruments are equipped with microprocessors and digital readout which permit calibration in direct concentration terms. If an instrument is not so equipped, prepare a calibration curve by plotting on linear graph paper the absorbance of standards versus concentration. Plot calibration curves for Al, Ba, and Ti based on original concentration of standard before adding KCl solution. Plot calibration curves for Mo and V based on original concentration of standard before adding $Al(NO_3)_3$ solution.

Analysis of samples: Rinse atomizer by aspirating water containing 1.5 mL concentration HNO_3/L and zero instrument. Atomize a sample and determine its absorbance. When determining Al, Ba and Ti, add 2 mL KCl solution to 100 mL sample before atomization. For Mo and V, add 2 mL $Al(NO_3)_3$ solution to 100 mL sample before atomization. Atomize a blank between sample or standard readings to verify baseline stability. Re-zero the instrument when necessary.

To one sample out of every ten (or one sample from each group of samples if less than ten are being analyzed) add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If little metal is present add an amount close to the middle of the linear range of the test. Recovery of the added metal should be between 85 and 115%.

Analyze an additional standard solution after every ten samples or with each batch of samples, whichever is less, to confirm that the test is in control.

Comparison with Other Methods:

This method is not as sensitive for barium, beryllium, and molybdenum as either the electrothermal AA method (SM-3113B) or the plasma emission methods (SM-3120B or EPA-6010A). However, it is the only AA technique available for vanadium although both plasma emission methods are applicable for vanadium analyses.

Analytes Covered by this Method:

Method 3111D covers 10 elements including four of the inorganic variables that are of interest to the National Contaminated Sites Remediation Program as shown in Table 29.

Comments on Use of this Method:

The sensitivity of flame absorption spectrometry is defined as the metal concentration that produces an absorption of 1%. The Instrument Detection Limit is the lowest concentration of analyte that an analytical instrument can detect and which is statistically different from the response obtained from the background instrumental noise. Sensitivity and detection limits vary with the instrument, the element determined, the complexity of the matrix, and the technique selected. The optimum concentration range usually starts from the concentration of several times the sensitivity and extends to the concentration at which the calibration curve starts to flatten.

Table 29. Analytes Covered Using SM 3111D

Element	CAS No.	Optimum Conc. Range (mg/L)	Inst. Det. Limit (mg/L)	Concentration Used (mg/L)	Relative Std. Dev. (%)	Relative Error (%)
Aluminum	7429-90-5	5-100	0.1	4.50	4.2	8.4
Barium*	7440-39-3	1-20	0.03	1.00	8.9	2.7
Beryllium*	7440-41-7	0.05-2	0.005	0.46	4.6	23.0
Molybdenum*	7439-98-7	1-20	0.1	9.5	11.6	1.3
Osmium	7440-04-2	Not listed	0.08	Not listed	Not listed	Not listed
Rhenium	7440-15-5	Not listed	0.5	Not listed	Not listed	Not listed
Silicon	7440-21-3	5-150	0.3	Not listed	Not listed	Not listed
Thorium	7440-29-1	Not listed	Not listed	Not listed	Not listed	Not listed
Titanium	7440-32-6	5-100	0.3	Not listed	Not listed	Not listed
Vanadium*	7440-62-2	2-100	0.2	Not listed	Not listed	Not listed

*Analytes targeted by the National Contaminated Sites Remediation Program.

Title:

Cold-Vapor Atomic Absorption Spectrometric Method, Method 3112B, for the Determination of Mercury.

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th. ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable to the determination of mercury in water and wastewater samples.

Sample Preparation:

Transfer 100 mL sample or portion diluted to 100 mL containing not more than 50 µg Hg/L to a 250 mL reaction flask. Add 5 mL concentrated H_2SO_4 and 2.5 mL concentrated HNO_3 to each flask. Add 15 mL $KMnO_4$ solution to each flask and let stand at least 15 minutes. Add 8 mL $K_2S_2O_8$ solution to each flask and heat for two hours in a water bath at 95°C. Cool to room temperature.

Add enough NaCl-hydroxylamine sulfate solution to reduce excess $KMnO_4$, then add 5 mL $SnCl_2$ solution and immediately attach flask to aeration apparatus. As Hg is volatilized and carried into the absorption cell, absorbance will increase to a maximum with a few seconds. As soon as recorder returns approximately to baseline, remove stopper holding the frit from reaction flask, and replace with a flask containing water. Flush system for a few seconds.

Instrumental Analysis:

The sample is introduced into an atomic absorption spectrophotometer following reaction and volatilization with a compressed air sweep into the absorption cell.

Instrumentation Required:

Atomic absorption spectrophotometer, consisting of a light source emitting the line spectrum of mercury and the associated accessories specifically designed for measurement of mercury by the cold vapor technique.

Interferences:

Samples containing high levels of chlorides or free chlorine present a major interference to this method. During the oxidation step, chlorides are converted to free chlorine, which absorbs at 253 nm. Remove all free chlorine before the Hg is reduced and swept into the cell by using an excess (25 mL) of hydroxylamine sulfate reagent. Remove free chlorine by sparging sample gently with air or nitrogen after adding hydroxylamine reducing solution. Use a separate tube and frit to avoid carryover of residual stannous chloride, which could cause reduction and loss of mercury.

Quality Control Requirements:

Transfer 100 mL of each of 1.0, 2.0, and 5.0 µg/L Hg standard solutions and a blank of 100 mL water to reaction flasks. Treat each flask according to the procedures outlined for samples and determine the absorbance of each and construct a standard curve by plotting peak height versus micrograms Hg.

Analyze a blank between sample or standard reading to verify baseline stability. Re-zero when necessary. To one sample out of every ten (or one sample from each group of samples if less than ten are being analyzed) add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If little metal is present add an amount close to the middle of the linear range of the test. Recovery of added metal should be between 100 $\pm$ 15%. Analyze an additional standard solution after every ten samples or with each batch of samples, whichever is less, to confirm that the test is in control.

Comparison with Other Methods:

This method is very sensitive and selective for mercury. The cold vapor technique is the only one recommended for mercury analyses.

Analytes Covered by this Method:

Method 3112B covers the determination of mercury which is an inorganic variable that is of interest to the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

The cold vapor atomic absorption spectrometric method can be used on samples containing not more than 5.0 µg Hg/L. Samples containing more than 50 µg Hg/L should be diluted before the sample in prepared for analysis.

Table 30. Analytes Covered Using SM 3112B

Element	CAS No.	Form	Concentration Used (µg/L)	Relative Standard Dev. (%)	Relative Error (%)
Mercury*	7439-97-6	Inorganic	0.34	22.6	21.0
		Inorganic	4.2	13.3	14.4
		Organic	4.2	8.6	8.4

*Analyte targeted by the National Contaminated Sites Remediation Program.

Title:

Electrothermal Atomic Absorption Spectrometric Method, Method 3113B, for the Determination of Metals.

Reference:

Standard Methods for the Examination of Water and Wastewater. 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is suitable for determination of micro quantities of aluminum, antimony, arsenic, barium, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, selenium, silver, and tin in water and wastewater samples.

Sample Preparation:

Before analysis, pretreat all samples as indicated below. Rinse all glassware with (1 + 1) HNO_3 and water. Carry out digestion procedures in a clean, dust-free laboratory area to avoid sample contamination. For digestion of trace aluminum, use polypropylene or TFE utensils to avoid leachable aluminum from glassware.

When Total recoverable metals are Al, Sb, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni Ag, and Sn, nitric acid will digest most samples adequately. Nitrate is an acceptable matrix for both flame and electrothermal atomic absorption. Some samples may require addition of perchloric, hydrochloric, or sulfuric acid for complete digestion. These acids may interfere in the analysis of some metals and all provide a poorer matrix for electrothermal analysis. Confirm metal recovery for each digestion and analytical procedure used. Quantitatively transfer digested sample to a 100-mL volumetric flask, add an appropriate amount of matrix modifier (if necessary, see Table 31), and dilute to volume with reagent water.

When total recoverable metals are As, Se, transfer 100 mL of a shaken sample, 1 mL of concentrated HNO_3, and 2 mL of 30% H_2O_2 to a clean, acid-washed 250 mL beaker. Heat on a hot-plate without allowing solvent to boil until volume has been reduced to about 50 mL. Remove from hot plate and let cool to room temperature. Add an appropriate concentration of nickel (see Table 31), and dilute to volume in a 100 mL volumetric flask with water.

Instrumental Analysis:

A discrete sample volume is dispensed into the graphite sample tube (or cup). Typically, determinations are made by heating the sample in three or more stages. First, a low current heats the tube to dry the sample. The second, or charring stage, destroys organic matter and volatilizes other matrix components at an intermediate temperature.

Finally, a high current heats the tube to incandescence and, in an inert atmosphere, atomizes the element being determined. Additional stages frequently are added to aid in drying and charring, and to clean and cool the tube between samples. The resultant ground-state atomic vapor absorbs monochromatic radiation from the source. A photoelectric detector measures the intensity of transmitted radiation, which is inversely proportional to the quantity of ground-state atoms in the optical path over a limited range.

Instrumentation:

Atomic absorption spectrophotometer, consisting of a light source emitting the line spectrum of an element (hollow-cathode lamp or electrodeless discharge lamp), a graphite furnace, a means of isolating an absorption line (monochromator or filter and adjustable slit), and a photoelectric detector with its associated electronic amplifying and measuring equipment. The instrument must have background correction capability. Use an electrically heated device with electronic control circuitry designed to carry a graphite tube or cup through a heating program that provides sufficient thermal energy to atomize the elements of interest. Fit the furnace into the sample compartment of the spectrometer in place of the conventional burner assembly. Use argon as a purge gas to minimize oxidation of the furnace tube and to prevent the formation of metallic oxides. Use graphite tubes with L'vov platforms to minimize interferences and to improve sensitivity.

Interferences:

Electrothermal atomization determinations are subject to significant interferences from molecular absorption as well as chemical and matrix effects. Use standard additions to compensate for matrix interferences. When making standard additions, determine whether the added species and the element being determined behave similarly under the specified conditions. Chemical interaction of the graphite tube with various elements to form refractory carbides occurs at high charring and atomization temperatures. Elements that form carbides are barium, molybdenum, nickel, titanium, vanadium, and silicon. Carbide formation is characterized by broad, tailing atomization peaks and reduced sensitivity. Using pyrolytically coated tubes for these metals minimizes the problem. For the analysis of aluminum, thorium treated L'vov platforms provide sharper peaks at low concentrations and enhance charring stability.

Quality Control Requirements:

Prepare standards for instrument calibration by dilution of the metal stock solutions. Prepare fresh standards daily. Prepare a blank and at least three calibration standards in the appropriate concentration range for correlating element concentration and instrument response. Match the matrix of the standard solutions to those of the samples as closely as possible. In addition, add the same concentration of matrix modifier (if required for sample analysis) to the standard solutions. Inject a suitable portion of each standard solution, in order of increasing concentration. Analyze each standard solution in triplicate to verify method precision. Analyze all samples except those demonstrated to be free of matrix interferences (based on recoveries of $100 \pm 15\%$ for known additions) using the method of standard additions. Analyze all samples at least in duplicate or until reproducible results are obtained. A variation of $\leq 10\%$ is considered acceptable reproducibility. Average the replicate values.

Comparison with Other Methods:

This method is more sensitive than the direct air-acetylene flame method (SM-3111B) and of comparable sensitivity with most elements to ICP (SM-3120B). However it is limited to surface water, groundwater, and wastewater whereas the EPA plasma emission method (EPA-6010A) is applicable to these matrices plus those of soils and sediments.

Analytes Covered by this Method:

This method covers 17 elements including 14 of the inorganic variables that are of interest to the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

Electrothermal atomic absorption permits determination of most metallic elements with sensitivities and detection limits from 20 to 1000 times better than those of conventional flame techniques without extraction or sample concentration. However, values may vary with the chemical form of the element being determined, sample composition, or instrumental conditions. Use of argon, rather than nitrogen, as the purge gas generally improves sensitivity and reproducibility. Hydrogen mixed with the inert gas may suppress chemical interference and increase sensitivity by acting as a reducing agent, thereby aiding in producing more ground-state atoms. Using pyrolytically coated graphite tubes can increase sensitivity for the more refractory elements. The optical pyrometer/maximum power accessory available on some instruments also offers increased sensitivity with lower atomization temperatures for many elements.

Table 31. Potential Matrix Modifiers for Electrothermal Atomic Absorption Spectrometry

Element	Matrix Modifers for Interference Removal	Matrix Modifiers as Enhancers
Al	$Mg(NO_3)_2$	$Ca(NO_3)$, $Ca_3(PO_4)_2$, H_2SO_4
Sb	$Ni(NO_3)_2$ & $Mg(NO_3)_2$	
As	$Mg(NO_3)_2$, $Ni(NO_3)_2$	
Be	$Al(NO_3)_2$, $Mg(NO_3)_2$	$Ca(NO_3)$
Cd	$NH_4H_2PO_4$ & $Mg(NO_3)_2$, $(NH_4)_2HPO_4$ & $Mg(NO_3)_2$, $(NH_4)_2SO_4$, & HNO_3,$(NH_4)S_2O_8$	
Cr	$Mg(NO_3)_2$	
Co	$Mg(NO_3)_2$, $NH_4H_2PO_4$, ascorbic acid	
Cu	NH_4NO_3, ascorbic acid	$MgSO_4$, $LaNO_3$
Fe	NH_4NO_3	
Pb	$NH_4H_2PO_4$,$(NH_4)HPO_4$,$Mg(NO_3)_2$, NH_4NO_3, ascorbic acid, oxalic acid, phosphoric acid, HNO_3, LaCl, $(NH_4)_2$EDTA	
Mn	Ascorbic acid, $Mg(NO_3)_2$, NH_4NO_3,	
Mo		HNO_3
Ni	$Mg(NO_3)_2$, $NH_4H_2PO_4$	
Se	$Ni(NO_3)_2$, $Ni(NO_3)_2$ & $Mg(NO_3)_2$, $Ni(NO_3)_2$ & $Cu(NO_2)$, $AgNO_3$, $(NH_4)_6Mo_7O_{24}$, $Fe(NO_3)_3$ $Fe(NO_3)_3$ & $Cu(NO_3)_2$	
Ag	$(NH_4)_2HPO_4$, $NH_4H_2PO_4$	
Sn	$(NH_4)_2HPO_4$ & $Mg(NO_3)_2$, $Ni(NO_3)_2$, ascorbic acid, NH_4NO_3	$Ca(NO_3)_2$

Table 32. Analytes Covered Using SM 3113B

Element	CAS No.	Est. Det. Limit (µg/L)	Optimum Conc. Range (µg/L)	Concentration Used (µg/L)	Overall Precision (% RSD)	Relative Error (%)
Aluminum	7429-90-5	3	20-200	28.0 125.0	124 49	54 39
Antimony*	7444-36-0	3	20-300	10.5 230.0	Not listed Not listed	28 19
Arsenic*	7440-38-2	1	5-100	9.78 227.0	37 13	22 10
Barium*	7440-39-3	2	10-200	56.5 418.0	43 28	44 0
Beryllium*	7440-41-7	0.2	1-30	0.45 10.9	15 26	11 9
Cadmium*	7440-43-9	0.1	0.5-10	0.43 12.0	5 41	37 5
Chromium (total)*	7440-47-3	2	5-100	9.87 236.0	24 24	4 9
Cobalt*	7440-48-4	1	5-100	29.7 420.0	17 17	1 8
Copper*	7440-50-8	1	5-100	10.1 234.0	31 19	2 0
Iron	7439-89-6	1	5-100	26.1 455.0	306 53	379 31
Lead*	7439-92-1	1	5-100	10.4 243.0	31 17	17 8
Manganese	7439-96-5	0.2	1-30	Not listed	Not listed	Not listed
Molybdenum*	7439-98-7	1	3-60	Not listed	Not listed	Not listed
Nickel*	7440-02-0	1	5-100	26.2 461.0	49 15	10 18
Selenium*	7782-49-2	2	5-100	10.0 235.0	32 18	6 0
Silver*	7440-22-4	0.2	1-25	0.45 13.6	368 59	534 5
Tin*	7440-31-5	5	20-300	Not listed	Not listed	Not listed

* Analytes targeted by the National Contaminated Sites Remediation Program

Title:

Manual Hydride Generation/Atomic Absorption Spectrometric Method, Method 3114B, for the Determination of Arsenic and Selenium.

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable to the determination of arsenic and selenium in water and wastewater samples by conversion to their hydrides by sodium borohydride reagent and aspiration into an atomic absorption atomizer.

Sample Preparation:

Add 50 mL sample to a 200 ml Berzelius beaker. Add 1 mL 2.5N H_2SO_4 and 5 mL 5% $K_2S_2O_8$. Boil gently on a pre-heated hot plate for approximately 30 to 40 minutes or until a final volume of 10 mL is reached. Do not let the sample go to dryness. Alternatively heat in an autoclave at 121°C for one hour in capped containers. After manual digestion, dilute to 50 mL for subsequent arsenic measurements and to 30 mL for selenium measurements.

Instrumental Analysis:

For determination of arsenic, add 5 mL concentrated HCl to 50 mL of the digested sample in a 200 mL Berzelius beaker and mix. Add 5 mL NaI pre-reductant solution, mix, and wait at least 30 minutes. Attach one Berzelins beaker at a time to the rubber stopper containing the gas dispersion tube for the purging gas, the sodium borohydride reagent inlet, and the outlet to the atomizer. Add 0.5 mL sodium borohydride reagent after the purging gas is established and all air is expelled from the reaction cell. The determination is complete once the instrument absorbance has reached a maximum and has returned to the baseline.

For determination of selenium, add 15 mL concentrated HCl to 30 mL of the digested sample in a 200 mL Berzelins beaker and mix. Heat for a predetermined period to 90 to 100°C. Alternatively, autoclave at 121°C in capped containers for 60 minutes, or heat for a predetermined time in open test tubes using a 90 to 100 °C hot water bath or an aluminum block digester. Add 0.50 mL sodium borohydride reagent. The determination is complete once the instrument absorbance has reached a maximum and returned to the baseline.

Instrumentation Required:

Atomic absorption spectrophotometer equipped with gas flow meters for argon and hydrogen, As and Se electrodeless discharge lamps with power supply, background correction at measurement wavelengths and appropriate strip-chart recorder. Also required is an atomizer and a reaction cell for producing arsenic or selenium hydrides.

Interferences:

Interferences are minimized because the arsenic and selenium hydrides are removed from the solution containing most potential interfering substances. Slight response variations occur when acid matrices are varied. Control these variations by treating standards and samples in the same manner. Low concentrations of noble metals (about 100 µg/L), concentrations of copper, lead, and nickel at or greater than 1 mg/L, and concentrations between 0.1 and 1 mg/L of hydride-forming elements may suppress the response of the arsenic and selenium hydrides.

Interferences by transition metals depends strongly on HCl concentration. Interferences are less pronounced at 4 to 6N HCl than at lower concentrations. The presence of arsenic or selenium in each other's matrices can cause similar suppression. Reduced nitrogen oxides resulting from HNO_3 digestion and nitrite also can suppress instrumental response for both elements. Large concentrations of iodide interfere with the selenium determination by reducing selenium to its elemental form.

Quality Control Requirements:

Before processing any samples and between each sample or standard, the analyst should demonstrate, through the analysis of a reagent water blank, that interferences from the analytical system are under control. Prepare standards for instrument calibration by dilution of the metal stock solutions with water containing the same acid concentration used for sample preservation. Prepare standards fresh daily.

To one sample out of every ten samples add a known amount of the metal of interest and reanalyze to confirm recovery. The amount of metal added should be approximately equal to the amount found. If little metal is present add an amount close to the middle of the linear range of the test. Recovery of the added metal should be 100 $\pm$ 15%. Analyze an additional standard solution after every ten samples or with each batch of samples, which ever is less.

Comparison with Other Methods:

This method has greater sensitivity with the two applicable elements than the plasma emission methods (SM-3120B and EPA-6010A) and about the same sensitivity as thermoelectric AA analysis (SM-3113B). This method is not applicable to soils and sediments.

Analytes Covered by this Method:

This method covers two of the inorganic variables, arsenic and selenium, that are of interest to the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

This method is limited to only two elements but may be useful for some water matrices that have interferences which other methods cannot overcome.

Table 33. Analytes Covered Using SM 3114B

Element	CAS No.	Method Det. Limit (µg/L)	Optimum Conc. Range (µg/L)
Arsenic*	7740-38-2	2	2-20
Selenium*	7782-49-2	2	2-20

* Analytes targeted by the National Contaminated Sites Remediation Program.

Title:

Inductively Coupled Plasma (ICP) Method, Method 3120B, for the Determination of Metals.

Reference:

Standard Methods for the Examination of Water and Wastewater, 17th ed. 1989. American Public Health Association.

Method Applicability:

This method is applicable for the determination of metals in water and wastewater samples.

Sample Preparation:

Transfer a measured volume of well-mixed, acid preserved sample appropriate for the expected metals concentration to a flask or beaker. Add 3 mL concentrated HNO_3. Place the flask or beaker on a hot plate and continuously evaporate to less than 5 mL, making certain that the sample does not boil and that no area of the bottom of the container is allowed to go dry. Cool and add 5 mL concentrated HNO_3. Cover the container with a watch glass and return to the hot plate. Increase the temperature of the hot plate so that a gentle reflux action occurs. Continue heating, adding additional acid as necessary, until digestion is complete (generally indicated when the digestate is light in color or does not change in appearance with continued refluxing). Evaporate to less than 5 mL and cool. Add 10 mL 1 + 1 HCl and 15 mL water per 100 mL anticipated final volume. Heat for an additional 15 minutes to dissolve any precipitate or residue. Cool, wash down beaker walls and watch glass with water, and filter to remove insoluble material that could clog the nebulizer. Alternatively centrifuge or let settle overnight. Adjust to a predetermined volume based on the expected metals concentrations.

Instrumental Analysis:

An ICP source consists of a flowing stream of argon gas ionized by an applied radio frequency field typically oscillating at 27.1 MHz. This field is inductively coupled to the ionized gas by a water-cooled coil surrounding a quartz "torch" that supports and confines the plasma. A sample aerosol is generated in an appropriate nebulizer and spray chamber and is carried into the plasma through an injector tube located within the torch. The sample aerosol is injected directly into the ICP. subjecting the constituent atoms to temperatures of about 6000 to 8000°K. The high temperature of the plasma excites atomic emission efficiently. Ionization of a high percentage of atoms produces ionic emission spectra.

Instrumentation Required:

The ICP source consists of a radio frequency (RF) generator capable of generating at least 1.1 KW of power, torch, tesla coil, load coil, impedance matching network, nebulizer, spray chamber, and drain. High-quality flow regulators are required for both the nebulizer argon and the plasma support gas flow. A peristaltic pump is recommended to regulate sample flow to the nebulizer. The spectrophotometer may be of the simultaneous (polychromator) or sequential (monochromator) type with air path, inert gas purged, or vacuum optics. A spectral bandpass of 0.05 nm or less is required. The instrument should permit examination of the spectral background surrounding the emission lines used for metals determination. It is necessary to be able to measure and correct for spectral background at one or more positions on either side of the analytical lines.

Interferences:

Interferences may be categorized as spectral or nonspectral. Spectral interferences are light emission from spectral sources other than the element of interest that may contribute to apparent net signal intensity. Sources of spectral interference include direct spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light from the emission of elements at high concentrations. Avoid line overlaps by selecting alternate analytical wavelengths. Avoid or minimize other spectral interference by judicious choice of background correction positions.

Nonspectral interferences include the following types. Physical interferences are effects associated with sample nebulization and transport processes. Changes in the physical properties of samples, such as viscosity and surface tension, can cause significant error. This usually occurs when samples containing more than 10% (by volume) acid or more than 1500 mg dissolved solids/L are analyzed using calibration standards containing $\leq$ 5% acid. If physical interference is present, compensate for it by sample dilution, by using matrix-matched calibration standards, or by applying the method of standard addition.

High dissolved solids content also can contribute to instrumental drift by causing salt buildup at the tip of the nebulizer gas orifice. Using pre-humidified argon for sample nebulization lessens this problem. Better control of the argon flow rate to the nebulizer using a mass flow controller improves instrument performance.

Chemical interferences are caused by molecular compound formation, ionization effects, and thermochemical effects associated with sample vaporization and atomization in the plasma. Normally these effects are not pronounced and can be minimized by careful selection of operational conditions. Chemical interferences are highly dependent on sample matrix and element of interest. As with physical interferences, compensate for them by using matrix matched standards or by standard addition.

Quality Control Requirements:

Calibrate instrument according to manufacturer's recommended procedures using calibration standards and blank. Aspirate each standard or blank for a minimum of 15 seconds after reaching the plasma before beginning signal integration. Rinse with calibration blank or similar solution for at least 60 seconds between each standard to eliminate any carryover from the previous standard.

Before analyzing samples, analyze instrument check standard. Concentration values obtained should not deviate from the actual values by more than ±5%. Begin each sample run with an analysis of the calibration blank, then analyze the method blank. This permits a check of the sample preparation reagents and procedures for contamination. Analyze samples, alternating them with analyses of calibration blank. Rinse for at least 60 seconds with dilute acid between samples and blanks. After introducing each sample or blank let system equilibrate before starting signal integration. Examine each analysis of the calibration blank to verify that no carry-over memory effect has occurred. If carry-over is observed, repeat rinsing until proper blank values are obtained. Analyze instrument check standard once per 10 samples to determine if significant instrument drift has occurred.

Comparison with Other Methods:

This method is similar in scope and sensitivity to the EPA plasma emission method (EPA-6010A) but is limited to low solid matrices of surface water, groundwater, and wastewater, whereas EPA-6010A is also applicable to soils and sediments. This method is more sensitive than atomic absorption methods with direct-aspiration for most elements and has the additional advantage of providing analytical data for many of them simultaneously. Both direct aspiration (SM-3111B) and electrothermal (SM-3113B) atomic absorption spectrometric methods provide analytical data for only one element at a time.

Analytes Covered by this Method:

Method 3120 covers 27 elements including 17 of the inorganic variables that are of interest to the National Contaminated Sites Remediation Program as shown in Table 34.

Comments on the Use of this Method:

Emission spectroscopy using inductively coupled plasma (ICP) is a rapid, sensitive, and convenient method for the determination of metals in water and wastewater samples. Dissolved metals are determined in filtered and acidified samples. Total metals are determined after appropriate digestion. Care must be taken to ensure that potential interferences are dealt with, especially when dissolved solids exceed 1500 mg/L. This, coupled with the extended dynamic range (four to six orders of magnitude for many elements), permits effective multi-element determination of metals.

Table 34. Analytes Covered Using SM 3120B

Element	CAS No.	Est. Inst. Det. Limit (µg/L)	Conc. Range (µg/L)	Accuracy (µg/L)	Precision (µg/L)
Aluminum	7429-90-5	40	69-4792	0.9273C+3.6	0.0559$\bar{x}$+18.6
Antimony*	7440-36-0	30	77-1406	0.7940C-17.0	0.1556$\bar{x}$-0.6
Arsenic*	7440-38-2	50	69-1887	1.0437C-12.2	0.1239$\bar{x}$+2.4
Barium*	7440-39-3	2	9-377	0.7683C+0.47	0.1819$\bar{x}$+2.78
Beryllium*	7440-41-7	0.3	3-1906	0.9629C+0.05	0.0136$\bar{x}$+0.95
Boron*	7440-42-8	5	19-5189	0.8807C+9.0	0.1150$\bar{x}$+14.1
Cadmium*	7440-43-9	4	9-1943	0.9874C-0.18	0.0557$\bar{x}$+2.02
Calcium	7440-70-2	10	17-47,170	0.9182C-2.6	0.1228$\bar{x}$+10.1
Chromium (total)*	7440-47-3	7	13-1406	0.9544C+3.1	0.0499$\bar{x}$+4.4
Cobalt*	7440-48-4	7	17-2340	0.9209C-4.5	0.0436$\bar{x}$+3.8
Copper*	7440-50-8	6	8-1887	0.9297C-0.30	0.0442$\bar{x}$+2.85
Iron	7439-89-6	7	13-9359	0.8829C+7.0	0.0683$\bar{x}$+11.5
Lead*	7439-92-1	40	42-4717	0.9699C-2.2	0.0558$\bar{x}$+7.0
Lithium	7439-93-2	4**	Not listed	Not listed	Not listed
Magnesium	7439-95-4	30	34-13,868	0.9881C-1.1	0.0607$\bar{x}$+11.6
Manganese	7439-96-5	2	4-1887	0.9417C+0.13	0.0324$\bar{x}$+0.88
Molybdenum*	7439-98-7	8	17-1830	0.9682C+0.1	0.0618$\bar{x}$+1.6
Nickel*	7440-02-0	15	17-47,170	0.9508C+0.4	0.0604$\bar{x}$+4.4
Potassium	7440-09-7	100**	347-14,151	0.8669C-36.4	0.0934$\bar{x}$+77.8
Selenium*	7782-49-2	75	69-1415	0.9363C-2.5	0.0855$\bar{x}$+17.8
Silicon	7440-21-3	20	189-9434	0.5742C-35.6	0.4160$\bar{x}$+37.8
Silver*	7440-22-4	7	8-189	0.4466C+5.07	0.5055$\bar{x}$-3.05
Sodium	7440-23-5	30**	35-47,170	0.9581C+39.6	0.2097$\bar{x}$+33.0
Strontium	7440-24-6	0.5	Not listed	Not listed	Not listed
Thallium*	7440-28-0	40	79-1434	0.9020C-7.3	0.1004$\bar{x}$+18.3
Vanadium*	7440-62-2	8	13-4698	0.9615C-2.0	0.0618$\bar{x}$+1.7
Zinc*	7440-66-6	2	7-7076	0.9356C-0.30	0.0914$\bar{x}$+3.75

* Analytes targeted by the National Contaminated Sites Remediation Program.
** Sensitive to operating conditions.

Title:

Inductively Coupled Plasma-Atomic Emission Spectroscopy. U.S. EPA Method 6010, Revision 0, September 1986.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 6010, Revision 0, September 1986. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is applicable to the determination of trace elements, including metals, in groundwater, soils, sludges, sediments, and other solid wastes. All matrices require digestion prior to analysis. The method of standard addition (MSA) must be used for the analysis of all sample digests unless either serial dilution or matrix spike addition demonstrates it is not required.

Sample Preparation:

Preliminary treatment of most matrices is necessary because of the complexity and variability of sample matrices. Water samples which have been prefiltered and acidified will not need acid digestion. Methods for acid digestion of waters for total recoverable or dissolved metals, acid digestions of aqueous samples and extracts for total metals, and acid digestion of sediments, sludges, and soils are summarized below.

Total Recoverable or Dissolved Metals in Water

To prepare surface and groundwater samples for determination of total recoverable and dissolved metals, transfer a 100-mL aliquot of well-mixed sample to a beaker. Add 2 mL of concentrated nitric acid and 5 mL of concentrated hydrochloric acid. Cover the sample with a watch glass and heat on a steam bath, hot plate, or other heating source at 90 to 95°C until the volume has been reduced to 15-20 mL. Remove the beaker from the hot plate and allow the solution to cool. Wash down the beaker walls and, when necessary, filter or centrifuge the sample to remove silicates and other insoluble materials. Adjust the final volume to 100 mL with reagent water.

Total Metals in Aqueous Samples

To prepare aqueous samples, soil and sediment extracts, and wastes that contain suspended solids, transfer a 100-mL aliquot of a well-mixed sample to a 150 mL beaker and add 3 mL of concentrated nitric acid. Cover the beaker with a watch glass and place on a hot plate or equivalent heating source and evaporate the solution to about 5 mL, making certain that the sample does not boil and that no portion of the bottom of the beaker is allowed to go dry. Cool the beaker and add another 3 mL portion of concentrated nitric acid, then cover it with a watch glass and increase the temperature until a gentle reflux action occurs. Continue heating and adding additional acid until sample digestion is complete, which is usually indicated when the digestate is light in color or does not change in appearance.

Next, uncover the beaker and evaporate the solution to about 3 mL. Then cool the solution and add a small quantity of 1:1 hydrochloric acid (10 mL/100 mL of final solution). Cover the beaker and reflux for 15 minutes. Wash down the beaker walls and filters or centrifuge the sample to remove silicates and other insoluble material. Filter the sample and adjust the final volume to 100 mL with reagent water and the final acid concentration to 10%.

Sediments, Sludges, and Soils

To prepare sediments, sludges and soil samples, mix the sample thoroughly and transfer 1 - 2 g to a conical beaker. Add 10 mL of 1:1 nitric acid, mix the slurry, and cover it with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 minutes without boiling. Allow it to cool, then add 5 mL of concentrated nitric acid, replace the watch glass, and reflux for 30 minutes. Repeat last step to ensure complete oxidation and then allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker.

Cool the sample and add 2 mL of water and 3 mL of 30% hydrogen peroxide. Cover the beaker with a watch glass and place on the hot plate for warming. Heat until effervescence subsides and then cool the beaker. Continue to add 30% hydrogen peroxide in 1 mL aliquots with warming until the effervescence is minimal but do not add more than a total of 10 mL of 30% hydrogen peroxide.

If the sample is being prepared for the analysis of Ag, Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Se, Tl, V, and Zn, then add 5 mL of concentrated hydrochloric acid and 10 mL of water and return the covered beaker to a hot plate for 15 minutes of additional refluxing without boiling. Dilute the sample to a 100 mL volume with water after cooling and filter or centrifuge to remove particulates.

Instrumental Analysis:

This method measures element-emitted light by optical spectrometry. Samples, following an appropriate acid digestion, are nebulized and the resulting aerosol is transported to the plasma torch. Element-specific atomic line emission spectra are produced by a radio-frequency inductively coupled plasma.

Instrumentation Required:

Inductively coupled argon plasma emission spectrometer capable of background correction.

Interferences:

Interferences may be categorized as spectral or non-spectral. Spectral interferences are caused by overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomenon, a stray light from the line emission of high concentration elements.

Spectral overlap can be compensated for by computer-correcting the raw data after monitoring and measuring the interfering element. Unresolved overlap requires selection of an alternative wavelength. Background contribution and stray light can usually be compensated for by a background correction adjacent to the analyte line.

Non-spectral interferences include physical and chemical interferences. Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity and surface tension can cause significant inaccuracies. Chemical interferences include molecular compound formation, ionization effects, and solute vaporization effects. Normally these effects are not significant and can be minimized by careful selection of operating conditions. Chemical interferences are highly dependent on matrix type and the specific analyte element.

Quality Control Requirements

Procedures should be in place for demonstrating that the laboratory is in control during each data collection activity. Laboratory control samples must be analyzed for each analytical method. A method blank should be analyzed with each batch of samples processed to assess contamination levels in the laboratory.

Procedures should be in place for documenting the effect of the matrix on method performance. When appropriate, there should be at least one matrix spike and either one matrix duplicate or one matrix spike duplicate per analytical batch. Procedures should be in place for determining the bias and precision of the method as well as the method detection limit, for the specific matrix type.

Dilute and reanalyze samples that are more concentrated than the linear calibration limit. Employ a minimum of one reagent blank per sample batch to determine if contamination or any memory effects are occurring. Whenever a new or unusual sample matrix is encountered, perform either a serial dilution test or a matrix spike addition test to ensure that neither positive or negative interferences are operating on any of the analyte elements. Check the instrument standardization by verifying calibration every 10 samples using a calibration blank and a check standard.

Comparison with Other Methods:

The capital equipment expense is more expensive than that required for atomic absorption spectrophotometry methods. However, multiple metals can be analyzed at once whereas atomic absorption spectrophotometry techniques only can analyze one metal at a time.

Analytes Covered by this Method:

Method 6010 covers 25 elements including 17 of the inorganic variables that are of interest to the National Contaminated Sites Remediation Program, as shown in Table 35.

Table 35. Analytes Covered Using U.S. EPA Method 6010, Rev. 0

Element	CAS No.	Est. Inst. Det. Limit (µg/L)	Spiked Concentration (µg/L)	Mean Reported Value	Precision (Rel. Std. Dec. %)
Aluminum	7429-90-5	45	60	62	33
Antimony*	7440-36-0	32	Not listed	Not listed	Not listed
Arsenic*	7440-38-2	53	22	19	23
Barium*	7440-39-3	2	Not listed	Not listed	Not listed
Beryllium*	7440-41-7	0.3	20	20	9.8
Boron*	7440-42-8	5	Not listed	Not listed	Not listed
Cadmium*	7440-43-9	4	2.5	2.9	16
Calcium	7440-70-2	10	Not listed	Not listed	Not listed
Chromium (total)*	7440-47-3	7	10	10	18
Cobalt*	7440-48-4	7	20	20	4.1
Copper*	7440-50-8	6	11	11	40
Iron	7439-89-6	7	20	19	15
Lead*	7439-92-1	42	24	30	32
Magnesium	7439-95-4	30	Not listed	Not listed	Not listed
Manganese	7439-96-5	2	15	15	6.7
Molybdenum*	7439-98-7	8	Not listed	Not listed	Not listed
Nickel*	7440-02-0	15	30	28	11
Phosphorus	7723-14-0	51	Not listed	Not listed	Not listed
Selenium*	7782-49-2	75	6	8.5	42
Silicon	7440-21-3	58	Not listed	Not listed	Not listed
Silver*	7440-22-4	7	Not listed	Not listed	Not listed
Sodium	7440-23-5	29	Not listed	Not listed	Not listed
Thallium*	7440-28-0	40	Not listed	Not listed	Not listed
Vanadium*	7440-62-2	8	70	69	2.9
Zinc*	7440-66-6	2	16	19	45

* Analytes targeted by the National Contaminated Sites Remediation Program

Comments on Use of this Method:

Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and model of the spectrometer. In a single laboratory evaluation, seven wastes were analyzed for 22 elements. The mean percent relative standard deviation from triplicate analyses for all elements and wastes was 9 ± 2%. The mean percent recovery of spiked elements for all wastes was 93 ± 6%. Spike levels ranged from 100 µg/L to 100 mg/L. The wastes included sludges and industrial wastewaters.

Title:

Chromium, Hexavalent (Colorimetric). U.S. EPA Method 7196, Revision 0, September 1986.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 6010, Revision 0, September 1986. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is used to determine the concentration of dissolved hexavalent chromium (Cr VI) in Extraction Procedure (EP) toxicity characteristic extracts and groundwaters. It may also be applicable to certain domestic and industrial wastes, provided that no interfering substances are present. Finally, this method may be used to analyze samples containing from 0.5 to 50 mg of Cr VI per liter.

Sample Preparation:

Transfer 95 mL of the sample to be tested to a 100 mL volumetric flask. Add 2 mL diphenylcarbazide solution and mix. Add H_2SO_4 solution to give a pH of 2 ± 0.5, dilute to 100 mL with Type II water, and let stand 5 to 10 minutes for full color development.

Instrumental Analysis:

Transfer an appropriate portion of the solution to a 1 cm absorption cell and measure its absorbance at 540 nm. Use Type II water as a reference.

Instrumentation Required:

Either a spectrophotometer for use at 540 nm, providing a light path of 1 cm or longer; or a filter photometer, providing a light path of 1 cm or longer and equipped with a greenish-yellow filter having maximum transmittance near 540 nm.

Interferences:

The chromium reaction with diphenylcarbazide is usually free from interferences. However, certain substances may interfere if the chromium concentration is relatively low. Hexavalent molybdenum and mercury salts also react to form color with the reagent; however, the red-violet intensities produced are much lower than those for chromium at the specified pH. Concentrations of up to 200 mg/L of molybdenum and mercury can be tolerated. Vanadium interferes strongly, but concentrations up to 10 times that of chromium will not cause trouble.

Quality Control Requirements:

Dilute samples if they are more concentrated than the highest standard or if they fall on the plateau of a calibration curve. Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring. Verify calibration with an independently prepared check standard every 15 samples. Run one spike duplicate for every 10 samples. The method of standard addition shall be used for the analysis of all EP extracts and whenever a new sample matrix is being analyzed.

Comparison with Other Methods:

No other methods were selected for comparison.

Analytes Covered by this Method:

Method 7196 covers the determination of hexavalent chromium which is an inorganic variable that is of interest to the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

Dissolved hexavalent chromium* in the absence of interfering amounts of substances such as molybdenum, vanadium, and mercury may be determined colorimetrically by reaction with diphenylcarbazide in acid solution. The reaction is very sensitive with the addition of an excess of diphenylcarbazide yielding a red-violet product with its absorbance measured photometrically at 540 nm.

*Analyte targeted by the National Contaminated Sites Remediation Program.

Title:

Mercury in Liquid Waste (Manual Cold Vapor Technique). U.S. EPA Method 7470A, Revision 1, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 7470A, Revision 1, November 1990. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is applicable to the determination of mercury in mobility-procedure extracts, aqueous wastes, and groundwater. It can also be used for analyzing certain solid and sludge-type wastes.

Sample Preparation:

Transfer 100 mL containing < 1.0 g of mercury to a 300 mL biological oxygen demand (BOD) bottle or equivalent. Add 5 mL of H_2SO_4 and 2.5 mL of concentrated HNO_3, mixing after each addition. Add 15 mL of potassium permanganate. Shake and add additional portions until the purple color persists for at least 15 minutes. Add 8 mL of potassium persulfate to each bottle and heat for 2 hours in a water bath at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. After at least 30 seconds, add 5 mL of stannous sulfate and immediately attach to the aeration apparatus.

Instrumental Analysis:

Allow the sample to stand without manual agitation while the circulating pump is allowed to run continuously. As mercury is volatilized, it is swept into the absorption cell and the absorbance will increase. As the recorder levels off, open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue aeration.

Instrumentation Required:

Atomic absorption spectrometer equipped with a mercury hollow cathode lamp or electrodeless discharge lamp. Also required is a cold vapor generator where the mercury vapor is passed through an absorption cell.

Interferences:

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/kg of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water. Copper has also been reported to interfere, but concentrations as high as 10 mg/kg had no effect in recovery studies.

Seawaters, brines, and industrial effluents high in chlorides require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine which also absorbs at 253.7 nm. Remove all free chlorine by using an excess (25 mL) of hydroxylamine sulfate reagent. Certain volatile organic materials that absorb at this wavelength may also cause interference.

Quality Control Requirements:

A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring a mid-range standard after every 10 samples. This value must be within 20% of the true value. At least one matrix spike and one matrix spike duplicate sample must be included in each analytical batch, as well as a laboratory control sample. For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis.

Comparison with Other Methods:

This method may be applicable for analyses of some sediment samples but it is primarily used for aqueous samples. It is quite similar to the Standard Method summary SM-3112B and has a larger range of QC data (Table 36) than the former method.

Analytes Covered by this Method:

Method 7470A covers the determination of mercury which is an inorganic variable that is of interest to the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

This method is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. The typical detection limit for this method is 0.0002 mg/L.

Table 36. Mercury QC Data Using Manual Cold Vapor Technique

Analyte Name	CAS No.	Spiked Conc. (µg/L)	Accuracy as % Bias	Standard Deviation (µg/L)
Mercury*	7439-97-6	0.21	66	0.276
		0.27	53	0.279
		0.51	32	0.541
		0.60	18	0.390
		3.4	0.34	1.49
		4.1	-7.1	1.12
		8.8	-0.4	3.69
		9.6	-5.2	3.57

* Analyte targeted by the National Contaminated Sites Remediation Program.

Title:

Mercury in Solid or Semisolid Waste (Manual Cold Vapor Technique). U.S. EPA Method 7471A, Revision 1, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 7471A, Revision 1, November 1990. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is applicable to the determination of total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix.

Sample Preparation:

Weigh triplicate 0.2 g portions of untreated sample and place in the bottom of a biological oxygen demand (BOD) bottle. Add 5 mL of reagent water and 5 mL of aqua regia. Heat for 2 minutes in a water bath at 95°C. Cool and add 50 mL reagent water and 15 mL potassium permanganate solution to each sample bottle. Mix thoroughly and place in the water bath for 30 minutes at 95°C. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate to reduce the excess permanganate. Add 55 mL of reagent water and 5 mL of stannous sulfate to each bottle. Immediately attach each bottle to the aeration apparatus.

Instrumental Analysis:

Allow the sample to stand without manual agitation while the circulating pump is allowed to run continuously. As mercury is volatilized, it is swept into the absorption cell and the absorbance will increase. As the recorder levels off, open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the stopper and frit from the BOD bottle, and continue aeration.

Instrumentation Required:

Atomic absorption spectrometer equipped with a mercury hollow cathode lamp or electrodeless discharge lamp. Also required is a cold vapor generator where the mercury vapor is passed through an absorption cell.

Interferences:

Potassium permanganate is added to eliminate possible interference from sulfide. Concentrations as high as 20 mg/kg of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water. Copper has also been reported to interfere, but concentrations as high as 10 mg/kg had no effect in recovery studies.

Seawaters, brines, and industrial effluents high in chlorides require additional permanganate because, during the oxidation step, chlorides are converted to free chlorine which also absorbs at 253.7 nm. Remove all free chlorine by using an excess (25 mL) of hydroxylamine sulfate reagent. Certain volatile organic materials that absorb at this wavelength may also cause interference.

Quality Control Requirements:

A calibration curve must be prepared each day with a minimum of a calibration blank and three standards. If more than 10 samples per day are analyzed, the working standard curve must be verified by measuring a mid-range standard after every 10 samples. This value must be within 20% of the true value. At least one matrix spike and one matrix spike duplicate sample must be included in each analytical batch, as well as a laboratory control sample. For each analytical batch select one typical sample for serial dilution to determine whether interferences are present. The concentration of the analyte should be at least 25 times the estimated detection limit. If all of the samples in the batch are below 10 times the detection limits, perform the spike recovery analysis.

Comparison with Other Methods:

This method is limited to mercury in soils and sediments. It is the only method summarized for analysis of this element in solid matrices.

Analytes Covered by this Method:

Method 7471A covers the determination of mercury which is an inorganic variable that is of interest to the National Contaminated Sites Remediation Program (see Table 37).

Table 37. Mercury QC Data Using EPA Method 7471A, Rev. 1

Analyte Name	CAS No.	Spiked Concentration (µg/g)	Recovery (% of True Value)	Standard Deviation (µg/g)
Mercury*	7439-97-6	0.30 0.87	97 94	0.02 0.03

* Analyte targeted by the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

This method is based on the absorption of radiation at 253.7 nm by mercury vapor. The mercury is reduced to the elemental state and aerated from solution in a closed system. The mercury vapor passes through a cell positioned in the light path of an atomic absorption spectrophotometer. The typical detection limit for this method is 0.0002 mg/L.

Title:

Sodium Adsorption Ratio (SAR).

Reference:

Canadian Water Quality Guidelines. 1987. Task Force on Water Quality Guidelines of the Canadian Council of Resource and Environmental Ministers. pp 4-6 to 4-7.

Method Applicability:

The Sodium Adsorption Ratio is a calculation rather than a method. Excess sodium in water relative to calcium and magnesium or relative to the total soluble salt content can adversely affect the soil structure and reduce the rate at which water moves into and through soil and can also reduce soil aeration.

Calculation of SAR:

The Sodium Adsorption Ratio* is calculated by:

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

where Na^{+} is the concentration of total sodium in milliequivalents per liter,

Ca^{++} is the concentration of total calcium in milliequivalents per liter, and

Mg^{++} is the concentration of total magnesium in milliequivalents per liter.

Sodium, calcium, and magnesium are not target analytes of the National Contaminated Sites Remediation Program but their analyses are required if the Sodium Adsorption Ratio is calculated. Standard Method 3113B or Standard Method 3120B are recommended for these analyses. Aqueous extractable solutions of these metal ions must be used for these analyses.

*The SAR is targeted by the National Contaminated Sites Remediation Program.

Title:

Tin (Atomic Absorption, Direct Aspiration). U.S. EPA Method 7870, Revision 0, September 1986.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 7870, Revision 0, September 1986. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is applicable to a large number of metals in drinking, surface, and saline waters, and domestic and industrial wastes, as well as groundwater, EP extracts, soils, sludges, sediments and other solid wastes which required digestion prior to analysis.

Sample Preparation:

Digestion of Soils, Sludges and Sediments:

Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh to the nearest 0.01 g and transfer to a conical beaker a 1.0 to 2.0 g portion of sample. Add 10 mL of a 1:1 water and HNO_3 solution, mix the slurry, and cover with a watch glass. Heat the sample to 95°C and reflux for 10 to 15 min without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, and reflux for 30 min. Repeat this last step to ensure complete oxidation.

Using a ribbed watch glass, allow the solution to evaporate to 5 mL without boiling, while maintaining a covering of solution over the bottom of the beaker. Allow the sample to cool. Add 2 mL of Type II water and 3 mL of 30% H_2O_2. Cover the beaker with a watch glass and return it to the hot plate for warming and to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides and cool the beaker. Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general appearance is unchanged. Do not add more than a total of 10 mL of 30% H_2O_2.

Add 5 mL of concentrated HCl and 10 mL of Type II water, return the covered beaker to the hot plate, and reflux for an additional 15 min without boiling. After cooling, dilute to 100 mL with Type II water. Particulates in the digestate should be removed by filtration, centrifugation or by allowing the sample to settle. Filter the solution through a Whatman #41 better paper and dilute to 100 mL with Type II water. Centrifuge at 2,000-3,000 rpm for 10 min to clear the supernatant. The diluted sample has an approximate acid concentration of 5% (v/v) HCl and 5% (v/v) HNO_3. Drinking water, free of particulates, may be analyzed directly.

Instrumental Analysis:

Allow the lamp to warm up for a minimum of 15 min, unless operated in a double-beam mode. During this period, align the instrument, position the monochromator at the correct wavelength, select the proper monochromator slit width, and adjust the current according to the manufacturer's recommendation. Subsequently, light the flame and regulate the flow of fuel and oxidant. Adjust the burner and nebulizer flow rate for maximum percent absorption and stability. Balance the photometer. Run a series of standards of the element under analysis. Construct a calibration curve by plotting the concentrations of the standards against absorbances. Set the curve corrector of a direct reading instrument to read out the proper concentration. Aspirate the samples and determine the concentrations either directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.

Instrumentation Required:

Atomic absorption spectrophotometer: single or dual-channel, single or double beam instrument having a grating monochromator, photomultiplier detector, adjustable slits, a wavelength range of 190-800 nm and provisions for interfacing with a strip-chart recorder. Also required is a tin hollow cathode lamp.

Interferences:

The most troublesome type of interference in atomic absorption spectrophotometry is usually termed "chemical" and is caused by lack of absorption of atoms bound in molecular combination in the flame. This phenomenon can occur when the flame is not sufficiently hot to dissociate the molecule or when the dissociated atom is immediately oxidized to a compound that will not dissociate further at the temperature of the flame.

The presence of high dissolved solids in the sample may result in an interference from nonatomic absorbance such as light scattering. If background correction is not available a nonabsorbing wavelength should be checked. Preferably, samples containing high solids should be extracted. Ionization interferences occur when the flame temperature is sufficiently high to generate the removal of an electron from a neutral atom, giving a positively charged ion. All metals are not equally stable in the digestate, and tin should be analyzed as soon as possible.

Spectral interference can occur when an absorbing wavelength of an element present in the sample but not being determined falls within the width of the absorption line of the element of interest. The results of the determination will then be erroneously high, due to the contribution of the interfering element to the atomic absorption signal. Interference can also occur when resonant energy from another element in a multi-element lamp, or from a metal impurity in the lamp cathode, falls within the bandpass of the slit setting when that other metal is present in the sample. This type of interference may sometimes be reduced by narrowing the slit width.

Quality Control Requirements:

A calibration curve must be prepared each day with a minimum of a reagent blank and three standards, verified by use of at least a reagent blank and one standard at or near the mid-range. Checks throughout the day must be within 20% of original curve.

If 20 or more samples per day are analyzed, the working standard curve must be verified by running an additional standard at or near the mid-range every 10 samples. Checks must be within ±20% of true value. At least one duplicate and one spike sample should be run every 20 samples, or with each matrix type to verify precision of the method.

Comparison with Other Methods:

This is the only method that is applicable to soils and sediments as well as surface waters. The standard methods summarized are only applicable for aqueous samples. The AA technique limits this method to the single element, tin.

Analytes Covered by this Method:

Method 7870 covers the determination of tin.*

Comments on Use of this Method:

Detection limits, sensitivity, and optimum ranges of the metals will vary with the matrices and models of atomic absorption spectrophotometers. A detection limit of 0.8 mg/L and a sensitivity of 4 mg/L have been obtained by direct aspiration. For clean aqueous samples, this detection limit may be extended downward with scale expansion and upward by using a less sensitive wavelength or by rotating the burner head. Detection limits by direct aspiration may also be extended through concentration of the sample and/or through solvent extraction techniques.

* A targeted analyte of the National Contaminated Sites Remediation Program.

Title:

Total and Amenable Cyanide (Colorimetric, Automated UV). U.S. EPA Method 9012, Revision 0, September 1986.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 9012, Revision 0, September 1986. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is used to determine the concentration of inorganic cyanide in an aqueous waste or leachate. It addresses total and amenable cyanides. Cyanide compounds that are amenable to chlorination include free cyanide as well as the complex cyanides.

Sample Preparation:

Pretreatment for Cyanides Amenable to Chlorination:

Two sample aliquots are required to determine cyanides amenable to chlorination. To one 500 mL aliquot, or to a volume diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with sodium hydroxide. This should be done in a fume hood.

Test for residual chlorine with potassium iodide-starch paper and maintain this excess for one hour, continuing agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional hypochlorite solution.

After 1 hour add 0.5 g portions of ascorbic acid until potassium iodide-starch paper shows no residual chlorine. Add an additional 0.5 g of ascorbic acid to ensure the presence of excess reducing agent.

Test for total cyanide in both the chlorinated and unchlorinated aliquots. The difference of total cyanide in the chlorinated and unchlorinated aliquots is the cyanide amenable to chlorination.

Distillation Procedure:

Place 500 mL of sample, or an aliquot diluted to 500 mL, in a 1 liter boiling flask and pipet 50 mL of sodium hydroxide into the absorbing tube. Add reagent water until the spiral is covered. Connect the boiling flask, condenser, absorber, and trap in the train. By adjusting the vacuum source, start a slow stream of air entering the boiling flask so that approximately two bubbles of air per second enter the flask through the air inlet tube.

Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper. If positive, treat the sample by adding 50 mL of bismuth nitrate solution through the air inlet tube after the air rate is set. Mix for 3 minutes prior to addition of sulfuric acid. If samples are suspected to contain nitrate and/or nitrite ions, add 50 mL of sulfamic acid solution after the air rate is set through the air inlet tube. Mix for 3 minutes prior to addition of sulfuric acid.

Slowly add 50 mL 1:1 water and sulfuric acid mixture through the air inlet tube. Rinse the tube with reagent water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride into the air inlet and wash down with a stream of water. Heat the solution to boiling. Reflux for 1 hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source. Drain the solution from the absorber into a 250 mL volumetric flask. Wash the absorber with reagent water and add the washings to the flask. Dilute to the mark with reagent water.

Instrumental Analysis:

Automated Colorimetric Determination:

Set up the manifold in a hood or a well-ventilated area. Allow the colorimeter and recorder to warm up for 30 minutes. Run a baseline with all reagents, feeding reagent water through the sample line. Place appropriate standards in the sampler in order of increasing concentration and complete loading of the sample tray with unknown samples. When the baseline is steady, begin the analysis.

In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction with Chloramine-T reagent at a pH less than 9 without hydrolyzing the cyanate. After the reaction is complete, color is formed upon the addition of pyridine-barbituric acid reagent. The concentration of NaOH must be the same in the standards, the scrubber solutions, and any dilution of the original scrubber solution to obtain color of comparable intensity.

Instrumentation Required:

The Reflux distillation apparatus consists of a 1 liter boiling flask with an inlet tube and provision for condenser. The gas absorber is a Fisher-Milligan scrubber. An automated continuous-flow analytical instrument includes a sampler, manifold with UV digestor, proportioning pump, heating bath with distillation coil, distillation head, colorimeter equipped with at 15 mm flow cell and 570 nm filter and a recorder.

Interferences:

Sulfides adversely affect the colorimetric procedures. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by addition of bismuth nitrate prior to distillation.

High results may be obtained for samples that contain nitrate and/or nitrite ions. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds will decompose under test conditions to generate hydrogen cyanide. The possible interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid.

Quality Control Requirements:

Employ a minimum of one blank per sample batch to determine if contamination or any memory effects are occurring. Verify calibration with an independently prepared check standard every 15 samples. Run one spike duplicate sample for every 10 samples. A duplicate sample is a sample brought through the whole sample preparation process. The method of standard additions should be used for the analysis of all samples that suffer from matrix interferences.

Comparison with Other Methods:

This method is essentually the same as EPA method 335.3 and either may be used with comparible results. The matrices listed for EPA-335.3 are drinking waters, surface waters, domestic and industrial wastes.

Analytes Covered by this Method:

Method 9012 covers the determination ot total cyanide and amenable cyanide which includes free cyanide. Both total cyanide and free cyanide are inorganic variables which are of interest to the National Contaminated Sites Remediation Program.

Comments on Use of this Method:

The method detects inorganic cyanides* that are present as either simple soluble salts or complex radicals. It is used to determine values for both total cyanide and cyanide amenable to chlorination (free cyanide). This method is not intended to determine if a waste is hazardous by the characteristic of reactivity.

No precision or accuracy data are available for this method.

* A targeted analyte of the National Contaminated Sites Remediation Program.

Title:

pH Electrometric Measurement. U.S. EPA Method 9040A, Revision 1, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 9040A, Revision 1, November 1990. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is applicable to the measurement of pH of aqueous wastes and those multi-phase wastes where the aqueous phase constitutes at least 20% of the total volume of the waste. The pH measurement requires some minimum water content.

Sample Preparation:

No specific sample preparation is required when determining the pH of an aqueous sample.

Instrumental Analysis:

Place the sample in a clean glass beaker using a sufficient volume to cover the sensing elements of the electrodes and to give adequate clearance for the magnetic stirring bar. Thoroughly rinse and gently wipe the electrodes prior to measuring pH of samples. Immerse the electrodes into the sample beaker or sample stream and gently stir at a constant rate to provide homogeneity and suspension of solids. Record the sample pH and temperature.

Instrumentation Required:

pH meter with glass electrode and a reference electrode.

Interferences:

The glass electrode is not generally subject to solution interferences from color, turbidity, collidal matter, oxidants, reductants, or high salinity. Sodium error at pH levels > 10 can be reduced or eliminated by using a low sodium error electrode. Coatings of oily material or particulate matter can impair electrode response.

Temperature effects on the electrometric determination of pH arise from two sources. The first is caused by the change in electrode output at various temperatures. This interference can be controlled with instruments having temperature compensation. The second source of temperature effects is the change of pH due to changes in the sample as the temperature changes. This is sample-dependent and cannot be controlled.

Quality Control Requirements:

No specific quality control procedures were listed for this method. Electrodes must be rinsed thoroughly between samples.

Comparison with Other Methods:

This method is more accurate than those based on colorimetric changes. Although instrumentation is more expensive than colormetric methods; it is of moderate cost and many samples can be processed accurately and inexpensively in a short period of time.

Analytes Covered by this Method:

Method 9040A covers the determination of pH*.

Comments on Use of this Method:

The pH of the sample is determined electrometrically using either a glass electrode in combination with a reference electrode or with a combination electrode. The measuring device is calibrated using a series of standard solutions of known pH. The corrosivity of concentrated acids and bases cannot be measured.

Table 38. Precision and Accuracy Versus pH

pH Units	Std. Dev. pH Units	Accuracy as Bias Percent	Accuracy as Bias pH Units
3.5	0.10	-0.29	-0.01
3.5	0.11	-0.00	
7.1	0.20	+1.01	0.07
7.2	0.18	-0.03	-0.002
8.0	0.13	-0.12	-0.01
8.0	0.12	+0.16	+0.01

* A general variable that is of interest to the National Contaminated Sites Remediation Program.

Title:

Specific Conductance. U.S. EPA Method 9050A, Rev. 1, November 1990.

Reference:

Test Methods for Evaluating Solid Waste (SW-846). U.S. EPA. 1983. Method 9050A, Revision 1, November 1990. Office of Solid Wastes, Washington, D.C.

Method Applicability:

This method is applicable to the measurement of the specific conductance of drinking waters, groundwaters, surface waters, saline waters, and domestic and industrial aqueous wastes. It is not applicable to solid samples or to organic samples.

Sample Preparation:

No specific sample preparation procedure is required when measuring the conductance of water samples.

Instrumental Analysis:

To determine the cell constant, rinse the conductivity cell with at least three portions of 0.01N potassium chloride solution. Adjust temperature of a fourth portion to 25.0 ± 0.1°C. Measure resistance of this portion and note temperature. Compute cell constant, C using the equation below.

$$C = (0.001\ 413)\ (R_{KCl})\ (1 + 0.0191)\ (t - 25)$$

where:

R_{KCl} = measured resistance in ohms; and
t = observed temperature in degrees C.

Rinse the cell with one or more portions of a sample. Adjust the temperature of a final portion to 25.0 ± 0.1°C, measure sample resistance or conductivity, and note the temperature. Report all conductivities at 25.0°C. When sample resistance is measured, conductivity at 25°C is calculated using the following equation:

$$K = \frac{(1\ 000\ 000)\ (C)}{R_m\ (1 + 0.0191)\ (t-25)}$$

where:

K = conductivity in µmho/cm;
C = cell constant in cm-L;
R_m = measured resistance of sample in ohms; and
t = temperature of measurement.

When sample conductivity is measured, conductivity at 25°C is:

$$K = \frac{K_m\ (1\ 000\ 000)(C)}{(1\ +\ 0.0191)\ (t\ -\ 25)}$$

where:

k_m = measured conductivity in µmho.

If the conductivity readout is in µmho/cm, then delete the factor 1,000,000 in the equation.

Instrumentation Required:

A self-contained conductivity instrument consisting of a source of alternating current, a Wheatstone bridge, null indicator, and a platinum electrode or non-platinum electrode specific conductance cell.

Interferences:

Platinum electrodes can degrade and cause erratic results. When this happens the electrode should be replatinized. The specific conductance cell can become coated with oil and other materials. It is essential that the cell be thoroughly rinsed between samples.

Quality Control Requirements:

An independently prepared check standard should be analyzed with each batch of samples to verify calibration. Analyze one duplicate sample for every 10 samples.

Comparison with Other Methods:

No other methods were compared with this method; it is a commonly used method for aqueous samples.

Analytes Covered by this Method:

Method 9050A covers the determination of specific conductance.*

Comments on Use of this Method:

The specific conductance of a sample is measured using a self-contained conductivity meter. When possible, samples are analyzed at 25°C. If samples are analyzed at different temperatures, temperature corrections must be made; many instruments provide automatic temperature-corrected readings.

*A general variable that is of interest to the National Contaminated Sites Remediation Program.

Table 39: Conductivity Versus Precision and Accuracy

Conductivity (µmho/cm)	No. of Results	Rel. Std. Dev. (%)	Relative Error (%)
147.0	117	8.6	9.4
303.0	120	7.8	1.9
228.0	120	8.4	3.0

Three synthetic samples were tested to produce the data in Table 39.

Appendix

Unpublished Analytical Methods

Unpublished Analytical Methods

The following are unpublished analytical methods used by various federal, provincial, and commercial laboratories.

Environment Canada, Conservation and Protection. 1991. Chlorinated Phenols. Gas Chromatographic - Diazomethane Derivative. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1990. Substituted Phenols. Gas Chromatographic/Mass Spectrometric. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1990. Polychlorinated Biphenyls. Gas Chromatographic. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1988. Fluoride. Specific Ion Electrode - Combined. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1990. Metals in Sediment. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1984. Cyanide. Tetracyanonickelate (II) - UV - Colorimetric. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1988. pH. Version 1.1. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1990. Conductivity. Version 2.0. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1987. Mercury in Water. Version 2.0. Laboratories, Pacific and Yukon Region.

Environment Canada, Conservation and Protection. 1990. Metals in Water. Laboratories, Pacific and Yukon Region.

Wastewater Technology Centre. 1989. The Determination of Organophosphorus Pesticides (OP) in Drinking Water by GC-AFID. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Organochlorine Pesticides (OC) and Polychlorinated Biphenyls (PCB) in Water by GC-ECD/MSD. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Polychlorinated Biphenyls (PCB), Organochlorines (OC), and Chlorobenzenes (CB) in Soils and Sediments by GLC-ECD. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of CDD and CDF in Ground Water and Aqueous Effluents by GC-MS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of CDD and CDF in Drinking Water by GC-MS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of 2,3,7,8-TCDD in Groundwater and Aqueous Effluents by GC-MS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of PCDD and PCDF in Drinking Water, Effluents, Incineration Fly Ash, Biological Samples, Soil and Sediments by HRGC-HRMS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Purgeable Organic Compounds in

Potable and Surface Waters by GC-FID and ECD. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Volatile Organohalides and Hydrocarbons in Sediments, Sludges and Kiln Dust by Headspace Capillary GC. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Polynuclear Aromatic Hydrocarbons in Surface Water, Drinking Water and Ground Water by HPLC. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Chlorophenols (CP) and Phenoxyacid Herbicides (PA) in Soils and Sediments by GC-ECD. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Chlorophenols and Phenoxyacid Herbicides in Water by Using Solid Phase Extraction and GC-ECD. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Extractable Organics in Water, Aqueous Effluent, Sediment and Soil by GC/MS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Conductivity, pH, and Alkalinity in Water and Effluents. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Conductivity in Soils and Sediments by Conductance Meter. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of pH in Soil and Sediment by Potentiometry. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Free Cyanide in Aqueous Samples by Colourimetry. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Total Cyanide in Solid Samples by Colourimetry. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Free Cyanide in Solid Samples by Colourimetry. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Total Cyanide in Aqueous Samples by Colourimetry. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Potable Waters by ICP-MS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Mercury in Water by AAS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1988. The Determination of Hexavalent Chromium in Waters, Landfill Leachates and Effluents by Colourimetry. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1988. The Determination of Arsenic, Selenium and Antimony in Water by HYD-FAAS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1988. The Determination of Boron in Water by ICP-OES. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Surface Waters by ICP AES. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Silver in Water by AAS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Fluoride in Water, Leachates, Effluents by Colourimetry. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Heavy Metals in Soils by AAS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1991. The Determination of Trace Metals in Soil by Sequential ICP-AES. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Fluoride in Soil, Sediments and

Mossbag Samples by Ion Selective Electrode (I.S.E.). Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Soil by ICP-AES. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Mercury in Soils, Sediments and Vegetation by AAS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1990. The Determination of Arsenic, Selenium and Antimony in Vegetation, Soils and Sediments by HYD-FAS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Heavy Metals in Sediments by AAS. Ontario Ministry of the Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Sediments by ICP-AES. Ontario Ministry of the Environment.

Ministère de l'Environnement du Québec. 1989. Eaux - Détermination des byphényles polychlorés, Extraction avec de l'hexane et purification avec florisil, Dosage par chromatographie en phase gazeuse.

Ministère de l'Environnement du Québec. 1988. Eaux - Détermination des cyanures totaux, Méthode colorimétrique automatisée avec la pyridine et l'acide barbiturique.

Ministère de l'Environnement du Québec. 1989. Eaux - Détermination du diquat et du paraquat, Extraction et purification avec C-18, Dosage par chromatographie en phase liquide.

Ministère de l'Environnement du Québec. 1987. Eaux - Détermination des fluorures, Méthode colorimétrique automatisée à l'alizarine.

Ministère de l'Environnement du Québec. 1990. Eaux - Détermination des hydrocarbures aromatiques polycycliques, Extraction et purification avec C-18 et Si, Dosage par chromatographie en phase liquide.

Ministère de l'Environnement du Québec. 1989. Eaux - Détermination des pesticides de type carbamates, Dosage par chromatographie en phase liquide avec dérivation post-colonne.

Ministère de l'Environnement du Québec. 1989. Eaux - Détermination des pesticides de type carbamates, Extraction et purification avec C-18, Dosage par chromatographie en phase liquide avec dérivation post-colonne.

Ministère de l'Environnement du Québec. 1989. Eaux - Détermination de pesticides de type organochlorés, Extraction avec de l'hexane et purification avec fluorisil.

Ministère de l'Environnement du Québec. 1989. Eaux - Détermination des pesticides suivants : Diethyle-atrazine, diethyl-simazine, atrazine, simazine, fonofos, diméthoate et carbofuran, Extraction avec C-18, Dosage par chromatographie en phase gazeuse.

Ministère de l'Environnement du Québec. 1989. Eaux - Détermination des pesticides suivants : Azinophos-méthyl, carbaryl, carbofurane, chlorothalonil, chlorpyrifos, chloroxuron, cyanazine, diazinon, fénitrothion, linuron, malathion, méthyl-parathion, métribuzine, parathion, phosalone, phosmet et tébuthiuron, Extraction liquide-solide, Dosage par chromatographie en phase gazeuse.

Ministère de l'Environnement du Québec. 1987. Eaux - Détermination du pH, Méthode électrométrique.

Ministère de l'Environnement du Québec. 1987. Eaux - Détermination du pH, Méthode électrométrique automatisée.

Ministère de l'Environnement du Québec. 1988. Eaux - Détermination des cyanures disponibles, Méthode colorimétrique automatisée avec la pyridine et l'acide barbiturique, Distillation manuelle.

Ministère de l'Environnement du Québec. 1988. Eaux - Détermination des cyanures totaux, Méthode colorimétrique automatisée avec la pyridine et l'acid barbiturique, Distillation manuelle.

Ministère de l'Environnement du Québec. 1990. Eaux - Détermination des fluorures, Méthode électrométrique.

Ministère de l'Environnement du Québec. 1990. Eaux - Détermination de l'arsenic. Méthode auto-

matisée par spectrophotométrie d'absorption atomique.

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