

United States
Environmental Protection
Agency

Office of
Research and Development
Washington, DC 20460

EPA/600/9-91/034
September 1991

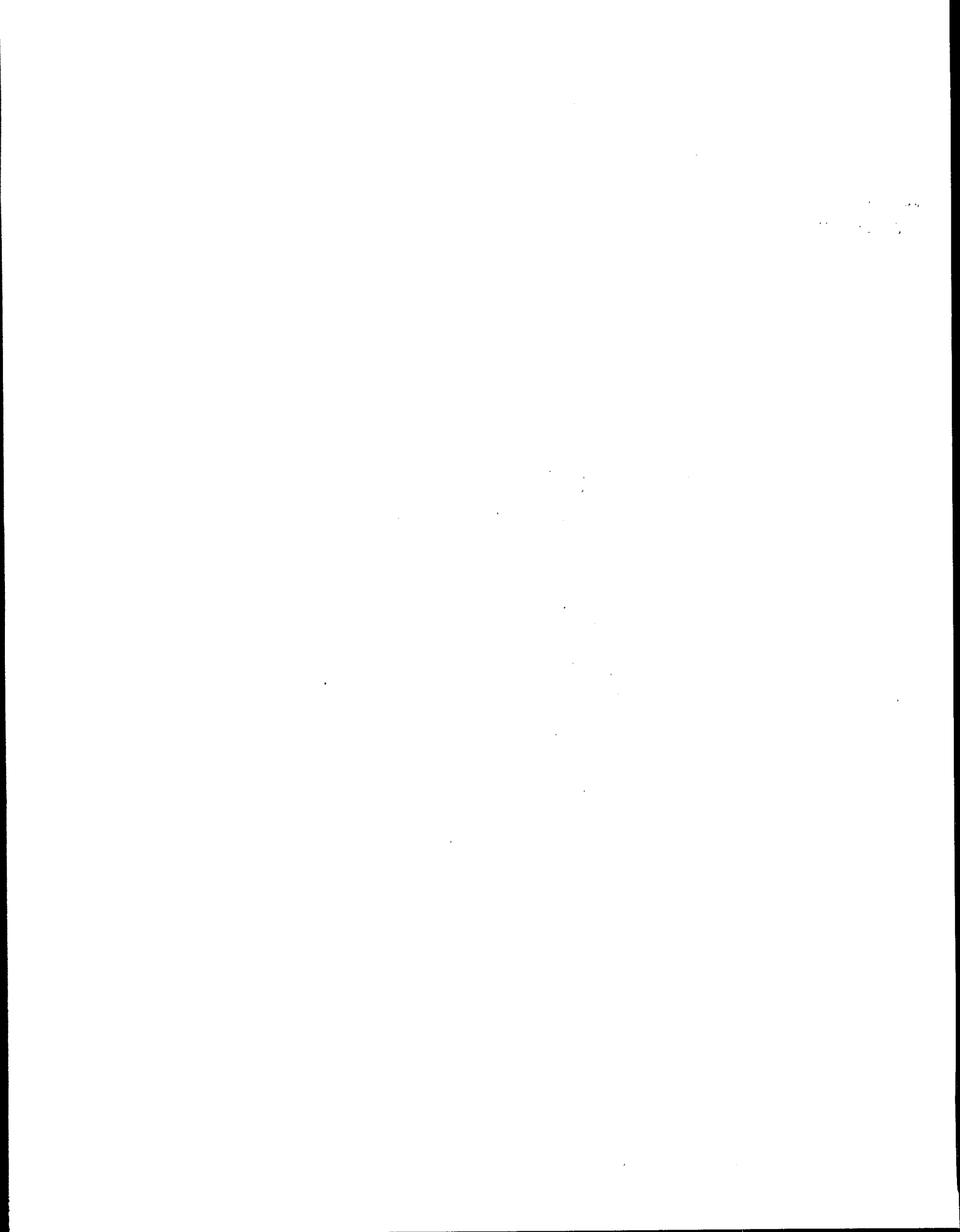


~ QUALITY CONTROL ~

Variability

In

Protocols



FOREWORD

Today's rapidly developing and changing technologies and industrial products and practices frequently carry with them the increased generation of materials that, if improperly dealt with, can threaten both public health and the environment. The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water systems. Under a mandate of national environmental laws, the Agency strives to formulate and to implement actions leading to a compatible balance between human activities and the ability of natural systems to support and to nurture life. These laws direct the EPA to perform research to define our environmental problems, measure the impacts, and search for solutions.

The Risk Reduction Engineering Laboratory is responsible for the planning, implementation, and management of research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of a quality assurance outreach program and provides a useful comparative index of several of the more frequently employed chemical analytical methodologies.

Within almost any project, the two resources which always seem to be in the shortest supply are time and money; to have more of either one is a welcome occurrence. It is toward this end that the document *Variability in Protocols* has been developed. By initially determining the objectives and requirements of a project, then having the procedures in place to accomplish them, as well as the quality control measures to ensure the reliability of the results, both time and money may be conserved. The compilation and summarization of the analytical methods contained in this document allow the user to compare the capabilities and requirements of each, thereby simplifying the decision-making process regarding which method to use in order to meet different requirements. In these ways, *Variability in Protocols* can facilitate the accomplishment of a project's goals by enabling more effective use of the allotted resources.

E. Timothy Oppelt, Director
Risk Reduction Engineering
Laboratory

ABSTRACT

The EPA Risk Reduction Engineering Laboratory's Quality Assurance Office, which published the popular pocket guide *Preparing Perfect Project Plans*, is now introducing another quality assurance reference aid. The document *Variability in Protocols (VIP)* was initially designed as a quick reference for personnel performing QA audits, but it also has found its place in serving as a reference source for laboratory managers as well as personnel reviewing or developing QA Project Plans.

Variability in Protocols contains tabular summaries of the quality control differences and similarities for some of the most frequently used analytical methods for water, soils, and other environmental samples. The document has been prepared in an attempt to bring together the separate methods that became a product of the major environmental statutes.

Noticeable differences between methods are evidenced in method detection limits, calibration methods, blanks, spikes, and several other parameters included in this summary. The tabular format provides quick and easy access to important, needed information - information that will increase one's knowledge about sets of methods such as SW-846, EPA 500 and 600 Series, Standard Methods, and others.

VIP can provide guidance when preparing Quality Assurance Project Plans. Managers, field sampling team members, auditors, and laboratory personnel alike will find this document helpful in determining the most suitable method of chemical analysis for their various purposes. As a quick reference tool, this document gives accurate information without the past necessity of searching through pages of methods, saving both time and money.

Inconsistency in quality control protocols doesn't have to be an obstacle, and with this creation, comparisons of methods can be effortless.

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ACKNOWLEDGEMENT

The extensive technical contributions of Tracey Vandermark of Maxwell Laboratories and Lauren Drees of IT Corporation are gratefully acknowledged. Contributors to and reviewers of this report were Thomas Clark of IT Corporation; and Robert Danner and Ann Kern of the USEPA.

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SW-846

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ABBREVIATIONS

CCC	Calibration Check Compound
CRDL	Contract Required Detection Limit
CRQL	Contract Required Quantitation Limit
CVAA	Cold Vapor Atomic Absorption
EDL	Estimated Detection Limit
EICP	Extracted Ion Current Profile
EQL	Estimated Quantitation Limit
FLAA	Flame Atomic Absorption
GFAA	Graphite Furnace Atomic Absorption
ICP	Inductively Coupled Plasma
ICS	Interference Check Standard
IDL	Instrument Detection Limit
LSE	Liquid-Solid Extraction
ID	Identification
IS	Internal Standard
MDL	Method Detection Limit
MS	Matrix Spike
MSA	Method of Standard Additions
MSD	Matrix Spike Duplicate
QC	Quality Control
R	Recovery
RF	Response Factor
RPD	Relative Percent Difference
RRT	Relative Retention Time
RSD	Relative Standard Deviation
RT	Retention Time
SD	Standard Deviation
SOW	Statement of Work
SPCC	System Performance Check Compound
SV	Semivolatile
SVOA	Semivolatile Organic Analysis
TCL	Target Compound List
VOA	Volatile Organic Analysis

DETERMINATION OF CHLORINATED HERBICIDES BY GC

Method - Parameter 1	SW-846 Method 8150A	EPA 500 Series Method 515.1	Standard Methods Method 6640
Applicability	Groundwater, soils, sediments and waste samples	Groundwater, surface, and drinking water	Surface waters, groundwater
Number of Analytes (1)	10 total	17 total	Not specified (includes Silvex, 2,4-D, 2,4,5-T and "similar" chlorinated phenoxy acid chemicals).
Method Validation (2)	Extract and analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 3 of method.	Extract and analyze a minimum of 4 replicates of QC check standard. Results must be within $\pm 30\%$ of values in Table 2 of method.	Not specified.
QC Check Standards	If MS/MSD results fall outside the ranges designated in Table 3 of method, a QC check standard must be analyzed and fall within those ranges.	Analyze a QC check standard with every 20 samples or one per sample set (all samples extracted within a 24-hour period). Compare %R to laboratory established limits, if available, or Table 2 of method.	Periodically determine recovery efficiency using QC check standard. Periodically is not defined in the method.
Method Detection Limit	MDLs listed in Table 1 of method. EQLs listed in Table 2 of method.	EDLs listed in Table 2 of method.	Varies with detector sensitivity, sample size, extract concentration.
Standard Solution Expiration (3)	Stock standards: 1 year Calibration standards: 6 months	Stock standards: 2 months Calibration standards: not specified	Not specified.
Initial Calibration	Minimum of 5 levels, lowest near but above MDL. If % RSD < 20, linearity assumed and average RF used.	Minimum of 3 levels (5 recommended), lowest near but above EDL. If %RSD < 20, linearity assumed and average RF used.	Prepare standard concentrations according to detector sensitivity and linearity. Number of standards used for calibration not specified.
Continuing Calibration	Mid-level calibration standard run every 10 samples. If not within $\pm 15\%$ of predicted response, recalibrate.	A calibration check standard must be analyzed at the beginning and end of analysis day (each at a different level). If not within $\pm 20\%$ of predicted response, recalibrate.	Inject same volume of herbicide methyl esters frequently to insure optimum operating conditions. Frequently is not defined in the method.
Surrogate Standards	One/two surrogates added to each sample (avoid use of deuterated analogs). Results must fall within laboratory established limits.	2,4-Dichlorophenylacetic acid (DCAA) at 0.5 $\mu\text{g}/\text{mL}$ extract. %R = 70 - 130.	Not specified.
Internal Standards	Optional; no standards specified.	Optional. If used, 4,4'-Dibromooctafluorobiphenyl (DBOB) at 0.25 $\mu\text{g}/\text{mL}$ extract.	Not specified.
Accuracy/Precision	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare results to Table 3 of method.	One MS per 10 samples or each batch of samples. %R=70-130 or laboratory established limits.	Analyze one set of duplicates with each batch of samples processed at the same time.
Blanks	One method blank per 20 samples or each batch of samples, whichever is more frequent.	One method blank with each batch of samples extracted or when new reagents used.	Periodically analyze a control blank to test the procedure. Periodically is not defined in the method.
Preservation/Storage Conditions	Sodium thiosulfate if residual chlorine present. Store at 4°C.	Mercuric chloride as bactericide. Sodium thiosulfate if residual chlorine present. Protect from light. Store at 4°C.	Store at 4°C.
Holding Time (4)	Extraction: 7 days (aqueous) 14 days (solid) Analysis: 40 days after extraction	Extraction: 14 days Analysis: 28 days after extraction	Extraction: 7 days Analysis: 40 days after extraction
Sample Volume (5)	1 liter (aqueous) 50 grams (solid)	1 liter	850 to 1000 mL

DETERMINATION OF CHLORINATED HERBICIDES BY GC

Method - Parameter 1	SW-846 Method 8150A	EPA 500 Series Method 515.1	Standard Methods Method 6640
Other Criteria (Method Specific)	<p>When doubt exists in compound identification, second column confirmation should be used.</p> <p>QC for extraction and cleanup according to specific methods used.</p>	<p>Laboratory Performance Check Sample analyzed daily to monitor instrument sensitivity, column performance, and chromatographic performance.</p> <p>When doubt exists in compound identification, second column confirmation should be used.</p>	<p>Use at least two columns for identification and quantification.</p>

Notes:

- (1) Analyte lists may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time, demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

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This material has been funded by the United States Environmental Protection Agency. Although it has been subject to Agency review, and has been approved for publication as an EPA document, it does not necessarily reflect EPA policy.

DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs BY GC

Method - Parameter 1	SW-846 Method 8080A	EPA 500 Series Method 508	EPA 600 Series Method 608	Standard Methods Method 6630	CLP PEST (Organic SOW)
Applicability	Groundwater, soils, sludges, and non-water miscible wastes	Groundwater and finished drinking water	Municipal and industrial discharges	Drinking water, surface and groundwater	Water, soil and sediment
Number of Analytes (1)	26 total	38 total (2 qualitative only)	25 total	19 listed (others possible). No PCBs.	28 total
Method Validation (2)	Extract and analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 3 of method.	Extract and analyze a minimum of 4 replicates of QC check standard. Results must be within $\pm 30\%$ of values specified in Table 2 of method.	Extract and analyze 4 replicates of QC check standards. Compare accuracy and precision results to Table 3 of method.	Not specified.	Not specified.
QC Check Standards	If MS/MSD results fall outside ranges designated in Table 3 of method, a QC check standard must be analyzed and fall within those ranges.	Analyze a QC check standard with every 20 samples or one per sample set (all samples extracted within a 24- hour period). Compare %R to established limits, if available, or Table 2 of method.	If MS results fall outside ranges designated in Table 3 of method, a QC check standard must be analyzed and fall within those ranges.	Periodically determine extraction efficiency to test procedure. Periodically is not defined in the method.	Not specified.
Method Detection Limit	MDLs listed in Table 1 of method. EQLs listed in Table 2 of method.	EDLs listed in Table 2 of method.	MDLs listed in Table 1 of method.	Varies with detector sensitivity, extraction/ clean-up efficiency, concentrations.	CRQLs for TCL listed in Exhibit C of SOW.
Standard Solution Expiration (3)	Stock standards: 1 year Calibration standards: 6 months	Stock standards: 2 months Calibration standards: not specified	Stock standards: 6 months Calibration standards: not specified.	Not specified.	Stock standards: 6 months Calibration standards: not specified
Initial Calibration	Minimum of 5 levels, lowest near but above MDL. If %RSD < 20, linearity assumed and average RF used.	Minimum of 3 levels (5 recommended), lowest near but above EDL. If %RSD < 20, linearity assumed and average RF used.	Minimum of 3 levels, lowest near but above MDL. If %RSD < 10, linearity assumed and average RF used.	Prepare standard concentrations according to detector sensitivity and linearity. Number of standards used for calibration not specified.	Three levels (except multi-components at one level) the lowest at the CRQL. The %RSD must be < 20.
Continuing Calibration	Mid-level calibration standard run every 10 samples. If not within $\pm 15\%$ of predicted response, recalibrate.	A calibration check standard must be analyzed at the beginning and end of analysis day (each at a different level). If not within $\pm 20\%$ of predicted response, recalibrate.	One or more calibration standards analyzed daily. If not within $\pm 15\%$ of predicted response, recalibrate.	Inject standards frequently to insure optimum operating conditions. Frequently is not defined in the method.	Blank and midpoint calibration standard are run once per 12 hour period. Standard must be within $\pm 25\%$ of predicted response.
Surrogate Standards	Two surrogates, decachlorobiphenyl and 2,4,5,6-Tetrachloro-m- xylene. Results must fall within laboratory established control limits.	4,4'-Dichlorobiphenyl (DCB) or others if acceptance criteria met. %R=70-130.	Not specified.	Not specified.	Two surrogates, Decachlorobiphenyl and 2,4,5,6- Tetrachloro-m- xylene. Advisory limits=60-150%.

DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs BY GC

Method - Parameter 1	SW-846 Method 8080A	EPA 500 Series Method 508	EPA 600 Series Method 608	Standard Methods Method 6630	CLP PEST (Organic SOW)
Internal Standards	Optional; no standards specified.	Optional. If used, penta- chloronitrobenzene or others if acceptance criteria met. Sample IS response must be >70% of standard response.	Optional; no standards specified.	Not specified.	Not required.
Accuracy/ Precision	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare results to Table 3 of method.	One MS per 10 samples or each sample batch, whichever is greater. Compare %R to lab established limits, if available, or Table 2 of method.	One MS per 10 samples from each site or 1 MS per month, whichever is more frequent. Compare %R to Table 3 of method.	Analyze one set of duplicates with each batch of samples processed at the same time.	One MS/MSD per sample batch or 1 per 20 samples. Six compounds are used for spiking; advisory limits in Exhibit D, Section III, Paragraph 16.4 of SOW.
Blanks	One method blank per 20 samples or each batch of samples	One method blank with each batch of samples extracted or when new reagents used.	One method blank with each batch of samples extracted or when new reagents used.	Periodically analyze a control blank to test the procedure. Periodically is not defined in the method.	One method blank per case, one per 20 samples, or one per sample batch. All compounds < CRQL
Preservation/ Storage Conditions	If residual chlorine present, add sodium thiosulfate. Store at 4°C.	Mercuric chloride as bactericide. Sodium thiosulfate if residual chlorine present. Store at 4°C.	Adjust pH to 5-9 if extraction not to be done within 72 hours of sampling. Add sodium thiosulfate if residual chlorine present and aldrin is being determined. Store at 4°C.	Store at 4°C.	Protect from light. Store at 4°C.
Holding Time (4)	Extraction: 7 days (aqueous) 14 days (solids) Analysis: 40 days after extraction	Extraction: 7 days Analysis: 14 days after extraction	Extraction: 7 days Analysis: 40 days after extraction	Extraction: 7 days Analysis: 40 days after extraction	Extraction: 5 days of sample receipt (aqueous) 10 days of sample receipt (solid) Analysis: 40 days after extraction
Sample Volume Required (5)	1 liter (aqueous) 30 grams (low level solid) 2 grams (medium level solid)	1 liter	1 liter	1 liter	1 liter (aqueous) 30 grams (low level solid) 1 gram (medium level solid)

DETERMINATION OF ORGANOCHLORINE PESTICIDES AND PCBs BY GC

Method - Parameter I	SW-846 Method 8080A	EPA 500 Series Method 508	EPA 600 Series Method 608	Standard Methods Method 6630	CLP PEST (Organic SOW)
Other Criteria (Method Specific)	<p>When doubt exists in compound identification, second column confirmation should be used.</p> <p>Check for dichlorodiphenyltrichloroethane (DDT) and endrin degradation. % breakdown must be < 20.</p>	<p>Laboratory Performance Check Sample analyzed daily to monitor instrument sensitivity, column performance, and chromatographic performance.</p> <p>When doubt exists in compound identification, second column confirmation should be used.</p>	<p>When doubt exists in compound identification, second column confirmation should be used.</p>	<p>When doubt exists in compound identification, second column confirmation should be used.</p>	<p>Second column confirmation is mandatory.</p> <p>Check for dichlorodiphenyltrichloroethane (DDT) and endrin degradation every 12 hours. % breakdown must be < 20.</p> <p>Analyze resolution check mixture prior to initial calibration.</p>

Notes:

- (1) Analyte lists may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time, demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons of QC check standards indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS

Method - Parameter 1	SW-846 Method 8270A	EPA 500 Series Method 525	EPA 600 Series Method 625	Standard Methods Method 6410	CLP SVOA (Organic SOW)
Applicability	Groundwaters, soils, sediments, sludges, and non-water miscible wastes	Drinking water and raw source water	Wastewater	Domestic, industrial wastewaters, natural and potable waters	Water, soil, and sediment
Number of Compounds (1)	227 total	43 total	81 total	81 total	64 total
Method Validation (2)	Extract and analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 6 of method.	Extract and analyze 4-7 replicates of QC check standard. %R=70-130. %RSD<30.	Extract and analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 6 of method.	Extract and analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 6410:V of method.	Not specified.
QC Check Standards	If MS/MSD results fall outside ranges designated in Table 6 of method, a QC check standard must be analyzed and fall within those ranges.	Analyze a QC check standard with every 20 samples or one per sample set. %R=70-130. Analyze QC sample from external source quarterly.	If MS results fall outside ranges in Table 6 of method, a QC check standard must be analyzed and fall within those ranges.	If MS results fall outside ranges in Table 6410:V of method, a QC check standard must be analyzed and fall within those ranges.	Not specified.
Method Detection Limit	EQLs listed in Table 2 of method.	MDLs listed in Tables 4, 5, and 6 of method.	MDLs listed in Tables 4 and 5 of method.	MDLs listed in Tables 6410:I and 6410:II of method.	CRQLs for TCL listed in Exhibit C of SOW.
Standard Solution Expiration (3)	Stock standards: 1 year Calibration standards: 1 year Daily continuing calibration standard: 1 week	Not specified.	Stock standards: 6 months Calibration standards: not specified	Stock standards: 6 months Calibration standards: not specified	Stock standards: 1 year Calibration standards: 1 year Daily continuing calibration standard: 1 week
Initial Calibration	Minimum of 5 levels, lowest near but above EDL. %RSD for CCCs < 30. RF for SPCCs > 0.05.	Six levels. %RSD must be < 30.	Minimum of 3 levels, lowest near but above MDL. If % RSD < 35, linearity assumed and average RF used.	Minimum of three levels, one near but above MDL. If % RSD < 35, linearity assumed and average RF used.	Five levels except for 8 compounds which only require 4 levels. Minimum RRF and maximum RSD criteria listed in Table 5 of Exhibit D/SV of SOW.
Continuing Calibration	Mid-level calibration standard run every 12 hours. RF for SPCCs > 0.05. RF of CCCs must be < 30% difference from initial calibration.	Mid-level calibration standard analyzed at the beginning of each 8 hour shift. RF must be within ± 30% of initial calibration.	One or more calibration standards analyzed each day. If not within ± 20% of predicted response, recalibrate.	One or more calibration standards analyzed each day. If not within ± 20% of predicted response, recalibrate.	A mid-level calibration standard is run every 12 hours. The % difference must be <25 from initial calibration.
Surrogate Standards	Nitrobenzene-d ₅ , 2-Fluorobiphenyl, p-Terphenyl-d ₁₄ , Phenol-d ₆ , 2-Fluorophenol, and 2,4,6-Tribromophenol. Recovery limits in Table 8 of method.	Perylene-d ₁₂ . Optional: Caffeine- ¹⁵ N ₂ and Pyrene-d ₁₀ .	Minimum of three from Table 8 of method. Results must fall within laboratory established control limits.	Minimum of 3 from Table 6410:IV of method. Results must fall within laboratory established control limits.	Same as 8270A plus 2-Fluorobiphenyl and Chlorophenol-d ₄ . Recovery limits listed in Table 6 of Exhibit D/SV of SOW.

DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS

Method - Parameter 1	SW-846 Method 8270A	EPA 500 Series Method 525	EPA 600 Series Method 625	Standard Methods Method 6410	CLP SVOA (Organic SOW)
Internal Standards	1,4-Dichlorobenzene-d ₄ , Naphthalene-d ₈ , Acenaphthene-d ₁₀ , Phenanthrene-d ₁₀ , Chrysene-d ₁₂ , and Perylene-d ₁₂ . RT must be within ± 30 seconds from last calibration; area must be -50 to +100%.	Acenaphthene-D ₁₀ , Phenanthrene-D ₁₀ , and Chrysene-D ₁₂ . Sample IS response must be >70% of standard response.	Optional. If used, minimum of 3 from Table 8 of method.	Minimum of 3 (some recommended in Table 6410:IV of method).	1,4-Dichlorobenzene-d ₄ , Naphthalene-d ₈ , Acenaphthene-d ₁₀ , Phenanthrene-d ₁₀ , Chrysene-d ₁₂ , and Perylene-d ₁₂ . RT must be within ± 30 seconds from last calibration; area must be -50 to +100%.
Accuracy/ Precision	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare results to Table 6 of method.	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. %R=70-130. %RSD < 30. Analyze duplicate QC check standards quarterly.	One MS per 20 samples from each site or 1 MS per month, whichever is more frequent. Compare %R to Table 6 of method.	One MS per 20 samples from each site. Compare results to Table 6410:V of method.	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent (only 11 compounds spiked). Compare results to Table 7 of Exhibit D/SV of SOW.
Blanks	One method blank per 20 samples or each batch of samples, whichever is more frequent.	One method blank with each batch of samples extracted.	One method blank with each batch of samples extracted or when new reagents used.	Not specified.	One method blank per 20 samples or each batch of samples, whichever is more frequent. Concentration < CRQL for all compounds but phthalates < 5X CRQL.
Preservation/ Storage Conditions	Sodium thiosulfate if residual chlorine. Store at 4°C.	If residual chlorine, add sodium sulfite or sodium arsenite. Adjust pH < 2 with HCl for unchlorinated water. Store at 4°C.	Sodium thiosulfate if residual chlorine. Store at 4°C.	Sodium thiosulfate if residual chlorine. Store at 4°C.	Protect from light. Store at 4°C.
Holding Time (4)	Extraction: 7 days (aqueous) 14 days (solids) Analysis: 40 days after extraction.	Extraction: 7 days Analysis: 30 days after extraction.	Extraction: 7 days Analysis: 40 days after extraction.	Extraction: 7 days Analysis: 40 days after extraction.	Extraction: 5 days of sample receipt (aqueous) 10 days of sample receipt (solid) Analysis: 40 days after extraction.
Sample Volume (5)	1 liter (aqueous) 30 grams (low level solid) 2 grams (medium level solid)	1 liter	1 liter	1 liter	1 liter (aqueous) 30 grams (low level solid) 1 gram (medium level solid)

DETERMINATION OF SEMIVOLATILE ORGANIC COMPOUNDS BY GC/MS

Method - Parameter 1	SW-846 Method 8270A	EPA 500 Series Method 525	EPA 600 Series Method 625	Standard Methods Method 6410	CLP SVOA (Organic SOW)
Other Criteria (Method Specific)	<p>Tuning: 50 ng decafluorotriphenylphosphine (DFTPP) initially and every 12 hours; acceptance criteria in Table 3 of method.</p> <p>Qualitative ID: All ions > 10% intensity must be $\pm 20\%$ of standard; ± 0.06 RRT units of standard RRT.</p> <p>Library searches may be made for the purpose of tentative identification.</p>	<p>Tuning: 5 ng decafluorotriphenylphosphine (DFTPP) at the beginning of each 8 hour shift; acceptance criteria in Table 1 of method.</p> <p>Qualitative ID: All ions > 10% intensity must be $\pm 20\%$ of standard ion; RT ± 10 seconds of standard RT.</p> <p>LSE cartridges must be checked for contamination.</p>	<p>Tuning: 50 ng decafluorotriphenylphosphine (DFTPP) at the beginning of each day; acceptance criteria in Table 9 of method.</p> <p>Qualitative ID: Characteristic ions for each analyte must maximize in the same scan or within 1 scan; relative peak heights of 3 characteristic ions must be $\pm 20\%$ of standard; RT (characteristic ions) within ± 30 seconds RT of analyte.</p> <p>Check column performance daily with benzidine and pentachlorophenol.</p>	<p>Tuning: 50 ng decafluorotriphenylphosphine (DFTPP) at the beginning of each day; acceptance criteria in Table 6410:III of method.</p> <p>Qualitative ID: Characteristic masses (Tables 6410:I and II) - each compound maximizes in same scan or within 1 scan; RT within ± 30 seconds of RT of standard; relative peak heights of 3 characteristic masses in EICPs within $\pm 20\%$ of relative intensities of masses in reference spectrum.</p> <p>Check column performance daily with benzidine and pentachlorophenol.</p>	<p>Tuning: 50 ng decafluorotriphenylphosphine (DFTPP) initially and every 12 hours; acceptance criteria in Table 1 of Exhibit D of SOW.</p> <p>Qualitative ID: same as for 8270A.</p> <p>Up to 20 compounds with responses > 10% of nearest internal standard are tentatively identified via a library search.</p>

Notes:

- (1) Analyte lists may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GC/MS

Method - Parameter 1	Internal Standards	Accuracy/Precision	Method	Blanks	Preservation/Storage Conditions	Holding Time (4)	Sample Volume Required (5)
SW-846 Method 8240A	Bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d ₅ . RT must be ± 30 seconds from last calibration; area must be -50 to 100%.	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare results to Table 6 of method.		One method blank per batch of samples, whichever is more frequent.	pH ≤ 2 with HCl. Sodium thiosulfate if residual chlorine. Store at 4°C.	14 days	5 mL (aqueous) 5 grams (solid)
EPA 500 Series Method 524.1	Fluorobenzene. Additional internal standards optional.	No MS required. Duplicate QC check standards analyzed quarterly.		One method blank per batch of samples processed together. One field blank per batch of samples.	pH ≤ 2 with HCl. Ascorbic Acid if residual chlorine. Collect all samples in duplicate. Store at 4°C.	14 days	25 mL (5mL may be used if MDLs can be achieved)
EPA 600 Series Method 624	Optional. If used, minimum of 3 from Table 3 of method.	One MS per 20 samples from each site or 1 per month, whichever is more frequent. Compare %R to Table 5 of method.		One method blank per day.	pH ≤ 2 with HCl. Sodium thiosulfate if residual chlorine. Store at 4°C.	14 days	5 mLs
Standard Methods Method 6210	Minimum of 3 from Table 6210:III of method.	One MS per 20 samples from each site. Compare results to Table 6210:IV of method.		One method blank per day.	pH ≤ 2 with HCl. Sodium thiosulfate if residual chlorine. Store at 4°C.	14 days	5 mLs
CLP VOA (Organic SOW)	Bromochloromethane, 1,4-difluorobenzene, and chlorobenzene-d ₅ . RT must be ± 30 seconds from last calibration; area must be -50 to 100%.	One MS per 20 samples or each batch of samples, whichever is more frequent (only 5 compounds spiked). Compare results to Table 7 of Exhibit D/VOA of SOW.		One method blank every 12 hours. Concentration <CRQL for all but methylene chloride, acetone, 2-butanone < 5X CRQL.	Protect from light. Store at 4°C.	10 days from sample receipt	5 mLs (aqueous) 5 grams (solid)

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GC/MS

Method - Parameter 1	SW-846 Method 8240A	EPA 500 Series Method 524.1	EPA 600 Series Method 624	Standard Methods Method 6210	CLP VDA (Organic SOW)
Applicability	Groundwaters, soils, sediments, sludges, non-water miscible wastes	Drinking water, raw source water	Wastewater	Most environ-mental water samples	Water, soil, and sediment
Number of Analytes (1)	74 total	48 total	31 total	31 total	33 total
Method Validation (2)	Extract and analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 6 of method.	Extract and analyze 4-7 replicates of QC check standard. %RSD<20. %R=80-120.	Extract and analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 5 of method.	Analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 6210/IV of method.	Not specified.
QC Check Standards	If MS/MSD results fall outside the ranges designated in Table 6 of method, a QC check standard must be analyzed and fall within those ranges.	Analyze a QC check standard with every 20 samples or one per sample set. %R=80-120.	If MS results fall outside the ranges designated in Table 5 of method, a QC check standard must be analyzed and fall within those ranges.	If MS results fall outside the ranges designated in Table 6210/IV of method, a QC check standard must be analyzed and fall within those ranges.	Not specified.
Method Detection Limit	ECLs listed in Table 2 of method.	MDLs listed in Table 3 of method.	MDLs listed in Table 1 of method.	MDLs listed in Table 6210/IV of method.	CROLs for TCL listed in Exhibit C of SOW.
Standard Solution Expiration (3)	Stock standards (except gases): 6 months. Stock gas standards: 2 months. Daily Calibration standards:	Stock standards (except gases): 4 weeks. Stock gas standards: 1 week. Aqueous calibration standards: 1 hour	Stock standards (except gases): 1 month. Stock gas standards: 1 week	Stock standards (except gases): 1 month. Stock gas standards: 1 week	Stock standards (except gases): 6 months. Stock gas standards: 2 months
Initial Calibration	Minimum of 5 levels, lowest near but above MDL. %RSD for CCCs < 30. RF for SPCCs > 0.30 (0.25 for bromoform)	3, 4, or 5 levels (depending on calibration range), lowest 2-10 times MDL. If %RSD<20, linearly assumed and average RF used.	Minimum of 3 levels, lowest near but above MDL. If %RSD < 35, linearly assumed and average RF used.	Minimum of three levels, one near but above MDL. If %RSD < 35, linearly assumed and average RF used.	Five levels. Minimum RRF and maximum RSD criteria listed in Table 2 of Exhibit D/NOA of SOW.
Continuing Calibration	Mid-level calibration standard run every 12 hours. RF for SPCCs same as for initial calibration. RF of CCCs must be < 25% difference from initial calibration.	Mid-level calibration standard analyzed at the beginning of each 8 hour shift. RF must be within ± 30% of initial calibration.	QC check standard analyzed each working day. Compare results to Table 5 of method.	QC check standard analyzed each working day. Compare results to Table 6210/IV of method.	A mid-level calibration standard is analyzed every 12 hours. The % difference must be < 25 from initial calibration.
Surrogate Standards	4-Bromofluorobenzene, 1,2-Dichloroethane-d ₄ , and Toluene-d ₈ . Recovery limits in Table 8 of method.	4-Bromofluorobenzene and 1,2-Dichloroethane-d ₄ . Recovery limits not specified.	Minimum of 3 from Table 3 of method. Results must fall within laboratory established control limits.	Minimum of 3 from Table 6210/III of method. Results must fall within laboratory established control limits.	4-Bromofluorobenzene, 1,2-Dichloroethane-d ₄ , and Toluene-d ₈ . Recovery limits in Table 6 of Exhibit D/NOA of SOW.

DETERMINATION OF VOLATILE ORGANIC COMPOUNDS BY GC/MS

Method - Parameter 1	SW-846 Method 8240A	EPA 500 Series Method 524.1	EPA 600 Series Method 624	Standard Methods Methods 6210	CLP VOA (Organic SOW)
Other Criteria (Method Specific)	<p>Tuning: 50 ng bromofluorobenzene (BFB) initially and every 12 hours; acceptance criteria in Table 3 of method.</p> <p>Qualitative ID: All ions > 10% intensity must be $\pm 20\%$ of standard; ± 0.06 RRT units of standard RRT.</p> <p>Library searches may be made for the purpose of tentative identification.</p>	<p>Tuning: 50 ng bromofluorobenzene (BFB) at the beginning of each 8 hour shift; acceptance criteria in Table 2 of method.</p> <p>Qualitative ID: All ions > 10% intensity must be $\pm 20\%$ of standard ion; sample RT within 3 SD of RT in calibration.</p>	<p>Tuning: 50 ng bromofluorobenzene (BFB) initially and every 12 hours; acceptance criteria in Table 2 of method.</p> <p>Qualitative ID: Three characteristic ions must be $\pm 20\%$ of standard & must maximize within 1 scan.</p>	<p>Tuning: 50 ng bromofluorobenzene (BFB) at the beginning of each day; acceptance criteria in Table 6210:II of method.</p> <p>Qualitative ID: Characteristic masses of each compound must reach the maximization point in same scan or within 1 scan; RT within 30 seconds of RT of authentic compound; relative peak height of 3 characteristic masses in EICP within 20% of relative intensities of masses in reference spectrum.</p>	<p>Tuning: 50 ng bromofluorobenzene (BFB) initially & every 12 hours; acceptance criteria in Table 1 of Exhibit D/VOA of SOW.</p> <p>Qualitative ID: Same as for 8240A.</p> <p>Up to 20 compounds with responses >10% of nearest IS are tentatively identified via a library search.</p>

Notes:

- (1) Analyte list may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time, demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons of QC check standards indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF AROMATIC VOLATILE ORGANIC COMPOUNDS BY GC

Method - Parameter 1	SW-846 Method 8020A	EPA 500 Series Method 503.1	EPA 600 Series Method 602	Standard Methods Method 6220
Applicability	Groundwater, soils, sludges, water-miscible and non-water miscible wastes	Drinking water, raw source water	Municipal and industrial discharge water	Most environmental water samples
Number of Analytes (1)	7 total (same as 602 and 6220)	28 total	7 total (same as 8020A and 6220)	7 total (same as 8020A and 602)
Method Validation (2)	Analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 3 of method.	Analyze 4-7 replicates of QC check standard. %R=80-120. %RSD < 20.	Analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 2 of method.	Analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 6220:II of method.
QC Check Standard	If MS/MSD results fall outside ranges designated in Table 3 of method, a QC check standard must be analyzed and fall within those ranges.	Analyze a QC check standard with every 20 samples or one per sample set. %R=80-120. Analyze QC check standard from external source quarterly.	If MS results fall outside ranges designated in Table 2 of method, a QC check standard must be analyzed and fall within those ranges.	If MS results fall outside ranges designated in Table 6220:II of method, a QC check standard must be analyzed and fall within those ranges.
Method Detection Limit	MDLs listed in Table 1 of method.	MDLs listed in Table 2 of method.	MDLs listed in Table 1 of method.	MDLs listed in Table 6220:I of method.
Standard Solution Expiration (3)	Stock standards: 6 months Calibration standards: 24 hours with no headspace.	Stock standards: 4 weeks Calibration standards: not specified	Stock standards: 1 month Calibration standards: daily	Stock standards: 4 weeks Calibration standards: 24 hours if zero headspace
Initial Calibration	Minimum of 5 levels, lowest near but above MDL. If %RSD < 20, linearity assumed and average RF used.	3, 4, or 5 levels (depending on calibration range), lowest 2-10 times MDL. If %RSD<10, linearity assumed and average RF used.	Minimum of 3 levels, lowest near but above MDL. If %RSD < 10, assume linearity and average RF used.	Minimum of 5 levels. If %RSD<10, linearity assumed and average RF used.
Continuing Calibration	Mid-level calibration standard run every 10 samples. If not within $\pm 15\%$ of predicted response, recalibrate.	Mid-level calibration standard analyzed at the beginning of each 8 hour shift. RF must be within $\pm 20\%$ of initial calibration.	QC check standard analyzed each working day. Compare results to Table 2 of method.	Analyze one or more calibration standards daily. If not within $\pm 20\%$ of predicted response, recalibrate.
Surrogate Standards	Add surrogates to encompass range of temperature program (five recommended surrogates are given in Section 5.7 of method).	Not specified.	Add surrogates to encompass range of temperature program (α, α, α -Trifluorotoluene is recommended).	α, α, α -Trifluorotoluene
Internal Standards	Optional. If used, α, α, α -Trifluorotoluene is recommended.	Optional. If used, α, α, α -Trifluorotoluene is recommended.	Optional. If used, α, α, α -Trifluorotoluene is recommended.	Optional. If used, α, α, α -Trifluorotoluene is recommended.
Accuracy/Precision	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare results to Table 3 of method.	No MS required. Analyze duplicates daily.	One MS per 10 samples from each site or 1 per month, whichever is more frequent. Compare %R to Table 2 of method.	One MS per 10 samples from each site or 1 per month, whichever is more frequent. Compare %R to Table 6220:II of method.

DETERMINATION OF AROMATIC VOLATILE ORGANIC COMPOUNDS BY GC

Method → Parameter ↓	SW-846 Method 8020A	EPA 500 Series Method 503.1	EPA 600 Series Method 602	Standard Methods Method 6220
Blanks	One method blank per 20 samples or each batch of samples.	One method blank per batch of samples processed at the same time. One field blank per batch of samples.	One method blank per day.	One method blank per day.
Preservation/ Storage Conditions	pH ≤ 2 with HCl. If residual chlorine, add sodium thiosulfate. Store at 4°C.	pH ≤ 2 with HCl. If residual chlorine, add ascorbic acid or sodium thiosulfate. Store at 4°C. Collect all samples in duplicate.	pH ≤ 2 with HCl. If residual chlorine, add sodium thiosulfate. Store at 4°C.	pH ≤ 2 with HCl. Add ascorbic acid if residual chlorine. Store at 4°C.
Holding Time (4)	14 days	14 days	14 days	14 days
Sample Volume Required (5)	5 mLs (aqueous) 5 grams (solid)	5 mLs	5 mLs	5 mLs
Other Criteria (Method Specific)	Second column confirmation is recommended.	Second column confirmation is recommended. Retention times must vary by <10% over 8 hour period.	Second column confirmation is recommended.	Second column confirmation is recommended.

Notes:

- (1) Analyte lists may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF HALOGENATED VOLATILE ORGANIC COMPOUNDS BY GC

Method - Parameter 1	SW-846 Method 8010A	EPA 500 Series Method 502.1	EPA 600 Series Method 601	Standard Methods Method 6230
Applicability	Groundwater, soils, sludge, water miscible liquid waste and non- water miscible waste	Drinking water, raw source water	Municipal and industrial discharge water	Most environmental water samples
Number of Analytes (1)	34 total	40 total	29 total (same as 6230)	29 total (same as 601)
Method Validation (2)	Analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 3 of method.	Analyze 4-7 replicates of QC check standard. %R=80-120. %RSD<20.	Analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 2 of method.	Analyze 4 replicates of QC check standard. Compare accuracy and precision results to Table 6230:III of method.
QC Check Standards	If MS results fall outside the ranges designated in Table 3 of method, a QC check standard must be analyzed and fall within those ranges.	Analyze a QC check standard with each sample batch. %R=80-120. Analyze a QC check standard from an external source quarterly.	If MS results fall outside the ranges designated in Table 2 of method, a QC check standard must be analyzed and fall within those ranges.	If MS results fall outside the ranges designated in Table 6230:II of method, a QC check standard must be analyzed and fall within those ranges.
Method Detection Limit	MDLs listed in Table 1 of method. EQLs listed in Table 2 of method.	MDLs listed in Table 2 of method.	MDLs listed in Table 1 of method.	MDLs listed in Table 6230:I of method.
Standard Solution Expiration (3)	Stock standards (except gases): 6 months Stock gas standards: 2 months Calibration standards: 24 hours if zero headspace.	Stock standards: 4 weeks Intermediate standards: 4 weeks Calibration standards: not specified	Stock standards, (except gases and 2- chloroethylvinyl ether): 1 month Stock gas standards and 2- chloroethylvinyl ether: 1 week Calibration standards: 24 hours if zero headspace.	Stock standards, (except gases and 2-chloroethylvinyl ether): 1 month Stock gas standards and 2- chloroethylvinyl ether: 1 week Calibration standards: 24 hours if zero headspace.
Initial Calibration	Minimum of 5 levels, lowest near but above MDL. If %RSD<20, linearity assumed and average RF used.	3, 4, or 5 levels (depending on calibration range), lowest 2-10X MDL. If %RSD<10, linearity assumed and average RF used.	Minimum of 3 levels, lowest near but above MDL. If %RSD<10, linearity assumed and average RF used.	Minimum of 3 levels, lowest near but above MDL. If %RSD<10, linearity assumed and average RF used.
Continuing Calibration	Mid-level calibration standard run every 10 samples. If not within ±15% of predicted response, recalibrate.	Analyze one or more calibration standards daily. If not within ±20% of predicted response, recalibrate.	QC check standard analyzed each working day. Compare results to Table 2 of method.	QC check standard analyzed each working day. Compare results to Table 6230:III of method.
Surrogate Standards	Bromochloromethane, 2-Bromo-1- chloropropane, and 1,4-Dichlorobutane. Results within lab established control limits.	Not specified.	Bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane	Bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane
Internal Standards	Optional. If used, exact compounds not specified, though same as used for surrogates may be appropriate.	Optional. If used, 1,4- Dichlorobutane or 2-Bromo-1-chloropropane. Area must be ±3 SD of calibration standards.	Optional. If used, surrogate compounds have been successfully used as internal standards.	Optional. Select one or more compounds similar in analytical behavior to compounds of interest.
Accuracy/ Precision	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. Compare results to Table 3 of method.	MS not required. Analyze duplicates daily.	One MS per 10 samples from each site or 1 per month, whichever is more frequent. Compare %R to Table 2 of method.	One MS per 10 samples from each site or 1 per month, whichever is more frequent. Compare %R to Table 6230:III of method.

DETERMINATION OF HALOGENATED VOLATILE ORGANIC COMPOUNDS BY GC

Method - Parameter 1	SW-846 Method 8010A	EPA 500 Series Method 502.1	EPA 600 Series Method 601	Standard Methods Method 6230
Blanks	One method blank per 20 samples or each batch of samples.	One method blank per batch of samples processed at the same time.	One method blank per day.	One method blank per day.
Preservation/ Storage Conditions	Sodium thiosulfate if residual chlorine. Store at 4°C.	pH \leq 2 with HCl. If residual chlorine, add ascorbic acid or sodium thiosulfate. Store at 4°C. Collect all samples in duplicate.	Sodium thiosulfate if residual chlorine. Store at 4°C.	pH \leq 2 with HCl. Add ascorbic acid if residual chlorine. Store at 4°C.
Holding Time (4)	14 days	14 days	14 days	14 days
Sample Volume Required (5)	5 mLs (aqueous) 5 grams (solid)	5 mLs	5 mLs	5 mLs
Other Criteria (Method Specific)	When doubt exists in compound identification, second column confirmation is recommended.	When doubt exists in compound identification, second column confirmation is recommended.	When doubt exists in compound identification, second column confirmation is recommended.	When doubt exists in compound identification, second column confirmation is recommended.

Notes:

- (1) Analyte lists may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF TOTAL AND AMENABLE CYANIDE

Method - Parameter 1	SW-846 Methods 9010A/9011	EPA Series Methods 335.1, 335.2	Standard Methods Methods 4500-CN C, D, E, and G	CLP CN (Inorganic SOW)
Applicability	Wastes and leachates	Drinking, surface, saline water, domestic and industrial wastes.	Wastewater and groundwaters	Water, soil, and sediments
Number of Analytes	Total CN and CN amenable to chlorination	Total CN and CN amenable to chlorination	Total CN and cyanide amenable to chlorination	Total CN only
Method Validation (1)	Not specified.	Not specified.	Not specified.	Not specified.
QC Check Standards	Verify calibration with an independent check standard. If not within $\pm 15\%$ of expected value, recalibrate.	Not specified.	Not specified.	Verify initial calibration with a distilled independent standard. %R=85-115%.
Method Detection Limit	0.02 mg/L	0.02 mg/L	0.02 mg/L	CRDL: 0.01 mg/L
Standard Solution Expiration (2)	Stock standard: Not specified Calibration standards: prepare daily	Stock standard: Not specified Calibration standards: prepare daily	Stock cyanide: check weekly Calibration standards: prepare daily	Stock cyanide: not specified Calibration standards: prepare daily
Initial Calibration	Colorimetric: 6 levels plus blank	Colorimetric: 6 levels plus blank	Colorimetric: Series of standards over range 0.2 - 6 μg CN plus blank	Colorimetric: Minimum of 3 levels plus a blank (one standard at CRDL).
Continuing Calibration	Colorimetric: verify curve with every sample batch by analyzing a mid-level concentration standard.	Not specified.	Colorimetric: Recheck calibration curve periodically, and each time new reagent used. Periodically is not defined in the method.	Colorimetric: Calibration checked after every 10 samples or 2 hours, whichever is more frequent. %R=85-115%.
Surrogate Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Internal Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Accuracy/Precision	One MS/MSD per sample batch	Do MS to check sample distillation efficiency; no frequency specified.	Not specified.	One MS and 1 duplicate for each sample batch. %R=75-125%. RPD<20%
Blanks	Titration - One reagent blank per sample batch Colorimetric - Calibration blank No distillation blank specified.	Titration - One reagent blank per sample batch Colorimetric - Calibration blank No distillation blank specified.	Titration: One reagent blank per sample batch Colorimetric: Calibration blank No distillation blank specified.	Titration: One reagent blank per sample batch Colorimetric: Calibration blanks after every 10 samples or 2 hours, whichever is more frequent Analyze a distillation blank with each sample batch.
Preservation/Storage Conditions	Aqueous: pH ≥ 12 with NaOH. Sodium arsenite or ascorbic acid if oxidizing agents. Store at 4°C. Solid: Store at 4°C.	pH ≥ 12 with NaOH. Ascorbic acid if oxidizing agents. Store at 4°C.	pH ≥ 12 with NaOH. Store at 4°C in dark. Sodium thiosulfate if oxidizing agent present.	Aqueous: pH ≥ 12 with NaOH. Ascorbic acid if oxidizing agents. Store at 4°C. Solid: Store at 4°C.
Holding Times (4)	14 days	14 days (24 hours when sulfide present)	14 days (24 hours when sulfide present)	12 days from sample receipt

DETERMINATION OF TOTAL AND AMENABLE CYANIDE

Method - Parameter 1	SW-846 Methods 9010A/9011	EPA Series Methods 335.1/335.2	Standard Methods Methods 4500-CN C, D, E, and G	CLP CN (Inorganic SOW)
Sample Volume Required (5)	Aqueous: 500 mLs (1000 mLs if both total and amenable CN) Solid: 1-5 grams (2-10 grams if both total and amenable CN)	500 mLs (1000 mLs if both total and amenable CN)	500 mLs (1000 mLs if both total and amenable CN)	500 mLs (aqueous) 1-5 grams (solid)
Other Criteria (Method Specific)	Distill a high and a low standard; results should be $\pm 10\%$ of undistilled concentration. If sulfides present, all standards must be distilled. If matrix interference, use MSA.	Distill a high and a low standard; results should be $\pm 10\%$ of undistilled concentration. If sulfides present, all standards must be distilled.	None.	Distill one mid-level standard; results must be $\pm 15\%$ of undistilled concentration.

Notes:

- (1) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (2) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (3) Unless otherwise indicated, holding times are from the date of sample collection.
- (4) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF TOTAL ORGANIC CARBON

Method - Parameter 1	SW-846 Method 9060A	EPA Series Method 415.1	Standard Methods Method 5310B
Applicability	Groundwater, surface and saline waters, domestic and industrial wastes	Groundwater, surface and saline waters; domestic and industrial wastes	Ground and surface waters, wastewater
Number of Analytes	No specific compounds; includes natural sugars, mercaptans, alkanes, low molecular weight alcohols and oils, cellulose fibers, oily matter adsorbed on silt.	No specific compounds; includes natural sugars, mercaptans, alkanes, low molecular weight alcohols and oils, cellulose fibers, oily matter adsorbed on silt.	No specific compounds; classes of organic compounds not specified.
Method Validation (1)	Not specified.	Not specified.	Not specified.
QC Check Standards	Verify calibration with an independently prepared check standard. No criteria specified.	Not specified.	Not specified.
Method Detection Limit	1 mg/L	1 mg/L	1 mg/L
Standard Solution Expiration (2)	Not specified.	Not specified.	Not specified.
Initial Calibration	Per instrument manufacturer's specifications.	Per instrument manufacturer's specifications.	Per instrument manufacturer's specifications.
Continuing Calibration	Not specified.	Not specified.	Not specified.
Surrogate Standards	Not applicable.	Not applicable.	Not applicable.
Internal Standards	Not applicable.	Not applicable.	Not applicable.
Accuracy/Precision	Analyze samples in quadruplicate.	Not specified.	Not specified.
Blanks	Method blanks analyzed; frequency not specified.	Method blanks analyzed; frequency not specified.	Method blanks analyzed; frequency not specified.
Preservation/Storage Conditions	pH \leq 2 with HCl or H ₂ SO ₄ . Protect from light & atmospheric O ₂ . Store at 4°C.	pH \leq 2 with HCl or H ₂ SO ₄ . Protect from light & atmospheric O ₂ . Store at 4°C.	pH \leq 2 with H ₂ SO ₄ or H ₃ PO ₄ <u>only</u> if inorganic carbon is later purged. Protect from light. Store at 4°C.
Holding Time (3)	28 days	28 days	28 days
Sample Volume Required (4)	Not specified.	Not specified.	Not specified.
Other Criteria (Method Specific)	None.	None.	None.

Notes:

- (1) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (2) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (3) Unless otherwise indicated, holding times are from the date of sample collection.
- (4) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF TRACE METALS BY FLAME AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

Method - Parameter 1	SW-846 Method 7000 Series	EPA Series Method 200 Series	Standard Methods Method 3000 Series	CLP (Inorganic SOW)
Applicability	Drinking, surface, saline waters, domestic and industrial wastes, extracts, soils, sludges, sediments, industrial and other solid wastes	Drinking, surface, and saline waters; domestic and industrial wastes	Drinking, surface, saline, groundwaters, and wastewaters	Water, soil, and sediment
Number of Analytes (1)	27 total	33 total	38 total	13 total
Method Validation (2)	Not specified.	Not specified.	Not specified.	Not specified.
QC Check Standards	Verify calibration with an independent check standard. %R=90-110.	Performance Sample: One (blind) sample analyzed per year for metals being determined; results within EPA control limits. OPTIONAL: Known reference standards analyzed once per quarter for metals being determined	Verify calibration with independent check standard. %R=95-105.	Initial calibration verified with independent standard. %R=90-110. Digested QC check standard analyzed with each sample batch. %R=80-120.
Method Detection Limit	Detection limits listed in Table 1 of method 7000A.	Detection limits listed in Table 1 of Metals Introductory chapter.	FLAA: IDLs listed in Table 3111.I of Method 3111A. GFAA: IDLs listed in Table 3113.II of Method 3113A.	CRDLs listed in Exhibit C of SOW. IDLs determined quarterly.
Standard Solution Expiration (3)	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.
Initial Calibration	Minimum of 3 levels plus a blank	Minimum of 3 levels plus a blank	Minimum of 3 levels plus a blank	Minimum of 3 levels plus a blank (one standard at CRDL).
Continuing Calibration	Analyze a mid-level calibration standard or QC check standard after every 10 samples. %R=80-120.	Analyze a low-level standard daily or every 20 samples, whichever is more frequent. %R=90-110.	Analyze a mid-level standard after every 10 samples. %R=90-110.	Analyze mid-level calibration standard after each 10 samples or every 2 hours, whichever is more frequent. %R=90-110.
Surrogate Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Internal Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Accuracy/Precision	One MS/MSD per batch of samples processed at the same time. %R=75-125. %RPD<20.	OPTIONAL: One duplicate sample per every 10 samples, or per each set of samples (if set contains < 10). Results within EPA control limits.	Spike samples prior to digestion (frequency not specified). %R=85-115. GFAA only: analyze all digestates in duplicate.	One MS and 1 duplicate per 20 samples or each sample batch, whichever is more frequent. %R=75-125. %RPD<20.
Blanks	One method blank per batch of samples processed at the same time. One calibration blank with curve.	Method blank not specified. Calibration blank with curve.	One method preparation blank per batch of samples processed at the same time. Analyze calibration blank after every 10 samples.	One method blank with very 20 samples or each sample batch, whichever is more frequent. Analyze calibration blanks after every 10 samples or 2 hours, whichever is more frequent.

DETERMINATION OF TRACE METALS BY FLAME AND GRAPHITE FURNACE ATOMIC ABSORPTION SPECTROSCOPY

Method - Parameter 1	SW-846 Method 7000 Series	EPA Series Method 2000 Series	Standard Methods Method 3000 Series	CLP (Inorganic S.O.W.)
Preservation/ Storage Conditions	Aqueous: pH \leq 2 with HNO ₃ Solid: Store at 4°C.	pH \leq 2 with HNO ₃	pH \leq 2 with HNO ₃	Aqueous: pH \leq 2 with HNO ₃ Solid: Store at 4°C.
Holding Time (4)	6 months	6 months	6 months	180 days from sample receipt
Sample Volume Required (5)	100 mLs (aqueous) 2 grams (solid)	100 mLs	100 mLs	100 mLs (aqueous) 2 grams (solid)
Other Criteria (Method-Specific)	Test for matrix interference with each matrix using serial dilution (if >25X detection limit) or post-digestion spike. Use standard additions to compensate for matrix interferences.	For GFAA, verify the absence of interferences by diluting and spiking each matrix. %R=90-110%. Use standard addition to compensate for matrix interferences.	Test for matrix interference with each matrix by analyzing undiluted and diluted samples.	CRDL standard run at beginning and end of run, or minimum of twice per 8 hours. All GFAA digestates injected in duplicate. %RPD<20. All GFAA digestates spiked to determine matrix interferences. If verified, MSA used.

Notes:

- (1) Analyte lists may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF MERCURY BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY

Method - Parameter 1	SW-846 Methods 7470/7471	EPA Series Methods 245.1/245.5	Standard Methods Method 3112B	CLP (Inorganic SOW)
Applicability	Drinking, surface, saline waters, domestic and industrial wastes, extracts, soils, sludges, sediments, industrial and other solid wastes	Drinking, surface, and saline waters, domestic and industrial wastes, soils, sediments, and sludges	Drinking, surface, saline, groundwaters, and wastewaters	Water, soil, and sediment
Number of Analytes	Hg only	Hg only	Hg only	Hg only
Method Validation (1)	Not specified.	Not specified.	Not specified.	Not specified.
QC Check Standards	Verify calibration with an independent check standard. %R=90-110.	Performance Sample: One (blind) sample analyzed per year for metals being determined; results within EPA control limits. OPTIONAL: Known reference standards analyzed once per quarter for metals being determined.	Verify calibration with independent check standard. %R=95-105.	Initial calibration verified with independent standard. %R=80-120. Digested QC check standard analyzed with each sample batch. %R=80-120.
Method Detection Limit	0.0002 mg/L	0.0002 mg/L	Not specified.	CRDL: 0.0002 mg/L
Standard Solution Expiration (2)	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.	Stock standards: Not specified. Calibration standards: Prepare fresh at time of analysis.
Initial Calibration	Five levels plus a blank	Six levels plus a blank	Three levels plus a blank	Four levels plus a blank
Continuing Calibration	Analyze a mid-level calibration standard or QC check standard after every 10 samples. %R=80-120.	Analyze a low-level standard daily or every 20 samples, whichever is more frequent. %R=90-110.	Analyze a mid-level standard after every 10 samples. %R=90-110.	Analyze mid-level calibration standard after each 10 samples or every 2 hours, whichever is more frequent. %R=80-120.
Surrogate Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Internal Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Accuracy/Precision	One MS/MSD per batch of samples processed at the same time. %R=75-125. %RPD<20.	OPTIONAL: One duplicate sample per every 10 samples, or per each batch of samples (if batch contains < 10). Results within EPA control limits.	Spike samples prior to digestion (frequency not specified). %R=85-115.	One MS and 1 duplicate per 20 samples or each sample batch, whichever is more frequent. %R=75-125. %RPD<20.

DETERMINATION OF MERCURY BY COLD VAPOR ATOMIC ABSORPTION SPECTROSCOPY

Method - Parameter 1	SW-846 Methods 7470/7471	EPA Series Methods 245.1/245.5	Standard Methods Method 3112B	CLP (Inorganic SOW)
Blanks	One method blank per batch of samples processed at the same time. One calibration blank with curve.	Method blank not specified. Calibration blank with curve.	One calibration blank with curve.	One method blank with every 20 samples or each sample batch, whichever is more frequent. Analyze calibration blanks after every 10 samples or 2 hours, whichever is more frequent.
Preservation/ Storage Conditions	Aqueous: pH \leq 2 with HNO ₃ Solid: Store at 4°C.	Aqueous: pH \leq 2 with HNO ₃ Solid: Store at 4°C.	pH \leq 2 with HNO ₃	Aqueous: pH \leq 2 with HNO ₃ Solid: Store at 4°C.
Holding Time (3)	28 days	28 days	28 days	26 days from sample receipt
Sample Volume Required (4)	100 mLs (aqueous) 0.2 grams in triplicate (solids)	100 mLs (aqueous) 0.2 grams in triplicate (solids)	100 mLs	100 mLs (aqueous) 0.2 grams in triplicate (solids)
Other Criteria (Method-Specific)	Use MSA to compensate for matrix interferences.	Use MSA to compensate for matrix interferences.	Use MSA to compensate for matrix interferences.	CRDL standard run at beginning and end of run, or minimum of twice per 8 hours.

Notes:

- (1) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (2) Indicates maximum usage time. If comparisons to QC check standards indicate a problem, more frequent preparation may be necessary.
- (3) Unless otherwise indicated, holding times are from the date of sample collection.
- (4) Minimum volume for analysis. Additional volumes are required for the generation of QC data.

DETERMINATION OF TRACE METALS BY ICP

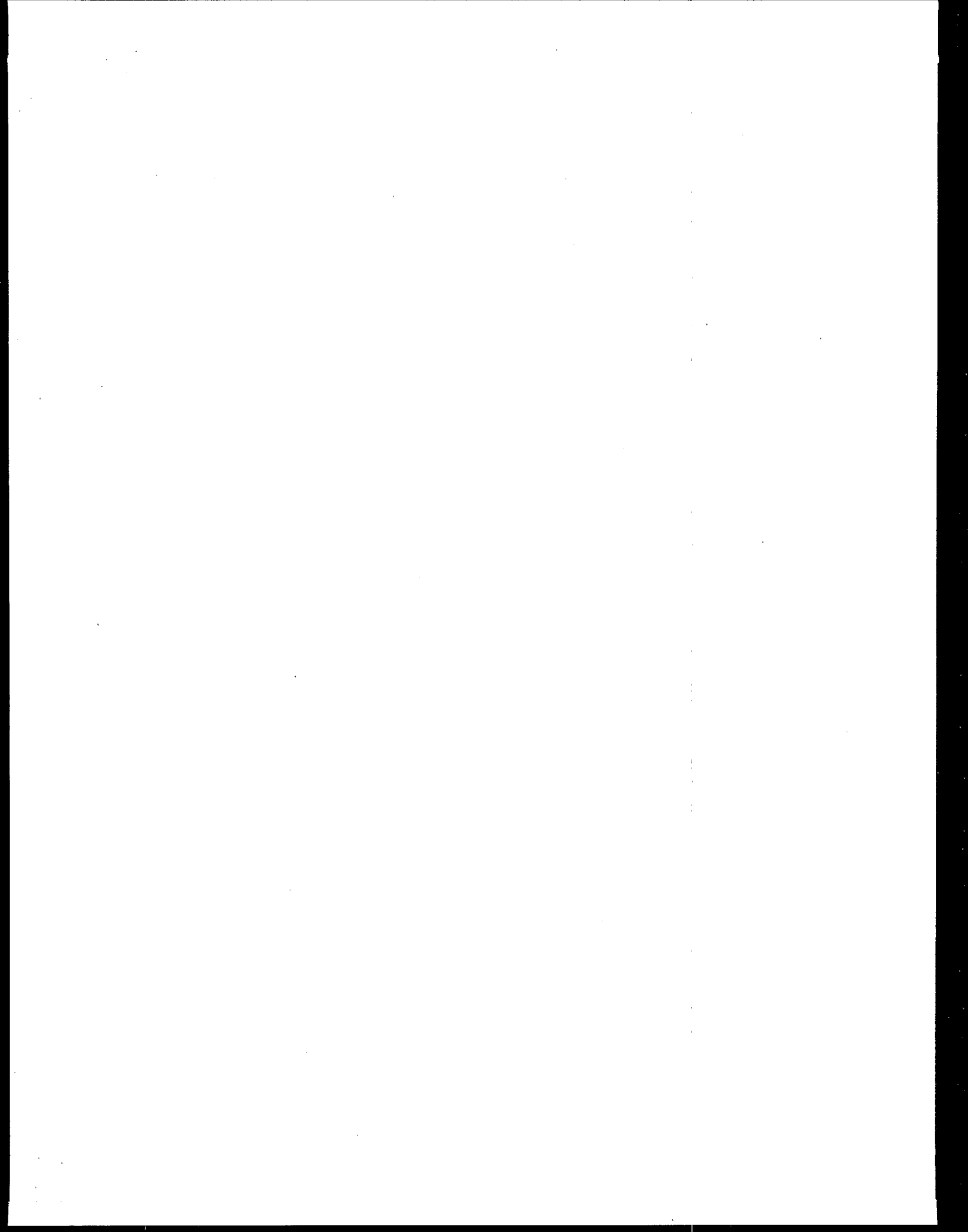
Method - Parameter 1	SW-846 Method 6010	EPA Series Method 200.7	Standard Methods Method 3120	CLP (Inorganic SOW)
Applicability	Nearly all matrices, including groundwater, extracts, industrial wastes, soils, sludges, sediments and solid wastes	Drinking water, surface, saline and industrial and domestic wastes	Water and wastewater	Water, soil, and sediment
Number of Analytes (1)	26 total	25 total (same as CLP)	27 total	25 total (same as 200.7)
Method Validation (2)	Not specified.	Not specified.	Not specified.	Not specified.
QC Check Standards	Verify calibration with an independently prepared check standard.	Verify calibration with QC check standard from external source. If recovery is not 95-105%, recalibrate.	Analyze QC check standard with each sample batch. %R=95-105 of expected values.	Initial calibration verified with independent standard. %R=90-110. Digested QC check standard analyzed with each sample batch. %R=80-120.
Method Detection Limit	IDLs listed in Table 1 of method. MDLs vary by matrix.	IDLs listed in Table 1 of method. MDLs vary by matrix.	IDLs listed in Table 3120.1 of method.	CRDLs list in Exhibit C of SOW. IDLs determined quarterly.
Standard Solution Expiration (3)	Not specified.	Not specified.	Not specified.	Not specified.
Initial Calibration	Per instrument manufacturer's specifications (should consist of 3 levels and a blank).	Per instrument manufacturer's specifications.	Per instrument manufacturer's specifications.	Per instrument manufacturer's specifications.
Continuing Calibration	Analyze mid-level calibration standard after each 10 samples. %R=90-110.	Analyze mid-level calibration standard after each 10 samples. %R=95-105.	Analyze 2 mg/L instrument check standard after each 10 samples. %R=95-105.	Analyze mid-level calibration standard after each 10 samples or every 2 hours, whichever is more frequent. %R=90-110.
Surrogate Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Internal Standards	Not applicable.	Not applicable.	Not applicable.	Not applicable.
Accuracy/Precision	One MS/MSD per 20 samples or each batch of samples, whichever is more frequent. %R=75-125. %RPD <20.	Not specified.	Not specified.	One MS and one duplicate per 20 samples or each sample batch, whichever is more frequent. %R=75-125. %RPD <20.
Blanks	One method blank per batch of samples processed at the same time. Analyze calibration blank after each 10 samples.	One method blank per batch of samples processed at the same time. Analyze calibration blank after each 10 samples.	Method blank analyzed; frequency not specified.	Analyze a method blank with every 20 samples or each sample batch, whichever is more frequent. Analyze calibration blanks after every 10 samples or 2 hours, whichever is more frequent.

DETERMINATION OF TRACE METALS BY ICP

Method - Parameter 1	SW-846 Method 6010	EPA Series Method 200.7	Standard Methods Method 3120	CLP (Inorganic SOW)
Preservation/ Storage Conditions	Aqueous: pH \leq 2 with HNO ₃ Solid: Store at 4°C.	pH \leq 2 with HNO ₃	pH \leq 2 with HNO ₃	Aqueous: pH \leq 2 with HNO ₃ Solid: Store at 4°C.
Holding Time (4)	6 months	6 months	6 months	180 days from sample receipt.
Sample Volume Required (5)	100 mLs (aqueous) 2 grams (solid)	100 mLs	100 mLs	100 mLs (aqueous) 2 grams (solid)
Other Criteria (Method Specific)	Analyze ICS at beginning and end of run or twice during 8 hour shift, whichever is more frequent. Results \pm 20% of true value. Reanalyze highest standard after calibration. Results \pm 5% of true value. For each new matrix, if analyte >10X IDL, dilute 1:4. Dilution should be \pm 10% of original.	Analyze ICS at beginning, end and periodically during run. Results within 1.5X SD of mean.	Determine interference correction factors each time samples are analyzed. Test for matrix interference with each matrix using serial dilution (>1mg/L) or post- digestion spike (<1mg/L).	ICS analysis: same as 6010A. CRDL standard run at beginning and end of run, or minimum of twice per 8 hours. Serial dilution analysis must be performed on a sample from each matrix. If concentration >50X IDL, must agree within \pm 10% of original. Verify linear ranges quarterly.

Notes:

- (1) Analyte lists may vary among methods; a smaller list in one method is not necessarily a subset of a larger list in another method.
- (2) Initial, one-time demonstration of ability to generate acceptable accuracy and precision.
- (3) Indicates maximum usage time. If comparisons to QC check standard indicate a problem, more frequent preparation may be necessary.
- (4) Unless otherwise indicated, holding times are from the date of sample collection.
- (5) Minimum volume for analysis. Additional volumes are required for the generation of QC data.



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