



# Application of Target Detection Limits and Designated Analytical Methods

*Remediation and Redevelopment Division  
Resource Materials*



**Prepared by:**  
Michigan Department of Environmental Quality  
Remediation and Redevelopment Division  
525 West Allegan Street  
Lansing, Michigan 48933  
March 2016



*In order to promote a consistent and informed approach for Michigan Department of Environmental Quality (MDEQ) staff, this document was developed to provide information to MDEQ staff and contractors for the application of the MDEQ published list of Target Detection Limits and Designated Analytical Methods.*

*This document is available as a technical reference to assist any party in the application of the MDEQ published list of Target Detection Limits and Designated Analytical Methods.*

*This document is explanatory and does not contain any regulatory requirements. It does not establish or affect the legal rights or obligations for groundwater modeling. It does not have the force or effect of law and is not legally binding on the public or the regulated community. Any regulatory decisions made by the MDEQ regarding groundwater modeling will be made by applying the governing statutes and Administrative Rules to relevant facts.*

Approved:

A handwritten signature in blue ink, appearing to read 'Robert Wagner', written over a horizontal line.

Robert Wagner, Chief  
Remediation and Redevelopment Division  
March 10, 2016

## Table of Contents

1.0	<a href="#">Introduction</a>	5
2.0	<a href="#">Target Detection Limits and Reporting Limits</a>	6
2.1	<a href="#">Use of Alternate Reporting Limits</a>	6
2.2	<a href="#">Elevation of Reporting Limits</a>	7
2.3	Project Planning	?
2.4	<a href="#">Application of Reporting Limits</a>	7
2.5	<a href="#">Contaminants with TDLs Higher than the Most Restrictive Criteria</a>	7
3.0	<a href="#">Designated Methods</a>	8
3.1	<a href="#">Confirmation of Contaminant Identities for Gas Chromatography Methods</a>	9
3.2	<a href="#">Ion Trap, Selected Ion Monitoring</a> , Single Ion Monitoring, and Mass Spectrometry/Mass Spectrometry (MS/MS) Procedures	9
4.0	<a href="#">Contaminants Without TDLs or Designated Methods</a>	9
5.0	<a href="#">Target Compound Lists</a>	9
6.0	<a href="#">Recommended Parameter List For Common Petroleum Products</a>	9
7.0	<a href="#">Soil Leaching Methods</a>	9
8.0	<a href="#">Sampling Methods For Volatile Organic Compounds in Soil</a>	12
8.1	<a href="#">Use of Procedures within Method 5035A</a>	12
8.1.1	<a href="#">Method 5035A, Section 8:</a> High Concentrations Soils Collected and Preserved in the Field	12
8.1.2	<a href="#">Method 5035A, Section 8:</a> High Concentration Soil Samples Collected Without Preservatives	13
8.1.3	<a href="#">Method 5035A, Section 8:</a> Low Concentration Soil Samples	13
8.1.4	<a href="#">Method 5035A:</a> Use of Soil Coring Storage Devices to Transfer Samples to the Laboratory	14
8.1.5	<a href="#">Method 5035A:</a> Use of Soil Coring Storage Devices for Leaching Purposed to Evaluate the Mobility of Volatiles in Soils	15
8.2	<a href="#">Laboratory Related Procedures and Documentation</a>	15
9.0	<a href="#">Data Records Retention</a>	15
	<a href="#">Appendix A</a> Definitions	17
	<a href="#">Appendix B</a> Recommended Parameters For Common Petroleum Products	18
	<a href="#">Appendix C</a> Cyanide Informational Materials	19
	<a href="#">Appendix D</a> Evaluating Exposure Due To Lead In Soils	27
	<a href="#">Appendix E</a> Measuring Non-Specific Petroleum Hydrocarbons	28
	<a href="#">Appendix F</a> MDEQ Requests For Review Of Laboratory Information	31
	<a href="#">Appendix G</a> Source Documents For Designated Methods	32



## **Summary**

This document is provided as a resource for environmental professionals involved in cleanup programs that rely upon the cleanup criteria developed pursuant to Part 201, Environmental Remediation, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (Part 201).

It provides:

- Information regarding the MDEQ specified target detection limits (TDLs) and analytical methods identified as capable of achieving the TDLs.
- A listing of the source documents for the designated methods.
- A recommended parameter list for common petroleum products.
- Information regarding MDEQ accepted soil leaching methods.
- Information regarding sampling methods for volatile organic compounds in soil.
- Background information on cyanide methods and criteria.
- Information regarding evaluation exposures due to lead in soils.
- Information regarding measuring non-specific petroleum products.
- Information regarding MDEQ requests for laboratory information and procedures as part of the supporting documentation to the data and conclusions of any submittal for MDEQ review and approval.



## 1.0 Introduction

This provides information pertaining to the application of the MDEQ published list of Target Detection Limits and Designated Analytical Methods in collection and evaluation of concentrations of hazardous substances in environmental media. The target detection limits (TDLs) and designated methods are applicable to environmental investigations, response activity, and corrective action performed pursuant to Part 201, Environmental Remediation, and Part 213, Leaking Underground Storage Tanks, of the Natural Resources and Environmental Protection Act, 1994 PA 451, as amended (Part 201 and Part 213).

The MDEQ is authorized to publish no more than once a year a list of Target Detection Limits and Designated Analytical Methods<sup>1</sup>. This list is integral in the development of the cleanup criteria because the TDL for a hazardous substance becomes the cleanup criteria when the TDL is greater than the risk-based criterion developed otherwise pursuant to Part 201<sup>2</sup>.

The tier 1 risk-based screening levels for Part 213 are the unrestricted residential and nonresidential generic cleanup criteria developed by the department pursuant to Part 201<sup>3</sup>. Therefore, the MDEQ list of Target Detection Limits and Designated Analytical Methods, the associated RRD procedures, and information provided within this reference, being components of the development of the cleanup criteria are applicable to Part 213 corrective actions.

The evaluation of sampling data to establish compliance with cleanup criteria relies upon data that reliably establishes a representative concentration of the hazardous substance in a given environmental medium. Prior to beginning site characterization and monitoring work data quality objectives should be established. Information on establishing appropriate objectives can be found in the U.S. EPA Guidance on Systematic Planning Using the Data Quality Objective Process EPA QA/G-4 (EPA/240/B-06/001 February 2006). Project planning should include development of a sampling plan. The sampling plan should include, appropriate to the situation, the following:

- Identification of the purpose and objectives of the sample collection.
- Identification of how the sample locations have been chosen to provide representative concentrations for soil samples located in the area affected by the release of hazardous substances and groundwater samples representative of the water moving in the aquifer, in the contaminant plume and/or the target zone where contaminants are expected to be located or to migrate.
- Establishment of reporting limits based on sampling objectives and relevant pathways. The MDEQ published list of Target Detection Limits and Designated Analytical Methods serves as the specifications for reporting limits when the most restrictive criterion for all pathways is applicable. Other reporting limits that may be necessary and should be provided to laboratories well in advance of the sample collection event to allow the laboratories to review and plan as appropriate.
- Standard Operating Procedures that detail the sample collection process.

---

<sup>1</sup> MCL 324.20101(1)(uu) Target detection limit

<sup>2</sup> MCL 324.20120a(10)

<sup>3</sup> MCL 324.21304a(2)



- Appropriate quality assurance to ensure data of sufficient quality is generated and appropriate quality control samples to measure and control data quality.

Any submittals for MDEQ review and approval that proposes sample collection or relies upon sampling data to establish compliance with cleanup criteria should either provide, or have readily available if requested, sufficient documentation to establish that the data quality objectives have been satisfied and the sample planning was adequate to allow reliance upon the data as representative. MDEQ staff may request supporting documentation to the data and conclusions of submittals ([See Appendix F](#)). Self-implemented response activity should maintain the supporting documentation.

## 2.0 Target Detection Limits and Reporting Limits

If you are not familiar with the statutory definition for the TDLs and how Reporting Limits are defined the definitions are provided in [Appendix A](#). In many cases, the numerical TDLs and reporting limits are the same. The following is provided to explain the relationship between the TDLs and reporting limits.

The TDLs have been established by the MDEQ for hazardous substances with generic cleanup criteria where available. Considerations for selecting a TDL are the capabilities of laboratories, methods published by government agencies, and the need to measure a hazardous substance at or below cleanup criteria. If the established TDL is greater than the risk-based value for a hazardous substance in a given environmental medium, the TDL shall be used as the cleanup criterion.

Reporting limits are the lowest levels that laboratories can measure quantitatively using the designated analytical methods of the published MDEQ Target Detection List and Designated Analytical Methods. The TDLs are the reporting limits required for the Part 201 and Part 213 programs. When possible, the TDLs are established to ensure that the most restrictive criterion for a hazardous substance can be measured.

For soil matrices, laboratory quantitative reporting limits should be equal to, or less than, the listed TDLs on a wet weight basis. Reported results are on a dry weight basis. For groundwater matrices, laboratory quantitative reporting limits should be equal to, or less than, the listed TDLs.

Achieving the TDL is critical for site investigation activities where the objective is characterization of the nature and extent of contamination. When the most restrictive criterion is applicable, the laboratories' reporting limits should be at or below the TDLs. For response activity and corrective action under Part 201 or Part 213, where there is no off-site migration and the goal is to determine compliance with applicable cleanup criteria, alternate reporting limits may be specified if the relevant pathways with the most restrictive cleanup criteria are appropriately determined to be "not relevant" thereby making the associated criteria not applicable.

### 2.1 Use of Alternate Reporting Limits

The TDLs in the MDEQ published list should be cited in project plans and provided to laboratories as specifications for reporting limits. Alternate reporting limits may be appropriate:



- When site-specific background levels or statewide default background levels for certain metals are substituted as the cleanup criteria. It may not be necessary to report data below the background levels.
- For response activity and corrective action under Part 201 or Part 213, when there is no off-site migration and the most restrictive criterion has been appropriately documented to not be applicable, reporting limits may be specified based on the most restrictive applicable criterion.
- When concentrations are determined for off-site waste disposal requirements.
- When sample concentrations lower than the TDL can be quantified for risk-based criteria lower than the TDL; i.e., the lower sample concentrations are within the analytical range of the method.

If alternative reporting limits are used for response activity or corrective actions that are submitted to the MDEQ for review and approval, supporting documentation for the use should be included as part of the submittal.

## **2.2 Elevation of Reporting Limits**

Reporting limits may be elevated above the TDLs because of matrix effects which can include interferences resulting from non-target compounds or high levels of target compounds, or interferences from species native to the sample matrices under investigation.

Supporting documentation for the use of elevated reporting limits should be provided as part of any response activity or corrective action submittal to the MDEQ for review and approval. Elevated reporting limits may be acceptable if the most restrictive cleanup criterion is not exceeded but may not be acceptable if the elevated reporting limit does exceed the most restrictive cleanup criterion. When reporting limits are increased and they exceed the cleanup criteria, it is necessary to further evaluate the elevated reporting limits. This may include a review of laboratory procedures to determine their appropriateness, re-analysis at other laboratories, further sample cleanups, modifications to methods, or other actions.

## **2.4 Application of Reporting Limits**

The concentrations quantitatively measured in groundwater samples may be compared directly to the generic cleanup criteria for groundwater. Quantitative concentrations for soils reported on a dry weight basis may be compared to the generic soil cleanup criteria, if applicable (See MDEQ Non-Aqueous Phase Liquid (NAPL) Characterization, Remediation, and Management for Petroleum Releases Resource Materials for further information). Concentrations are expressed in parts per billion (ppb), when possible, to allow direct comparison to the generic criteria. The concentrations quantitatively measured in air or soil gas may be compared directly to appropriate vapor intrusion screening levels. Information regarding use of the screening levels is available in MDEQ Policy and Procedure: 09-017 Guidance for the Vapor Intrusion Pathway. Concentrations of contaminants in air are routinely reported in units of parts per billion by volume (ppbv) or micrograms per cubic meter of air ( $\mu\text{g}/\text{m}^3$ ). These units are not interchangeable; they require conversion from one to the other. To assist, screening levels are provided in both units to facilitate comparison without conversion.

## **2.5 Contaminants with TDLs Higher than the Most Restrictive Criteria**

For contaminants that have TDLs greater than the most restrictive criterion (i.e., where the risk based criteria is lower than the TDL), it is important that laboratories follow reporting



requirements and report results down to the TDL, at a minimum. When reported results are below the TDL and are reliable, the results should be appropriately coded to indicate estimations. For any response activity or corrective actions submitted for MDEQ review and approval, explanation of the coding and any supporting document for use of estimated concentrations should be included as part of the submittal.

### 3.0 Designated Methods

The MDEQ published list of designated analytical methods includes multiple methods when more than one method has been judged capable of achieving the TDL. A list of source documents for the designated methods is included in [Appendix F](#). Published revisions of the listed methods may be used.

The designated methods for soil and groundwater matrices in the MDEQ published list are primarily from Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Edition 3 (SW-846), and those approved by the U.S. EPA for the federal Safe Drinking Water Act (SDWA) and the federal Clean Water Act (CWA), as provided in 40 CFR Part 122, 136, et al.<sup>4</sup> Methods in SW 846 and 40 CFR Part 122, 136, et al., not otherwise designated in the MDEQ published list are alternate methods that may be used if applied to the matrices they were designed to analyze and the method requirements for reporting and preservation are met. Occasionally alternate methods may be required if the results from samples collected are to be used to establish compliance to the programs administered by the SDWA or CWA. The designated methods for air and soil gas matrices are primarily from the publication Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air, Second Edition, (EPA/625/R-96/010b), by the Office of Research and Development of the U.S. EPA. Other validated and published methods for air or soil gas matrices from nationally recognized organizations may also be used; National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) methods for individual contaminants may be used provided the reporting limit allows comparison to the risk based screening levels.

Other alternative methods may be proposed to be included as designated methods, or for use on a case-by-case site-specific basis. Proposed methods will need to be well documented and provide reproducible quality data. MDEQ acceptance of alternative methods is recommended prior to implementation of response activity or corrective action.

For any response activity or corrective action submitted to the MDEQ for review and approval, explanation of the use of any of the alternative methods, including those listed as acceptable when conditions are met, should be included as part of the submittal. Self-implemented response activity should maintain supporting documentation for the use of any alternative method.

---

<sup>4</sup> Federal Register, Part III, Environmental Protection Agency, 40 CFR Part 122, 136, et al., Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; National Primary Drinking Water Regulations; National Secondary Drinking Water Regulations; Analysis and Sampling Procedures; Final Rule, March 12, 2007.





When designated methods are applied to contaminants not included in the compound list for the published method, method performance validations for those contaminants should be provided to the MDEQ as part of any response activity or corrective action submittal for MDEQ review and approval.

### **3.1 Confirmation of Contaminant Identities for Gas Chromatography Methods**

Confirmation of the contaminants' identities using mass spectrometry is preferred when measuring specific chemicals and when the TDL can be met. When mass spectrometry is not used, other confirmation techniques should be used whenever possible. Techniques that are routinely used are dual column analyses and confirmation using GC/MS for a select number of samples.

### **3.2 Selective Ion Monitoring**

Ion monitoring techniques using a single ion or more can be used to detect and measure contaminants when reporting limits cannot be attained using the GC/MS full scan technique and acceptable method performance can be met with selective ion monitoring (SIM). Documentation supporting the use of SIM should be part of any response activity or corrective action submitted for MDEQ review and approval.

### **4.0 Contaminants Without TDLs or Designated Analytical Methods**

Proposed TDLs and analytical methods should be submitted to the MDEQ for review and approval for contaminants with established risk-based criteria but not TDLs and for designated analytical methods or contaminants for which no cleanup criteria have been established. The submittal of proposed analytical methods will need to include detailed descriptions of the methods and method performance validations.

### **5.0 Target Compound List**

Target compound lists (TCLs) refer to the list of compounds that a laboratory routinely analyzes and reports using a specified method. The MDEQ Lab TCLs are provided on the MDEQ website ([MDEQ Lab TCLs](#)). The MDEQ Lab TCLs represent those compounds analyzed during state funded investigations. These lists are provided for informational purposes only. In some situations it may be necessary to conduct analyses for compounds not included on these lists.

### **6.0 Recommended Parameter List For Common Petroleum Products**

In addition to the MDEQ Lab TCLs, a recommended parameter list for common petroleum products was previously published as part of former Storage Tank Division Operational Memorandum No. 14. MDEQ has been requested to maintain this list by external users. The list is available as [Appendix B](#). The list should be used for site characterization purposes to identify the contaminants of concern which require action. Care should be taken to ensure that the more mobile groundwater contaminants are accounted for during the site characterization process.

### **7.0 Soil Leaching Methods**

If soil concentrations do not exceed the applicable generic criteria then leachate testing is not necessary. If soil concentrations exceed applicable generic soil criteria based upon leaching of hazardous substances into groundwater, leachate testing is an alternative to demonstrate



compliance. Leachate concentrations are determined by a method that best represents in-situ conditions<sup>5</sup>. Information regarding the test methods identified as acceptable by rule, and additional methods and specifications that have been judged by the MDEQ to best represent in-situ conditions follows:

- Toxicity Characteristic Leaching Procedure (TCLP), U.S. EPA Method 1311, July 1992, as set forth in SW-846. Buffered acetic acid solutions at pH 2.88 or 4.93 are used for leaching soils to determine the concentrations of metals, semi-volatiles, pesticides, and volatiles that can be leached. This method is not acceptable for leaching soils to determine the concentrations of cyanides, sulfides, and hexavalent chromium that can be leached.
- Synthetic Precipitation Leaching Procedure (SPLP), U.S. EPA Method 1312, September 1994, as set forth in SW-846. Extraction Fluid #1, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> solutions at pH 4.20, is used for leaching soils to determine the concentrations of metals, semi-volatiles, and pesticides that can be leached. Extraction Fluid #3, reagent water, is used for leaching soils to determine the concentrations of cyanides, sulfides, volatiles, and hexavalent chromium that can be leached.
- ASTM Neutral Leach Procedure, ASTM D3987-85 (2004). Reagent water is used for leaching soils to determine the concentrations of semi-volatiles, pesticides, cyanide, sulfides, and hexavalent chromium that can be leached. This method is not acceptable for leaching soils to determine the concentrations of metals and volatiles that can be leached. This procedure provides for reporting the leachable contaminant levels in terms of the weight of the soil (mg/Kg). However, in order to use this soil leaching procedure for the purpose of evaluating contaminant mobility and potential impact on groundwater, leachable contaminant levels are converted to be reported in terms of the volume of the leaching fluid, in milligram per liter (ug/L) units. This requirement should be conveyed to the laboratory prior to sample analysis.
- ASTM D5233-92 (2004), ASTM Single Batch. Buffered acetic acid solutions at pH 2.88 or 4.93 are used to leach soils and determine the concentrations of metals, semi-volatiles, and pesticides that can be leached. This method is not acceptable for leaching soils to determine the concentrations of volatiles, cyanides, sulfides, and hexavalent chromium that can be leached. This method is useful for large particle-sized materials. Any monolith subject to this method also is evaluated with ASTM D4842-89 to evaluate freeze-thaw effects.

Proposals for use of other standard methods may be made to the MDEQ for consideration. Other proposed methods need to be well documented and produce reproducible, quality data. Preference will be given to methods which are developed by the U.S. EPA or national organizations such as ASTM International (formerly the American Society for Testing and Materials).

If contaminants in the soils have the potential to be characteristically hazardous, e.g., the total concentrations exceed the screening value of 20 times the TCLP regulatory limit, then TCLP testing may be necessary to determine the applicability of Part 111, Hazardous Waste

---

<sup>5</sup> R 299.22(2) Generic cleanup criteria for soil based on leaching of hazardous substances into groundwater



Management, of NREPA (Part 111) and the associated administrative rules. Soils determined to be hazardous waste are subject to regulation under Part 111.

Leachate testing is not necessary to demonstrate compliance with applicable criteria if soil concentrations do not exceed the applicable generic soil criteria based upon leaching of hazardous substances into groundwater. If the leachate concentration generated by background soils, or the background groundwater concentration is greater than the generic criteria, the background concentration is used in place of the risk-based value as the cleanup criterion. Background soils and background groundwater concentrations represent background conditions not impacted by a release at or regionally proximate to, the facility<sup>6</sup>.

If leachate analysis data is relied upon, to assure that soils do not pose a threat of aquifer contamination, the concentration of a hazardous substance in soil needs to be below that which produces a concentration in soil leachate that is equal to or less than the most restrictive applicable groundwater criteria. The concentration in soil needs to be established to determine what concentrations do not leach above applicable criteria. An analysis of samples of the same soils needs to be conducted, in accordance with an appropriate acceptable method, to determine concentrations of contaminants in the soils prior to leaching. Options for soil collection include collecting enough soil to allow separation into aliquots of sufficient size that analysis of total and leached concentrations of the contaminants can be conducted; or for this comparison, soil may be collected using an acceptable soil coring device with preparation or freezing within 48 hours of collection ([Section 8.1.5](#) contains additional information regarding the use of soil coring devices). Holding time should be carefully monitored. A separate soil sample cannot be subsequently collected after leaching is conducted and used to determine concentrations of total contaminants. The laboratory data for total concentrations of the contaminants in the soils needs to be provided along with the laboratory data for concentrations leached from the soil.

Soil sample collection and preservation specifications for volatiles analysis require different collection methods to obtain samples appropriate for both leachate and soil analyses. Specifications for the appropriate collection of samples to determine total concentrations of volatile contaminants in soil, or to determine volatile contaminants leached from soil are available in [Section 8.0](#).

### **Integrity of Soils**

The crushing, cutting, grinding, sieving and filtering, or other procedures that may alter the physical soil characteristics are not appropriate for soil leachate sampling. Such procedures may be appropriate for leachate testing of other types of materials, such as brick and concrete.

### **Quality Control**

Leachate analysis should have associated quality control as provided by the method being used.

---

<sup>6</sup> MCL 324.20101(1)(e) Background concentration



## **8.0 Sampling Methods For Volatile Organic Compounds in Soil**

This section provides additional information concerning the collection and preservation of soil samples using the procedures in the U.S. EPA SW-846 Method 5035A for analysis of volatile organic compounds (VOCs), commonly referenced as methanol preservation procedures. The evaluation of sampling data to determine compliance with risk based cleanup criteria or to manage exposures requires data that reliably establish representative concentrations of the hazardous substances in a given environmental media. To produce reliable representative analytical results for VOCs, the MDEQ implemented the use of the methanol preservation procedures for soil samples on April 30, 1998.

The requirements for collection and preservation of samples using the U.S. EPA Method 5035A are based on the latest revision of that method. To ensure representative sampling data, samples for analysis should be collected into the analytical jars or vials directly from the sampling device as quickly as possible to minimize the loss of VOCs due to volatilization. Soil samples (both discreet and incremental) should not be transferred from the sampling device to a secondary container (e.g., sample bottle, zip lock bag, aluminum foil, or sampling bowls) for future sample collection. Field screening may be used to decide which discrete samples will be submitted for analysis. For field screening, it is recommended that soil samples be split; with an undisturbed sample portion appropriately and quickly preserved and stored, and the remainder available for field screening. When performing incremental sampling for VOCs, each increment should immediately be added to the analytical jar containing methanol. Data from samples that are compromised during collection will not be considered representative of site conditions.

Applicable contaminants that can be measured are listed within the method. Other contaminants may be included if method performance data exist for the contaminant demonstrating the accuracy, precision, and detection that can be measured, and supporting documentation is part of any response activity or corrective action submittal for MDEQ review and approval. Laboratory chain-of-custody documents should clearly identify the preservative(s) used for each of the VOC samples collected.

### **8.1 Use of Procedures within Method 5035A**

The high concentration procedure described in Method 5035A, using methanol as a preservative and preserving samples in the field, is the preferred method for the collection of soils and analyses of VOCs. U.S. EPA Office of Solid Waste issued a memorandum titled Clarification Regarding Use of SW-846 Methods, August 7, 1998 that provided clarifications to method 5035. The clarifications are reflected in the MDEQ expectations for the collection and analyses of soils using the preferred procedure, and other procedures described in Method 5035A as provided below.

#### **8.1.1 Method 5035A, Section 8:**

##### **High Concentration Soils Collected and Preserved in the Field (MDEQ preferred procedure)**

The MDEQ accepts results generated using the methanol preservation procedure described for high concentration soils using Method 5035A for site investigations, response activity, and corrective action provided the method requirements listed below are followed and documented:



- Samples are preserved with methanol in the field using a procedure consistent with that provided in Method 5035A.
- Approximately 10 grams of soil are collected.
- The methanol is added immediately in the field with the collection of the sample.
- The methanol covers the soil. If more methanol needs to be added, it is better to double the amount if ampoules are used to establish the amount of methanol. Otherwise, the amount of methanol added needs to be measured. This will affect the reporting limits. Documentation of the amount of methanol added in the field logbook is provided to the laboratory.
- The ratio of methanol volume to soil weight is equal to or greater than one.
- Samples are sonicated for at least 20 minutes prior to analysis.
- An aliquot of methanol is taken after sonication and stored for analysis.
- The sample preserved with methanol is not used for analysis of volatiles once the aliquot of methanol is taken unless the original aliquot cannot be used.
- Results are reported, corrected for moisture, and miscibility of methanol with water.
- The Laboratory Standard Operating Procedures are provided.
- MDEQ published Target Detection Limits and Designated Analytical Methods have been followed.

#### **8.1.2 Method 5035A, Section 8:**

##### **High Concentration Soil Samples Collected Without Preservatives**

The MDEQ does not accept soil VOC analytical results to demonstrate compliance with applicable criteria if the soil samples have not been preserved. When the nature of the sample prevents sampling by the accepted procedures described in this document and bulk sampling is the only option that can be used, the results should be evaluated by a procedure approved by the RRD. Concentrations of contaminants from samples collected using the bulk sampling procedure (i.e., without preservation) should be interpreted as “the minimum concentration of contaminant.” When used in this context, the results can be used to demonstrate that the applicable criteria have been exceeded. However, if the results are less than the criteria, they cannot be used to demonstrate compliance with criteria for Part 201 or Part 213.

#### **8.1.3 Method 5035A, Section 8:**

##### **Low Concentration Soil Samples**

The MDEQ accepts results generated using the procedure described in Method 5035A for low concentration soil samples for site investigations, response activity, and corrective action. Careful review of the low level concentration provisions of Method 5035A and consultation with the laboratory should occur prior to sample collection. Acceptance of the results will depend upon adherence to the requirements in Method 5035A being met and those listed below being documented:

- The samples are not exposed to the atmosphere from collection to analyses.
- The sealed containers are attached directly to the analytical instrumentation.
- Sodium bisulfate is used as a preservative or information regarding soil conditions that validates the use of no chemical preservative is provided.
  - When soils are known or suspected to contain high levels of carbonate materials, test samples of the soils representative of sample locations should be collected in the field into a vial containing sodium bisulfate to check for effervescence. If there is

a slight amount of gas generated (several mL) as long as the vial is sealed quickly any loss of volatiles should be minimal and sample preservation with sodium bisulfate would be acceptable. If a rapid or vigorous reaction occurs, low level concentrations samples may be collected in vials without chemical preservation (e.g., using reagent grade water).

- When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative may not be strong enough to reduce the pH to below 2. Soils collected for low concentration preservation should be tested for alkalinity, in addition to effervescence. If the soils are strongly alkaline or highly calcareous, additional steps may be required to preserve the samples.
- Under the best of circumstances all samples should be chemically preserved in some manner. If chemical preservation is not possible and samples for VOC analytes are collected in reagent grade water, unless analyzed immediately on-site, there needs to be documentation that the soils are not undergoing biological degradation. If target analytes are not subject to biodegradation samples using reagent waters may be transported to the laboratory for analysis. The rationale for not chemically preserving samples and special considerations for analysis of such samples needs to be clearly documented.

Documentation of the use of alternative preservatives, as narrative text and the sample result report, should be part of any response activity or corrective action submitted for MDEQ review and approval.

#### **8.1.4 Method 5035A:**

##### **Use of Soil Coring Storage Devices to Transfer Samples to the Laboratory**

The MDEQ does not recommend the use of soil coring storage devices to transport soils to the laboratories when the primary purpose is to identify total volatile contaminants or to demonstrate compliance with cleanup criteria, except to evaluate the leaching of volatiles from soils as provided in Section 8.1.5. To document the use of soil coring storage devices will provide representative results the following should be part of any response activity or corrective action submittal for MDEQ review and approval.

- Scientific studies are available that demonstrate the device to be effective for the use intended. The manufacturer of the device should be contacted regarding studies that prove them effective.
- Demonstration of the effectiveness of the devices to retain volatile chemicals for the specific chemicals of concern at the facility. Demonstration of the effectiveness of the devices proposed to be used can be accomplished using duplicate sampling. The demonstration needs to include duplicate samples collected using methanol preservation in the field. Duplicate samples should be collected for a minimum of one sample, or for at least one of every five samples collected.
- Written protocols are established regarding the use of the devices to collect and store samples and to preserve samples at the laboratory.
- Confirmation samples are collected using methanol preservation in the field. Confirmation samples should be collected for a minimum of two samples, or for at least two from every ten samples collected.
- All requirements of Method 5035A regarding the use of the samplers have been met.



### 8.1.5 Method 5035A:

#### Use of Soil Coring Storage Devices for Leaching Purposes to Evaluate the Mobility of Volatiles in Soils

Soil coring devices are used to evaluate the leaching of volatiles from soils as follows:

A soil coring storage device, documented to be effective for retaining the volatiles that are to be analyzed, is used for collecting a 25 gm ( $\pm$  3 gm) soil sample. The sample weight is determined in the field by subtracting the device weight from the weight of the device with the soil. Exposing the soil to the environment to obtain the weight either in the field or in the laboratory is not acceptable. Two options are available for leachate testing:

1. The soil can be collected, cooled to  $\leq 6^\circ$  C for transfer to the laboratory, and extruded from the coring device directly into the leaching fluid within 48 hours of collection.
2. The sample can be cooled to  $\leq 6^\circ$  C for transfer to the laboratory, sent to the laboratory within 48 hours and frozen at  $< -20$  to  $-7^\circ$  C. The sample is leached within 14 days.

After completion of the leaching procedure, an aliquot of leachate is immediately collected and preserved as a volatile organic water sample. If large sample sizes are required, multiple coring devices should be used.

### 8.2 Laboratory Related Procedures and Documentation

The laboratory selected is expected to have written Standard Operating Procedures that require information regarding the handling of methanol preserved soils. The laboratory should first be contacted regarding their specific requirements, but at a minimum the following documentation needs to be included:

- Quality of the methanol used.
- Percent of moisture in the samples (determined using separate vial/container with just soil).
- Dates and times samples were collected.
- Dates samples were received at the laboratory.
- Sample weights.
- Actual ratios of methanol-to-soil.
- Sonication dates and times.
- Minutes of sonication, if different from 20 minutes.

### References

U.S. EPA Office of Solid Waste Memorandum regarding Clarification Regarding Use of SW-846 Methods, August 7, 1998

### 9.0 Data Records Retention

The required retention times after submittal to the MDEQ of a Part 201 No Further Action Report or Part 213 Closure Report are established by statute<sup>7</sup>. The documents, data and reports include the raw data relied upon not summaries.

---

<sup>7</sup> Section 20114d(7) and Section 21312a(1)(d) of the NREPA



## Appendices

- [Appendix A:](#) Definitions
- [Appendix B:](#) Recommended Parameters for Common Petroleum Products
- [Appendix C:](#) Cyanide Informational Materials
- [Appendix D:](#) Evaluating Exposure Due to Lead in Soils
- [Appendix E:](#) Measuring Non-Specific Petroleum Hydrocarbons
- [Appendix F:](#) MDEQ Requests For Review Of Laboratory Information
- [Appendix G:](#) Source Documents For Designated Methods





## Appendix A

### Definitions

Key definitions for terms used in this document:

NREPA:	The Natural Resources and Environmental Protection Act, 1994 PA 451, as amended
Part 201:	Part 201, Environmental Remediation, of NREPA
Part 213:	Part 213, Leaking Underground Storage Tanks, of NREPA
MDEQ:	Michigan Department of Environmental Quality
MDEQ Lab:	Michigan Department of Environmental Quality, Environmental Lab
RRD:	Remediation and Redevelopment Division
U.S. EPA:	United States Environmental Protection Agency
Criteria or Criterion:	Includes the cleanup criteria for Part 201 and the Risk-Based Screening Levels as defined in Part 213
DRO:	Diesel Range Organics
Facility:	Includes "facility" as defined in Part 201 and "site" or "property" as defined in Part 213
GC/MS:	Gas chromatography with mass spectrometry
GRO:	Gasoline Range Organics
HEM:	Hexane Extractable Material
Method 5035A:	U.S. EPA SW-846 Method 5035A, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," Test Method for Evaluating Solid Waste, Physical/Chemical Methods, SW-846, United States Environmental Protection Agency, Office of Solid Waste and Emergency Response, Draft Revision 1, July 2002.
NAPL	Nonaqueous-phase liquids or a nonaqueous-phase liquid solution composed of 1 or more organic compounds that are immiscible or sparingly soluble in water.
ORO:	Oil Range Organics
Purge-and-Trap:	Refers to the analytical procedure that is commonly used for measuring volatile organic compounds. Chemicals used in this procedure are certified to be uncontaminated with the target compounds analyzed. Methanol certified as such is referred to as "purge-and-trap" grade methanol.
Reporting Limit:	The lowest level that can be reliably achieved within specified limits of precision and accuracy under routine laboratory conditions and based on quantitation, and normal operation of the laboratory.
Sonication:	The procedure for mixing the soil with methanol using sound waves.
TDLs:	Target detection limits as defined in Part 201 [Section 20101(1)(uu)] means the detection limit for a hazardous substance in a given environmental medium that is specified by the MDEQ on a list that it publishes not more than once a year. The TDL for a given hazardous



**Remediation and Redevelopment Division**  
Michigan Department of Environmental Quality

substance is greater than or equal to the method detection limit for that hazardous substance.

TRPHs:

Total Recoverable Petroleum Hydrocarbons

VOCs:

Volatile Organic Compounds.



Appendix B

Recommended Parameters For Common Petroleum Products

Parameters	Leaded Gasoline <sup>1</sup>	Unleaded Gasoline <sup>2</sup>	Petro. Solv <sup>3</sup>	Light Distillate Oils <sup>4</sup>	Residual Oils <sup>5</sup>	Used Motor	Waste Oils <sup>7</sup>	Unknown
BTEX	X	X	X	X		X	X	X
Trimethylbenzene Isomers (TMB) <sup>8</sup>	X	X	X	X	X	X	X	X
MTBE		X						X
1,2-Dibromoethane <sup>1</sup> (ethylene dibromide)	X					X	X	X
1,2-Dichloroethane <sup>1</sup>	X					X	X	X
PNAs <sup>9</sup>			X	X	X	X		X
Naphthalene/ 2-methylnaphthalene	X	X						X
Cadmium <sup>10</sup>						X	X	X
Chromium <sup>10</sup>						X	X	X
Lead <sup>10</sup>	X					X	X	X
Volatile Halocarbons <sup>11</sup>						X	X	X
PCBs							X	X
Diesel Range Organics (DRO) <sup>12</sup>			X	X	X	X	X	X
Gasoline Range Organics (GRO) <sup>12</sup>	X	X	X					X
Oil Range Organics (ORO) <sup>12</sup>					X	X	X	X



**Footnotes:**

1. 1,2-dichloroethane and 1,2-dibromoethane may be present in leaded gasoline and leaded aviation gasoline and should be analyzed for if believed to be present.
2. This category includes aviation gasoline, regular, mid-grade and premium unleaded fuels or any fuel blend containing MTBE.
3. Petroleum solvents include petroleum spirits, mineral spirits, VM and P naphthas and stoddard solvent.
4. Light distillate oils include fuel oils #1, #2, diesel oils #1-D, #2-D, kerosene, Jet A and jet propellants (JP) #4, #7 and #8.
5. Residual oils include residual fuel oils #4, #5 and #6 (Bunker C), lubricating oils and hydraulic fluids. Most of these fluids are mineral oil based and can be measured by methods identified above. However, some hydraulic fluids are synthetic or water based and will not be detected by these methods.
6. Used oil is any oil that has been refined from crude or synthetic oil and as a result of use becomes unsuitable for its original purpose due to loss of original properties, or presence of impurities. Used motor oils may be suitable for further use and may be economically recyclable. Used motor oils include spent motor oils, other lubricating oils and hydraulic oils from the servicing of automotive vehicles which are not contaminated by cleaning solvents or halogenated solvents.
7. Waste oil is defined as “used oil” that has been contaminated by spilling, or by mixing with other waste, hazardous or otherwise.
8. Trimethylbenzene (TMB) isomers include 1,2,3- TMB, 1,2,4- TMB and 1,3,5- TMB.
9. PNAs include the 16 priority pollutant PNAs listed in Method 8310 plus 2-methylnaphthalene.
10. Metals are measured as totals.
11. Measurement of volatile halocarbons in used motor oil releases is not required if there is documentation that cleaning solvents and sources of volatile halocarbons have been excluded from used motor oil.
12. Gasoline Range Organics (GRO) are defined as compounds eluting from the GC between C6 (n-hexane) and C10 (n-decane); Diesel Range Organics are defined as compounds between n-alkane ranges C10-C20; Oil Range Organics are defined by as compounds n-alkane ranges C20-C34. (See [Appendix E](#) for additional information)



## Appendix C

### Cyanide Information Materials

This document provides background information relevant to the analytical methods designated by the MDEQ Remediation and Redevelopment Division (RRD) for measuring cyanide in environmental media and the generic cleanup criteria for cyanide to which the reported concentrations are compared.

Footnote (P) in the Part 201 Cleanup Criteria Requirement for Response Activity Rules [R 299.49(1)(P)], reads as follows:

“Amenable cyanide methods [U.S. EPA Method 335.1] or method OIA-1677[available cyanide] shall be used to quantify cyanide concentrations for compliance with all groundwater criteria. Total cyanide methods or method OIA-1677[available cyanide] shall be used to quantify cyanide concentrations for compliance with soil criteria. Industrial/commercial direct contact criteria may not be protective of the potential for release of hydrogen cyanide gas. Additional land or resource use restrictions may be necessary to protect for the acute inhalation concerns associated with hydrogen cyanide gas.”

### Human and Environmental Health Aspects

Cyanides comprise a wide range of inorganic and organic compounds of varying chemical complexity all of which contain the cyano group, a carbon atom triply bonded to a nitrogen atom ( $-C\equiv N$ ). Hydrogen cyanide (HCN) and the cyanide anion ( $CN^-$ ) are collectively referred to as “free cyanide” and are the most toxic chemical forms of cyanides, regardless of the parent chemical form that they may be generated from. Some parent cyanide molecules can release free cyanide more readily than others under environmental conditions. Free cyanide is the basis of the generic Part 201 risk-based cleanup criteria. The severity of cyanide’s toxic effects will be dependent, in part, on the chemical form and physical state of the parent cyanide molecule as well as the route and duration of exposure of the receptor.

The generic soil direct contact criterion of 12 parts per million (ppm) for residential land use is protective of acute ingestion of cyanide contaminated soil by a child. The generic soil direct contact criterion of 250 ppm for nonresidential land use is protective for the generation of hydrogen cyanide gas. Cyanide concentrations of 760 ppm are acceptable for nonresidential land uses if a site specific demonstration is made that releasable cyanide in soil when exposed to pH conditions between 2 and 12.5, will not generate toxic gases, vapors, or fumes in a quantity sufficient to present a danger to human health or the environment. Cyanide concentrations of 760 ppm for nonresidential land use are protective of acute ingestion of cyanide contaminated soils by an adult. Site-specific circumstances at nonresidential properties where land-use patterns indicate that children may be present and engage in activities which pose a risk may warrant the development of site specific criterion or the application of the residential criterion to nonresidential properties.

## Cyanide Use

Cyanide can be chemically classified into inorganic and organic forms. Inorganic forms of cyanides occur in gas, aqueous, and solid physical states. Organic cyanides are typically found in the aqueous state. Examples of some different forms of cyanides are presented in Table 1.

HCN is a colorless or pale blue liquid or gas with a faint bitter almond-like odor. In an aqueous solution, it is a weak acid (Pesce, 1993). HCN is primarily used as a chemical intermediate in the manufacture of acrylates, synthetic fibers, plastics, and inorganic cyanide salts. It is also used as an agricultural fumigant and has various uses in the electroplating and mining industries (Cohrssen, 2001).

**Table 1 Chemical and Physical Forms of Cyanides (modified from Ghosh, 2005)**

Physical State	Chemical Form	Example	
Inorganic	Gas	Free cyanide Cyanide halogens	HCN CNCl, CNBr
	Aqueous	Free cyanide Weak metal-cyanide complexes Strong metal-cyanide complexes Cyanate Thiocyanate	HCN, CN <sup>-</sup> CdCN <sup>-</sup> Fe(CN) <sup>-4</sup> <sub>6</sub> CNO <sup>-</sup> SCN <sup>-</sup>
	Solid	Alkali earth metal-cyanides Alkali earth metal-metal-cyanides Other metal-metal-cyanides	NaCN K <sub>3</sub> Fe(CN) <sub>6</sub> Fe <sub>4</sub> (Fe(CN) <sub>6</sub> ) <sub>3</sub>
Aqueous	Organocyanides	CH <sub>3</sub> CN	

Simple alkali earth-cyanide complexes, such as sodium (NaCN) and potassium cyanide (KCN), are solid or crystalline hygroscopic salts that are highly soluble in water, and will readily dissolve to form free cyanide. Simple inorganic cyanide salts are widely used in precious metal recovery and electroplating processes, and to a lesser extent in case-hardening of steel, and production of dye, printing, and photography products (IPCS, 2004). They are also used in the manufacture of many organic and inorganic chemicals (e.g., nitriles, carboxylic acids, amides, esters, amines, and heavy metal cyanides) and in the production of chelating agents (Pesce, 1993).

Metal-cyanide complexes of varying complexity can occur in aqueous or solid forms. Sodium ferrocyanide (Na<sub>4</sub>(Fe(CN)<sub>6</sub>) and ferric ferrocyanide (Fe<sub>4</sub>(Fe(CN)<sub>6</sub>)<sub>3</sub>) are metal cyanide solids used as anti-caking agents in road salt, with the ferric form responsible for the blue coloration of road salt (Wong-Chong, 2005). Ferrocyanides are also used in the manufacture of textile dyes, photography reagents, detergents, and pesticides. Complex metal-cyanide complexes themselves are less toxic than free cyanide; however, their dissociation in solution can release free cyanide as well as the respective metal cation, which can also be toxic. In solution, iron-cyanide complexes can decompose to release free cyanide when exposed to ultraviolet light.

## Sources of Cyanide

Anthropogenic sources of environmental cyanide contamination are diverse. Atmospheric cyanide releases include chemical manufacturing and processing industries such as metallurgical industries and metal plating, and extraction of gold and silver from low-grade ores.

Other sources include volatilization from cyanide wastes disposed of in landfills and waste ponds, emissions from municipal solid waste incinerators, biomass burning, fossil fuel combustion (including vehicle emissions), agricultural fumigation activities, and the production of coke or other coal carbonization procedures.

Non-point sources of cyanide released to surface and groundwater can result from cyanide-containing road salt run-off, migration from landfills, and agricultural and atmospheric fallout and washout (ATSDR, 2006). Point sources of cyanide release to surface and groundwater include discharges from gold mining plants, wastewater treatment works, iron and steel production, and organic chemical industries (IPCS, 2004).

The principal natural sources of cyanides include over 2,000 fruit and vegetable plant species that produce cyanogenic glycosides (e.g., amygdalin, linamarin, prunasin, dhurrin, lotaustralin, and taxiphyllin) that can release free cyanide via hydrolysis (Ghosh, 2005; IPCS, 2004). Among these food sources, cassava (tapioca, manioc) and sorghum are staples for millions of people in many tropical countries. HCN is also released into the atmosphere by natural biogenic processes in higher plants, bacteria, and fungi (ATSDR, 2006).

## Dissociation of Metal-Cyanide Complexes

Cyanide is very reactive, readily forming simple salts with alkali earth cations and ionic complexes of varying stability with numerous transition metal cations. The primary risks from cyanide-containing metal complexes result from their potential to dissociate or decompose, releasing toxic free cyanide into the environment. Those complexes that are readily dissociable pose much more risk than those with low dissociation potential.

The degree to which metal cyanides dissociate has been determined for many of the transition metal-cyanide complexes that may be found in the environment and is based on their respective chemical stability in weak acid solutions (Dzombak, 2005). Strong metal-cyanide complexes have low dissociation potential, while weak metal-cyanide complexes are readily dissociable in a weak acid solution. Table 2 summarizes some metal cyanide forms found in the environment and their potential to dissociate.

For the purpose of clarifying the terms “Total” and “Available” as related to the laboratory analysis of cyanide (see below), cyanide from all chemical forms in Table 2 are measured using the *Total* cyanide analytical methods. Cyanide from weak metal-cyanide complexes is measured using *Available* cyanide analytical methods.



**Table 2 Dissociation Potential and Cyanide Analysis of Some Metal Cyanides**

<b>Stability in Weak Acid Solution</b>	
<b>Weak</b>	<b>Strong</b>
Cadmium Copper Mercury Nickel Silver Zinc	Iron Cobalt Gold
<b>Available</b>	
<b>Total</b>	

**Forms of Cyanide in the Environment**

Cyanide is released into the atmosphere mainly as HCN gas and, to a lesser extent, as particulate cyanides (ATSDR, 2006). Once in the atmosphere, these cyanides demonstrate long residence times and have the potential to be transported significant distances from their respective emission sources.

Cyanide most commonly exists in water as HCN, although other forms can occur, as even the stable metal-cyanide complexes become readily soluble in the mixed presence of alkali cyanides. The concentration of free cyanide that can be present in water is a function of water chemistry, primarily pH and temperature. HCN has a pKa value of 9.23 (Ghosh, 1999). Therefore, at a pH of 7, over 99% of the free cyanide in solution will exist as HCN. Because of its high vapor pressure, volatilization from surface water is a significant fate process for HCN, and possibly the alkali metal cyanides (ATSDR, 2006).

The most prevalent forms of cyanide in soil are the metal-cyanide complexes, of which the iron cyanides make up the majority. Iron cyanides, dominated by ferrocyanide, may comprise over 97% of total cyanides in either weathered or unweathered soils. Iron cyanides are very stable and are not expected to significantly dissociate or decompose to form free cyanide under normal environmental soil conditions. Industries that use or have disposed of cyanides on-site may treat cyanide-containing wastes with iron compounds to stabilize them as iron cyanides. Other metal cyanides common to soils, such as zinc and copper cyanides, may pose more of a risk as they can more readily dissociate, releasing free cyanide. The metal cyanides, including iron cyanide, are highly soluble in water. These cyanides can leach into the groundwater, though this is not considered a significant fate process.

**Measurement of Cyanide in Groundwater**

To adequately protect the public and environment from risks associated with exposure to free cyanide, it may be necessary to measure cyanide concentrations in environmental samples; specifically, those cyanide compounds that can readily dissociate and release free cyanide.





The analytical methods presented in the MDEQ published list of Target Detection Levels and Designated Analytical Methods for analyzing free cyanide generated from weak acid dissociable cyanide complexes, which include U.S. EPA Method 335.1 (Cyanides, Amenable to Chlorination) and U.S. EPA Method OIA-1677 or ASTM D6888-04 (Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry). Despite their different analytical approaches, each of these methods measures the cyanide from the same weak metal-cyanide complexes.

Footnote (P) states that the *Amenable* cyanide methods or OIA 1677 shall be used to measure cyanide in groundwater. However, the MDEQ recognizes that *Amenable* methods have several disadvantages. Identified issues related to the *Amenable* cyanide methods include: they are subject to interferences, the detection capability is insufficient for comparison to the most restrictive criterion, the methods' accuracy is questionable, and false negative results can occur. The *Amenable* methods do not measure the concentrations of cyanide from strong metal-cyanide complexes such as the iron, cobalt, and gold cyanides. The U.S. EPA Method OIA-1677 measures the same cyanide compounds as the *Amenable* methods but is more economical, has better detection capabilities, demonstrates fewer interferences, and has superior accuracy and precision, therefore it is the preferred designated analytical method. The footnote requirements will be revised as part of the current cleanup criteria update process.

### Measurements of Cyanide in Soils

Footnote (P) states that *Total* cyanide methods or the U.S. EPA Method OIA-1677 shall be used to measure cyanide concentrations in soils for comparison to the generic

Part 201 cleanup criteria. *Total* cyanide methods measure cyanide from both the weak and strong metal-cyanide complexes presented in Table 2. Other cyanide complexes not listed in Table 2 may be measured using the *Total* cyanide method. Cyanide concentrations measured using a *Total* cyanide method may overestimate the potential risk from free cyanide because this method includes cyanide from strong metal-cyanide complexes (e.g., iron cyanides) that are not expected to significantly contribute to free cyanide formation in the environment. The U.S. EPA Method OIA-1677 measures cyanide from free cyanide and weak metal-cyanide complexes (i.e., *Available* cyanides). When *Total* cyanide concentrations exceed the generic Part 201 soil cleanup criteria for cyanide, it is appropriate to utilize the U.S. EPA Method OIA-1677 to measure *Available* cyanide for comparison to the generic cleanup criteria. When possible, both measurements should be conducted on the same soil or soil extraction sample.

### Interpretation of Total and Available Cyanide Measurements

Free cyanide and all cyanide complexes in Table 2 are measured using *Total* cyanide methods, while only free cyanide and the weak metal-cyanide complexes are measured using *Available* cyanide methods. The most prevalent forms of metal cyanides in the environment are the iron cyanides, making up at least 97% of the cyanides in soils. Although the relative percent of the different cyanide compounds in water is unknown, it is expected to be high for iron cyanides based on their solubility and stability. Because the *Total* cyanide methods include the iron cyanides while *Available* cyanide methods do not, it is expected that the differences in concentrations measured by these two different methods may be considerable



and, in most cases, represent the levels of iron cyanides. If a site has a history of operations involving cobalt and/or gold, then the difference between the concentrations measured using *Total* and *Available* cyanide methods may be primarily due to the iron, cobalt, and gold cyanides.

### Analytical Methods to Distinguish Metal-Cyanide Complexes

There is a lack of methodology that can separate and measure concentrations of the individual metal-cyanide complexes in environmental samples. SW-846 Method 9015 (Metal Cyanide Complexes by Anion Exchange Chromatography and UV Detection) can resolve the metal-cyanide complexes presented in Table 3; however, this method is new and has not been used to any significant extent for cyanide analyses. Locating an environmental laboratory capable of conducting the method may be difficult.

**Table 3 Speciated Forms of Cyanide**

Cyanide Complex	Common Name
$[\text{Ag}(\text{CN})_2]^-$	Dicyanoargentate(I)
$[\text{Au}(\text{CN})_2]^-$	Dicyanoaurate(I)
$[\text{Co}(\text{CN})_6]^{3-}$	Hexacyanocobaltate(III)
$[\text{Cu}(\text{CN})_3]^{2-}$	Tricyanocuprate(I)
$[\text{Fe}(\text{CN})_6]^{3-}$	Hexacyanoferrate(III) or Ferricyanide
$[\text{Fe}(\text{CN})_6]^{4-}$	Hexacyanoferrate(II) or Ferrocyanide
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II)

### Other Considerations for Sites Contaminated with Cyanides

Free cyanide may decompose to form nitrate and ammonia (ATSDR, 2006). When high levels of cyanides are encountered, evaluation of nitrate and ammonia in groundwater should also be considered.

Industries that dispose of cyanide-containing wastes may treat them in various ways to reduce potential free cyanide production. Several chemical by-products of these treatment processes can result, most which are not listed in the Part 201 cleanup criteria tables. The most widely used commercial treatment process for cyanide-containing wastes, alkaline chlorination, reacts cyanide and chlorine in an alkaline solution, converting the cyanide into the less toxic cyanate ( $\text{CNO}^-$ ) via a cyanogen chloride ( $\text{CNCl}$ ) intermediate (Pesce, 1993). Cyanogen chloride is a highly toxic gas. Cyanates are soluble in water and can leach from soils into groundwater. Cyanates and cyanogen chloride are not currently listed in the Part 201 cleanup criteria tables.

Cyanides that come into contact with polysulfides and sulfur can easily be converted into thiocyanates, which are less toxic than free cyanide (Pesce, 1993). High levels of thiocyanates have been found in contaminated groundwater at sites where mining operations occur



(ATSDR, 2006). Thiocyanates are water soluble and can leach from soils into the groundwater. Thiocyanates are not currently listed in the Part 201 cleanup criteria tables.

## References

Agency for Toxic Substance and Disease Registry (ATSDR). 2006. *Toxicological Profile for Cyanide*. U.S. Department of Health and Human Services.

Cohrssen, B. Cyanides and Nitriles in *Patty's Toxicology*. Fifth Edition. E. Bingham et al. Eds. John Wiley & Sons, Inc. New York. 2001.

Dzombak, D.A. et al. Physical-Chemical Properties and Reactivity of Cyanide in Water and Soil in *Cyanide in Water and Soil: Chemistry, Risk and Management*. D.A. Dzombak et al., Eds. CRC Press. Boca Raton. 2005.

Ghosh, R.S. et al. 1999. Equilibrium Precipitation and Dissolution of Iron Cyanide Solids in Water. *Env. Eng. Sci.* 16(4): 293-313.

Ghosh, R.S. et al. Physical and Chemical Forms of Cyanide in *Cyanide in Water and Soil: Chemistry, Risk and Management*. D.A. Dzombak et al., Eds. CRC Press. Boca Raton. 2005.

International Program on Chemical Safety (IPCS). 2004. *Concise International Chemical Assessment Document 61: Hydrogen Cyanide and Cyanides: Human Health Aspects*. <http://www.inchem.org/documents/cicads/cicads/cicad61.htm#4.1>

Pesce, L.D. Cyanides in *Encyclopedia of Chemical Technology*. M. Howe-Grant Ed. John Wiley & Sons, Inc. New York. 1993. Pages 753-82.

Wong-Chong, G.M. et al. Introduction in *Cyanide in Water and Soil: Chemistry, Risk and Management*. D.A. Dzombak et al., Eds. CRC Press. Boca Raton. 2005.



## Appendix D

### Evaluating Exposure Due to Lead in Soils

The amount of lead in a soil sample has historically been evaluated by analyzing its total lead concentration. However, current evidence indicates that the lead concentration in the fine soil fraction, defined as less than 250 microns ( $\mu\text{m}$ ) in size, is more appropriate for comparison to soil direct contact and inhalation pathway criteria.

In 2003, the State of Michigan's *Childhood Lead Poisoning Prevention: A Call to Action* directed the MDEQ to review the most recent toxicological and other pertinent data to determine if the current Part 201 residential soil lead cleanup criterion is protective and to determine the most appropriate method of soil sampling. The U.S. EPA's review of lead data<sup>8</sup> from CERCLA sites demonstrated that the lead concentrations in the fine fraction often exceeded the total lead concentrations in the respective soil samples. The MDEQ's review of Michigan-specific lead data demonstrated findings similar to the U.S. EPA's conclusions.

Incidental ingestion is the major pathway of human exposure to lead in soil and dust. An inherent assumption of this exposure pathway is that the ingested soil and dust fraction is best represented by the lead concentration in the particle size fraction that sticks to the hands. Several studies indicate that the particle size fraction of soil and dust that sticks to the hands is the fine soil fraction and that a reasonable upper-bound for this fraction is 250  $\mu\text{m}$ . This is also the particle size fraction that is most likely to accumulate in the indoor environment, as a result of deposition of wind-blown soil and transport of soil on clothes, shoes, pets, toys, and other objects. Fine fraction soil lead concentration data were used in the calibration of the U.S. EPA's Integrated Exposure Uptake Biokinetic (IEUBK) Model for Lead in Children, as well as in the characterization of lead bioavailability from soil using either *in vivo* or *in vitro* studies. The MDEQ's residential Part 201 soil lead cleanup criterion is based on these resources.

While it is generally expected that fine soil fractions will be "enriched" in lead compared to their respective coarse or total soil fractions, in certain cases, the opposite situation may occur. In some soils, the coarse or total soil fraction may contain higher concentrations of lead. When coarser materials contain high lead concentrations, concerns about the future degradation of these coarser materials into finer particles should be addressed when developing response actions.

The MDEQ studied the relationship between total measured and fine fraction lead for the purposes of identifying a total measured lead concentration below which the fine fraction concentration is not expected to exceed 400 ppm, the residential soil lead criterion. The identification of 75 ppm as the corresponding total measured lead concentration threshold is based upon a data set submitted to the MDEQ for review in 2007. To further define the relationship between total measured lead and fine fraction lead concentrations, total measured and fine fraction soil lead paired data may be submitted to the RRD Toxicology Unit for evaluation.

---

<sup>8</sup> EPA Short Sheet: TRW Recommendations for Sampling and Analysis of Soil at Lead Sites EPA #540-F-00-010, OSWER #9285.7-38, April 2000



## Appendix E

### Measuring Non-Specific Petroleum Hydrocarbons

Summaries of the analytical methods and their application to petroleum type materials are provided.

**Table 1 Designated Screening Methods for Identifying the Presence of Petroleum Products or Petroleum-Related Materials**

<b>Contaminant</b>	<b>Method</b>
Gasoline Range Organics	Method 8015B/C GC/MS
Diesel Range Organics	Method 8015B/C/D GC/MS
Oil Range Organics	Method 8015B/C/D GC/MS
Hydrocarbon Patterns	Method 8015B/C/D GC/MS
TRPH, Infrared (soils)	8440
Petroleum Hydrocarbons, HEM (soils)	9071B
Petroleum Hydrocarbons, HEM Non-Polar Material (waters)	1664
Petroleum Hydrocarbons HEM Polar Material (waters)	1664

### Evidence of Petroleum Hydrocarbon Compounds

Using the methods identified in the MDEQ published list, the measurement of non-specific petroleum hydrocarbons in contaminated soil or groundwater are gross quantities without identification of specific contaminants and do not substitute for contaminant-specific analyses and comparison to cleanup criteria or risk based screening levels.

The amounts of petroleum hydrocarbons measured may be useful in evaluating the magnitude of petroleum contamination, determining the absence or presence of NAPL, determining the nature of the product (i.e., carbon range), to estimate the degree of NAPL saturation in the pore space of the soil, to aid in the delineation of the NAPL body, to determine whether the comparison to generic criteria is appropriate, and evaluating aesthetic concerns at a facility (See MDEQ Non-Aqueous Phase Liquid (NAPL) Characterization, Remediation, and Management for Petroleum Releases Resource Materials for additional information).

The groups of petroleum hydrocarbons measured by these non-specific methods are entirely method defined, and hence, results depend entirely on the method. To provide comparable data once petroleum hydrocarbons are quantified using a specific method the same method needs to be used for the analysis of all subsequent samples. It is not appropriate to compare results from different methods.

### Methods For Quantifying Hydrocarbons

Commonly used methods to measure petroleum hydrocarbons include:

- Methods Based on Petroleum Hydrocarbons Extractable using HEM.
- Method Based on Petroleum Hydrocarbons Extractable using Supercritical Carbon Dioxide and Infrared Measurements.

- Methods Based on Number of Carbons on Petroleum Hydrocarbon Compounds.

The specific designated analytical methods on the MDEQ published list are provided in Table 1, Designated Screening Methods for Identifying the Presence of Petroleum Products or Petroleum Related Materials for easy reference. Methods other than those on the MDEQ published list may be proposed for use as described in Section 3.0 Designated Methods.

### **Methods Based on Petroleum Hydrocarbons Extractable Using HEM**

*Method 1664 (waters): Using both HEM Polar Material and HEM Non-Polar Material.*

Polar material includes relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, and related materials. Non-polar material includes petroleum products other than polar materials. This method is not applicable to the measurement of materials that volatilize at temperatures below approximately 85° C. Lighter petroleum hydrocarbons (e.g., gasoline, #2 fuel oil) may be partially lost in the solvent removal operation used in this method. Some crude oils and heavy fuel oils contain a significant percentage of materials that are not measured because of their insolubility in n-hexane. This method is capable of measuring polar hydrocarbons and non-polar hydrocarbons in the range of 5-1,000 mg/L, and may be extended to higher levels by analysis of a smaller sample volume collected separately. The method detection limit is 1.4 mg/L, and the minimum level of quantitation is 5.0 mg/L. Results generally are reported as Petroleum Hydrocarbons, HEM Polar Material; or Petroleum Hydrocarbons, HEM Non-Polar Material. Common abbreviations are HEM Polar and HEM Non-Polar.

*Method 9071B (soils): Using HEM Material.*

The material sampled should be amenable to chemical drying and solvent extractions with hexane using a Soxhlet apparatus. Method 9071B is suitable for extracting relatively non-volatile hydrocarbons, vegetable oils, animal fats, waxes, soaps, greases, biological lipids, and related materials. Method 9071B is not recommended for measuring materials that volatilize at temperatures below 85° C. Lighter petroleum hydrocarbons (e.g., gasoline, #2 fuel oil) may be partially lost during the solvent removal process. Some crude oils and heavy fuel oils may contain materials that are not soluble in n-hexane, and recovery of these materials may be low. Results generally are reported as HEM Material.

### **Method Based on Petroleum Hydrocarbons Extractable Using Supercritical Carbon Dioxide and Infrared Measurements**

Method 8440 is used for the measurement of the group of petroleum hydrocarbons referred to as TRPHs. This group represents those petroleum hydrocarbons extracted with supercritical carbon dioxide using Method 3560, where interferences are removed with silica gel, and measurements made using infrared spectroscopy. Method 8440 is not applicable to the measurement of gasoline and other volatile petroleum fractions because of evaporative losses. Method 8440 can detect the TRPHs at concentrations of 10 mg/L in extracts. This translates to 10 mg/Kg in soils when a 3 gram sample is extracted by supercritical fluid extraction (assuming 100 percent extraction efficiency) and the final extract volume is 3 mL. Determination of the TRPHs is a measure of mineral oils only and does not include the biodegradable animal greases and vegetable oils captured in oil and grease measurements. These non-mineral oil contaminants may cause positive interferences with infrared analysis if they are not completely removed by the silica gel cleanup. Results generally are reported as TRPH.



## Methods Based on Number of Carbons on Petroleum Hydrocarbon Compounds

*GRO, DRO, and ORO:* Gas chromatography is used to separate petroleum hydrocarbon compounds based essentially on the number of carbons on the hydrocarbon compound, the order of separation being from lowest to highest carbons. All compounds from the environmental sample that are measured within a specified calibrated range, and based on specific compounds with known numbers of carbon atoms, are then quantified and reported as a group. Each group was established from knowledge of the abundance of the hydrocarbons in various types of petroleum products commonly encountered at the contaminated sites, such as gasoline, diesel, and oil products. For purposes of this document, those groups are GRO, DRO, and ORO.

Gasoline Range Organics (GRO) are defined by this method as compounds eluting from the GC between C6 (n-hexane) and C10 (n-decane).

Diesel Range Organics are defined by this method as compounds eluting from the GC between n-alkane ranges C10-C20.

Oil Range Organics are defined by this method as compounds eluting from the GC between n-alkane ranges C20-C34.

The GRO results may be another tool to use in evaluating releases of petroleum solvents, gasoline, kerosene, #2 fuel oil, and aviation type fuels. The DRO results may be useful for evaluating releases of products such as fuel oils, diesel fuels, and lubricating oils. The ORO results may be useful for evaluating releases of heavy oils, including crude oil or weathered oils.

The GRO, DRO, and ORO concentrations are defined by the method's analytical strategies used to separate them. The concentrations reported by the various methods are method-specific; therefore, the concentrations measured by any one method cannot be compared to concentrations obtained by other methods. If a specific method has been used historically to track cleanups, then the use of that method should be continued for comparative purposes.

Environmental samples may contain mixtures of petroleum products or the product released at a site may not be known. In these instances, all three organic ranges should be requested for analysis.



## Appendix F

### MDEQ Requests For Review Of Laboratory Information

An MDEQ project manager may request to review any of the following laboratory information or procedures as part of the supporting documentation to the data and conclusions of a submittal. Requests are made in writing, address specific information, and include an explanation of the reason that the information is being requested.

**I. Methods** - All laboratory methods used should be clearly identified, including preservation, preparatory and analytical methods. Lab standard operation procedures (SOPs), including SOPs for extraction, cleanup and corrective actions, based on these reference methods should be available with the data.

**II. Holding Times/Sampling Handling** - All holding times specified in the method should be strictly followed.

- The chain of custody should clearly document the sample preservation method(s), sample collection times, date of sample receipt in the lab, temperature at time of receipt and name of person who received the sample.
- Lab data sheets should contain date of sample receipt in the lab, date of each progressive analytical procedure, and the name of the analyst performing the procedure and should be included in the report.
- Proper preservation (e.g., temperature and pH) should be checked and maintained from sample receipt to analysis and any discrepancies noted.

**IIIa. Quality Control (QC) Data** - data required by the EPA reference method should be available. Written comments should be included regarding any general difficulty with the procedure or "outliers" in the QC data. In general the following information should be available, where appropriate.

- Blanks - Trip and field blanks should be available. Laboratory reagent blanks (method blanks) should be prepared and analyzed at the appropriate frequency. When detections of target analytes are encountered in blank samples, the source of contamination needs to be evaluated and the potential impact of the contamination on data quality should be described in the sample results. It is recognized that it is nearly impossible to remove all potential sources of contamination in the laboratory environment; however contamination must be minimized using all means available. As a general rule, method blanks should not contain more than five times the target detection limit for common laboratory contaminants (e.g., methylene chloride and ketones for volatiles analysis, certain phthalates for the semivolatile analyses). Blank subtraction is not permitted. Documentation to include batch quality control for blanks should be available upon request.
- Surrogate Recoveries - Should be performed when appropriate and meet the reference method specifications and statistically derived lab control limits. If surrogate outliers are observed, the laboratory must justify acceptance of the data, or take corrective action to remedy the outlier, including restandardization and re-evaluation of instruments performance parameters. If reanalysis demonstrates a similar surrogate result (outlier),





then the laboratory should document the reanalysis and qualify the data. Matrix interference is assumed to be the cause of the outlier.

- Lab Control Sample Recoveries - Should be performed using prepared "known" samples which have documented concentrations of the analytes of interest. Such recoveries should be within reference method specifications and within lab specific statistically derived control limits. Documentation for lab control samples that includes chromatograms and quantification reports should be available upon request.
- Matrix Spiked Recoveries - Should be acceptable by statistically derived control limits or properly qualified when limits are not met. If matrix spike outliers are observed, the laboratory must take corrective action (e.g., qualify data, reanalyze). If reanalysis demonstrates a similar matrix spike result (outlier), then the laboratory should document the reanalysis and matrix interference is assumed to be the cause of the outlier. Documentation of statistically derived control limits for matrix spikes should be available upon request.
- Duplicate Analyses - should be acceptable by protocol or lab specific statistically derived control limits.
- Method Detection Limit (MDL) Calculations - should include data and method used to calculate the MDL according to the method described in 40 CFR Part 136, [Appendix B](#) and should be available upon request.

**IIIb. Quality Assurance Sample Results** - Quality Assurance (QA) samples are periodically analyzed by laboratories as an external check on performance, all results should be available. Performance on QA samples is an indication of the lab's ability to perform a certain analysis and is potentially useful to evaluate a lab's capabilities. Examples of QA reference sample are EPA, National Bureau of Standards, commercially available standards, and various intercomparison studies.

**IV. Calibration Data** - All data and information should be available to demonstrate that the analytical system was properly calibrated at the time of analysis including calibration method, frequency, source of standards, concentration of standards, response factors, linear range, check standards, and check standard control limits.

## Appendix G

### Source Documents For Designated Methods

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Edition 3 (SW-846)	
Method	Title
3060A	Alkaline Digestion for Hexavalent Chromium
4030	Soil Screening for Petroleum Hydrocarbons by Immunoassay
4035	Soil Screening for Polynuclear Aromatic Hydrocarbons by Immunoassay
6000	SW-846 Manual, Chapter 3 and 6000 Series Methods
6850	Perchlorate in Water, Soils and Solid Wastes Using High Performance Liquid Chromatography/Electrospray Ionization/Mass Spectrometry



**Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,  
U.S. Environmental Protection Agency, Office of Solid Waste and  
Emergency Response, Edition 3 (SW-846)**

6860	Perchlorate in Water, Soils and Solid Wastes Using Ion Chromatography/Electrospray Ionization/Mass Spectrometry
7000	SW-846 Manual, Chapter 3 and 7000 Series Methods
7195	Chromium, Hexavalent (Coprecipitation)
7196A	Chromium, Hexavalent (Colorimetric)
7197	Chromium, Hexavalent (Chelation/Extraction)
7198	Chromium, Hexavalent (Differential Pulse Polarography)
7199	Chromium, Hexavalent by Ion Chromatography
7580	White Phosphorus by Solvent Extraction and Gas Chromatography
8011	1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane by Microextraction and Gas Chromatography
8015C	Non-halogenated Organics Using Gas Chromatography
8015D	Non-halogenated Organics Using GC/FID
8021B	Halogenated and Aromatic Volatiles by Gas Chromatography Using Electrolytic Conductivity and Photoionization Detectors in Series: Capillary Column Technique
8031	Acrylonitrile by Gas Chromatography
8032A	Acrylamide by Gas Chromatography
8033	Method 8033, Acetonitrile by Gas Chromatography with Nitrogen-Phosphorus Detection
8041A	Phenols by Gas Chromatography
8061A	Phthalate Esters by Capillary Gas Chromatography With Electron Capture Detector (GC/ECD)
8070A	Nitrosamines by Gas Chromatography
8081B	Organochlorine Pesticides and PCBs as Aroclors by GC: Capillary Column Technique
8082A	Polychlorinated Biphenyls (PCBs) by Gas Chromatography
8095	Explosives by Gas Chromatography
8121B	Chlorinated Hydrocarbons by Gas Chromatography: Capillary Column Technique
8131	Aniline and Selected Derivatives by Gas Chromatography
8141B	Organophosphorus Pesticides by Gas Chromatography: Capillary Column Technique
8151A	Chlorinated Herbicides by GC Using Methylation or Pentafluorobenzoylation, Derivation: Capillary Column Technique



### Source Documents For Designated Methods

**Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,  
U.S. Environmental Protection Agency, Office of Solid Waste and  
Emergency Response, Edition 3 (SW-846)**

Method	Title
8260B	Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique
8270C	Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS): Capillary Column Technique
8270C Ion Trap	This reference is simply to point out that the Method 8270C above allows the use of the ion trap technology and may be needed to reach low detection limits
8270C SIM	This reference is simply to point out that the selective ion procedure can be used in Method 8270C above and may be needed to reach low detection limits
8290A	Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs), by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)
8310	Polynuclear Aromatic Hydrocarbons (HPLC and UV or fluorescence detectors)
8315A	Determination of Carbonyl Compounds by HPLC
8316	Acrylamide, Acrylonitrile, and Acrolein by High Performance Liquid Chromatography
8318A	N-Methylcarbamates by HPLC
8321B	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection
8325	Solvent Extractable Nonvolatile Compounds by High Performance Liquid Chromatography/Particle Beam/Mass Spectrometry (HPLC/PB/MS)
8330A	Nitroaromatics and Nitramines by HPLC
8430	Analysis of Bis(2-chloroethyl) Ether and Hydrolysis Products by Direct Aqueous Injection GC/FT-IR (Gas Chromatography/Fourier Transform Infrared Spectrometer)
8440	Total Recoverable Petroleum Hydrocarbons by Infrared Spectrophotometry
9010B	Total and Amenable Cyanide
9012A	Total and Amenable Cyanide (Colorimetric, Automated UV)
9013A	Cyanide Extraction Procedure for Solids and Oils
9030B	Acid-Soluble and Acid-Insoluble Sulfides
9034	Titrimetric Procedure for Acid-Soluble and Acid-Insoluble Sulfides
9035	Sulfate (Colorimetric, Automated, Chloranilate)
9036	Sulfate (Colorimetric, Automated, Methylthymol Blue, AA II)
9040C	pH Electrometric Measurement
9045D	Soil and Waste pH
9050A	Specific Conductance
9056	Determination of Inorganic Anions by Ion Chromatography



**Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Edition 3 (SW-846)**

9058	Determination of Perchlorate Using Ion Chromatography with Chemical Suppression Conductivity Detection
9071B	n-Hexane Extractable Material (HEM) for Sludge, Sediment, and Solid Samples
9212	Potentiometric Determination of Chloride in Aqueous Samples with Ion-Selective Electrode

**Source Documents For Designated Methods**

**Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Edition 3 (SW-846)**

Method	Title
9214	Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode
9215	Potentiometric Determination of Sulfide in Aqueous Samples and Distillates with Ion-Selective Electrode
9250	Chloride (Colorimetric, Automated Ferricyanide AAI)
9251	Chloride (Colorimetric, Automated Ferricyanide AAI)
9253	Chloride (Titrimetric, Silver Nitrate)

**Environmental Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Athens, Georgia 30613**

Method	Title
100.1	Analytical Method for Determination of Asbestos Fibers in Water

**U.S. Environmental Protection Agency**

Method	Title
EPA/600/R-93-116	Method for the Determination of Asbestos in Bulk Building Materials. July 1993. (NTIS / PB93-218576). [Updated and replaces interim version in 40 CFR 763 Subpart F Appendix A. Available from NTIS.]

**California Environmental Protection Agency, Air Resource Board**

Method	Title
CARB 435	Method 435, Determination of Asbestos Content of Serpentine Aggregate, Adopted: June 6, 1991

**Guidelines Establishing Test Procedures for the Analysis of Pollutants, 40 CFR Part 136, Appendix A, Revised: July 1990**

Method	Title
605	Benzidines



**EPA: Volatile/Semivolatile Organic Compounds by Isotope Dilution GC/MS, U.S. EPA, Office of Water Regulations and Standards, Ind. Tech. Div., Edition: June 1989**

Method	Title
1624	Volatile Organic Compounds by Isotope Dilution GC/MS

**Analytical Methods for the National Sludge Survey, U.S. Environmental Protection Agency, Office of Water (WH-585), Edition: September 1990**

Method	Title
1613	Tetra-through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, Rev B

**Source Documents For Designated Methods**

**Standard Methods for the Examination of Water and Wastewater**

Method	Title
SM 2120 B/C/E	Color
SM 2340 B	Hardness by Calculation (Ca and Mg results)
SM 2540 C	Total Dissolved Solids Dried at 180° C
SM 2550 B	Laboratory and Field Methods
SM 3500-Cr D/E	Chromium
SM 4500-CN F	Cyanide-Selective Electrode Method
SM 4500-O G	Oxygen, (Dissolved), Membrane Electrode Method (field determination)
SM 5210 B	Biochemical Oxygen Demand
SM 6651	Glyphosate Herbicide

**Methods for the Determination of Organic Compounds in Drinking Water and Supplement I, III, U.S. EPA, EMSL, Cincinnati, Ohio 45268, Edition: December 1988 and July 1990**

Method	Title
504.1	1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-chloropropane (DBCP) in Water by Microextraction and Gas Chromatography
507	Determination of Nitrogen and Phosphorous-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorous Detector
515.1	Determination of Chlorinated Acids in Water by Gas Chromatography with an Electron Capture Detector
515.2	Determination of Chlorinated Acids in Water Using Liquid-Solid Extraction and Gas Chromatography with an Electron Capture Detector
515.4	Method 515.4, Determination of Chlorinated Acids in Drinking Water by Liquid-Liquid Microextraction, Derivatization, and Fast Gas Chromatography with Electron Capture Detection, Revision 1.0, April 2000
524.2	Method 524.2, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry
525.2	Determination of Organic Compounds in Drinking Water by Liquid-Solid Extraction and Capillary Column Gas Chromatography/Mass Spectrometry
531.1	Measurement of N-Methylcarbamoylazines and N-Methylcarbamates in Water by



**Methods for the Determination of Organic Compounds in Drinking Water and Supplement I, III, U.S. EPA, EMSL, Cincinnati, Ohio 45268, Edition: December 1988 and July 1990**

<b>Method</b>	<b>Title</b>
	Direct Aqueous Injection HPLC with Post Column Derivatization, Revision 3.1
547	Determination of Glyphosate in Drinking Water by Direct-Aqueous-Injection HPLC, Post-Column Derivatization, and Fluorescence Detection
548	Determination of Endothall in Drinking Water by Aqueous Derivatization, Liquid Solid Extraction, and Gas Chromatography with an Electron Capture Detection
549	Determination of Diquat and Paraquat in Drinking Water by Liquid-Solid Extraction and HPLC with UV Detection
551.1	Determination of Chlorination Disinfection By-products, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid-Liquid Extraction and Gas Chromatography with Electron Capture Detection
552.3	Determination of Haloacetic Acids and Dalapon in Drinking Water by Liquid-Liquid Microextraction, Derivatization and Gas Chromatography with Electron Capture Detection, EPA 815-B-03-002, Revision 1.0, July 2003

**U.S. EPA, Office of Research and Development, U.S. EPA, Cincinnati, Ohio 45268**

<b>Method</b>	<b>Title</b>
415.3	Determination of Total Organic Carbon and Specific UV Absorbance at 254 nm in Source Water and Drinking Water, Revision 1.0, June 2003

**Official Methods of Analysis, Association of Official Analytical Chemists 957.18, Edition 15, 1990**

<b>Method</b>	<b>Title</b>
983.01	Urea and Methyleneureas
957.18	Microdetermination of Phosphorus, Kjeldahl Digestion Method

**U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460**

<b>Method</b>	<b>Title</b>
Kelada-01	Kelada Automated Test Methods For Total Cyanide, Acid Dissociable Cyanide, and Thiocyanate, Revision 1.2
OIA-1677	Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry, August 1999, EPA-821-R-99-013
200.2	Revision 2.8: Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements, October 1999, EPA-821-R-99-018
1614	Brominated Diphenyl Ethers in Water, Soil, Sediment, and Tissue by HRGC/HRMS



**U.S. Environmental Protection Agency, Office of Water, Office of Science and Technology Engineering and Analysis Division (4303), 401 M Street SW, Washington, DC 20460**

Method	Title
1631E	Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry
1631E (mod)	EPA-821-R-01-013, January 2001, Appendix to Method 1631 Total Mercury in Tissue, Sludge, Sediment, and Soil by Acid Digestion and BrCl Oxidation
1664	Test Method 1664: Guidelines Establishing Test Procedures for the Analysis of Oil and Grease and Non-Polar Material

**U.S. Environmental Protection Agency, Office of Water (4304T), 1200 Pennsylvania Avenue, NW, Washington, DC 20460**

Method	Title
1668	EPA-821-R-00-002, Method 1668, Revision A, Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS
EPA-821-R-02-012	<a href="#">Short-Term Methods for Measuring the Acute Toxicity of Effluents and Receiving Waters to Freshwater and Marine Organisms, Edition 5, October 2002, with Errata Sheet.</a>
EPA-821-R-02-013	<a href="#">Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms, Edition 4, October 2002, with Errata Sheet.</a>

**Source Documents For Designated Methods**

**Methods for the Determination of Nonconventional Pesticides in Industrial Wastewater, U.S. EPA, Office of Water, Engineering and Analysis Division, WH-552, Edition: April 1992**

Method	Title
1656	The Determination of Organo-Halide Pesticides in Municipal and Industrial Wastewater
608.2	The Determination of Certain Organochlorine Pesticides in Municipal and Industrial Wastewater
619	The Determination of Triazine Pesticides in Municipal and Industrial Wastewater
629	The Determination of Cyanazine in Municipal and Industrial Wastewater
632.1	Method 632.1, The Determination of Carbamate and Amide Pesticides in Municipal and Industrial Wastewater

**Methane Procedures**

Method	Title
RSKSOP-175	Standard Operating Procedure, Sample Preparation and Calculation for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique, R.S. Kerr Environmental Research Laboratory, U.S. EPA, 1994



**MOSA. Methods of Soil Analysis**

Part 1. 1986. Klute, A., ED. American Society of Agronomy, Madison, Wisconsin

**Gee, G.W., Bauder, J.W.**

Gee, G.W., Bauder, J.W., 1986, Particle-Size Analysis. In: Klute, A. (ED.), Methods of Soil Analysis: Part 1. Physical and Mineralogical Methods, Edition 2; Agronomy, 9. Soil Science Society of America, Madison, USA, 383-411

**Walkley-Black Method**

Instruments are available that utilize a form of the Walkley-Black digestion method. The following documents provide the original method and some modifications.

Walkley, A., and Black, 1934. An examination of the Degtijareff Method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 37:29-38

Walkley, A., 1947. A critical examination of a rapid method for determining organic carbon in soils: Effect of variations in digestion conditions and of inorganic soil constituents. Soil Sci. 63:251-257

Jackson, M.L., 1958. Soil Chemical Analysis. 214-221

Schollenberger, C.J., 1927. A Rapid Approximate Method for Determining Soil Organic Matter. Soil Sci. 24:65-68

**Source Documents For Designated Methods**

<b>Methods for Chemical Analysis of Water and Wastes, U.S. EPA, EMSL, Cincinnati, Ohio 45268</b>	
<b>Method</b>	<b>Title</b>
120.1	Conductance, Specific Conductance, Revision 1982
180.1	Determination of Turbidity by Nephelometry, Revision 2.0, 1993
200.8	Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma – Mass Spectrometry, Revision 5.4, 1994
218.6	Determination of Dissolved Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography, Revision 3.3, 1994
245.1	Determination of Mercury in Water by Cold Vapor Atomic Absorption Spectrometry, Revision 3.0, 1994
245.2	Mercury (Automated Cold Vapor Technique), Issued 1974
245.7	Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, Revision 2.0, 2005
300.0	The Determination of Inorganic Anions in Water by Ion Chromatography, Revision 2.1, 1993
300.1	The Determination of Inorganic Anions in Water by Ion Chromatography, Revision 1.0, 1997
310.2	Alkalinity (Colorimetric, Automated, Methyl Orange), Revision 1974
314	Method 314.0, Determination of Perchlorate in Drinking Water Using Ion Chromatography





**Methods for Chemical Analysis of Water and Wastes, U.S. EPA, EMSL, Cincinnati, Ohio 45268**

- 335.1 Cyanides, Amenable To Chlorination (Titrimetric; Spectrophotometric)
- 335.4 Determination of Total Cyanide by Semi-Automated Colorimetry, Revision 1.0, 1993
- 350.1 Nitrogen, Ammonia (Colorimetric, Automated Phenate), Revision 2.0, 1993
- 350.2 Nitrogen, Ammonia (Colorimetric, Titrimetric, Potentiometric – Distillation Procedure)
- 350.3 Nitrogen, Ammonia (Potentiometric, Ion Selective Electrode)
- 351.1 Kjeldahl Nitrogen, Revision 1978
- 351.2 Kjeldahl Nitrogen, Revision 2.0, 1993
- 353.2 Nitrogen, Nitrate-Nitrite, Colorimetric, Automated, Cadmium Reduction, Revision 2.0, 1993
- 365.1 Phosphorus, Total, Revision 2, 1993
- 365.3 Phosphorus, Total, Issued 1978
- 365.4 Phosphorous, Total (Colorimetric, Automated, Block Digester, AAll), Issued 1974

**Methods for Chemical Analysis of Water and Wastes, U.S. EPA, EMSL, Cincinnati, Ohio 45268**

Method	Title
375.2	Sulfate (Colorimetric, Automated Colorimetry), Revision 2.0, 1993
376.1	Sulfide, Titrimetric, Iodine
376.2	Sulfide (Colorimetric, Methylene Blue)
410.3	Method 410.4, The Determination of Chemical Oxygen Demand by Semi-Automated Colorimetry, Revision 1978
410.4	Method 410.4, The Determination of Chemical Oxygen Demand by Semi-Automated Colorimetry, Revision 2, 1993
603	Acrolein and acrylonitrile

**ASTM Standards, American Society of Testing Materials**

Method	Title
D 2937-10	Standard Test Method for Density of Soil in Place by the Drive-Cylinder Method
D 2487-11	Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System)
D 2216-10	Standard Test Methods for Laboratory Determination of Water (Moisture) Content of Soil and Rock by Mass
D 2488-09a	Standard Practice for Description and Identification of Soils (Visual-Manual Procedure)
D 3987-12	Standard Practice for Shake Extraction of Solid Waste with Water
D 6888-09	Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection
D 7511-12	Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection
D 7284-	Standard Test Method for Total Cyanide in Water by Micro Distillation followed by



### ASTM Standards, American Society of Testing Materials

Method	Title
08e1	Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection
D 421-85(2007)	Standard Practice for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants
D 422-63(2007)	Standard Test Method for Particle-Size Analysis of Soils

### Compendium Methods for the Determination of Toxic Organic Compounds

Method	Title
TO-4A	Compendium Method TO-4A
TO-10A	Compendium Method TO-10A
TO-13A	Compendium Method TO-13A
TO-15	Compendium Method TO-15
TO-17	Compendium Method TO-17

### NIOSH Manual of Analytical Methods (NMAM)

Method	Title
S141	Diisopropylamine
S283	Dieldrin
1003	Hydrocarbons, Halogenated
2002	Amines, Aromatic
2005	Nitroaromatic Compounds
2017	Aniline, o-Toluidine, and Nitrobenzene
2518	Hexachloro-1,3-Cyclopentadiene
3513	Tetranitromethane
3800	Organic and Inorganic Gases by Extractive FTIR Spectrometry
5503	Polychlorobiphenyls
5510	Chlordane
6015	Ammonia
6016	Ammonia by Ion Chromatography

### OSHA Sampling and Analytical Methods

D188	Ammonia in Workplace Atmospheres - Solid Sorbent
67	Chlordane
PV2064	N,N-Dimethylaniline
7	Organic Vapors