

	Remediation and Redevelopment Division POLICY AND PROCEDURE		DEPARTMENT OF ENVIRONMENTAL QUALITY
Original Effective Date: October 22, 2004 Revised Date: March 10, 2016 Reformatted Date: March 10, 2016	Subject: Standard Operating Procedure for Sample Preservation, Sample Handling, and Holding Time		Category: <input checked="" type="checkbox"/> Internal/Administrative <input type="checkbox"/> External/Non-Interpretive <input type="checkbox"/> External/Interpretive
	Program Name: Part 201, Environmental Remediation Part 213, Leaking Underground Storage Tanks		Type: <input type="checkbox"/> Policy <input checked="" type="checkbox"/> Procedure <input type="checkbox"/> Policy and Procedure
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A Michigan Department of Environmental Quality (MDEQ) Policy and Procedure cannot establish regulatory requirements for parties outside of the MDEQ. This document provides direction to MDEQ staff regarding the implementation of rules and laws administered by the MDEQ. It is merely explanatory; does not affect the rights of, or procedures and practices available to, the public; and does not have the force and effect of law.

PURPOSE

This Standard Operating Procedure (SOP) is explanatory and provides direction to MDEQ staff and their contractors pertaining to general sample collection, preservation, handling and holding time information. Appendix 1 provides MDEQ staff with tables that are a summary of the designated analytical methods requirements for sample preservation, sample handling, and holding time specifications, current at the time of issuance. This document is intended to assist with the implementation of the MDEQ published list of Target Detection Limits and Designated Analytical Methods, Application of the Target Detection Limits and Designated Analytical Methods Reference Materials, and the Standard Operating Procedure for Methanol Preservation in the Field (RRD 35). In designating the analytical method, the appropriate sample collection preparation techniques included within the method are also designated. This document contains expectations for MDEQ staff and their contractors for implementation of the designated analytical methods. As part of the sample planning efforts a project manager should review and incorporate current specifications from the MDEQ Lab or the designated analytical methods. This SOP is available as a technical reference that may be informative and may be used as a reference by parties outside of the MDEQ when collecting samples for analysis.

DEFINITIONS

Acronyms and 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 Laboratory
RRD:	Remediation and Redevelopment Division
U.S. EPA:	United States Environmental Protection Agency
Holding Time:	The length of time a sample can be held after collection and prior to analysis without significantly affecting the analytical results. Holding times vary with the analyte, sample matrix, and analytical methodology used to quantify the analyte's concentration.

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SOP FOR SAMPLE PRESERVATION, SAMPLE HANDLING, AND HOLDING TIMES

Sample Scheduling

MDEQ RRD field staff and contractors submitting environmental samples to the MDEQ Lab should schedule samples with the MDEQ Lab by completing and submitting a current Sample Scheduling form at least one week in advance of submitting samples to DEQ-ENV-Labschedule@michigan.gov. Contact the MDEQ Lab at 517-335-9800 for additional help. The MDEQ Lab's current Sample Scheduling form can be found at http://www.michigan.gov/deq/0,4561,7-135-3307_4131_4154-143557--,00.html.

The MDEQ uses laboratory contracts to obtain laboratory services that are not provided or cannot be completed by the MDEQ Lab (See RRD Procedure for Use of Laboratory Contracts RRD-2). The MDEQ project manager must identify the services the MDEQ Lab has the capability to perform. The MDEQ Analysis Request Sheets and Sample Scheduling form can be used to identify these services. Services that can be scheduled by the MDEQ Lab are sent to the MDEQ Lab. Services that cannot be scheduled by the MDEQ Lab must be obtained through the contract laboratories.

Sample Containers and Preservatives

Containers and preservatives should be obtained from the laboratory performing the analysis, when possible. Otherwise, arrangements must be made with the laboratory to ensure the sample containers and preservatives to be used are appropriate. Sample containers obtained from the MDEQ Lab should be ordered at least two weeks prior to sampling. Preservatives must be provided with an appropriate identification for traceability, safety information, instructions for use if necessary, and the expiration date. Sufficient information for preservatives must be recorded into field logbooks as samples are collected so that each preserved sample is cross-referenced with the added preservative(s). Safety Data Sheets for the preservatives are available from the MDEQ Lab webpage; and can be found at: http://www.michigan.gov/deq/0,4561,7-135-3307_4131_4154-197798--,00.html.

Appendix 1 contains details regarding sample containers, bottle codes, and preservatives. The table details are those specified by the MDEQ Lab at the date this document was written. The current MDEQ Lab bottle order/field supplies form should be used for sample planning efforts and can be found at: http://www.michigan.gov/documents/deq/deq-ess-lab-rls_280175_7.xls.

Use of Chemical Preservatives

Chemical preservatives should be used in their recommended dosages. If a little preservative is good, more is not necessarily better. Preservatives must be replaced at intervals specified by the manufacturer, laboratory, whenever contamination is suspected, or upon expiration. Chemical preservatives should not be added to soil samples, except when specified in a sampling protocol, e.g., methanol preservation of soils analyzed for volatile organic compounds. Chemical preservatives should never be added to unknown or untreated liquid waste and to samples of unknown matrix or source. Violent reactions can occur as acids are added to basic waste, or conversely when bases are added to acidic waste. Adding acids to samples containing high cyanide or sulfide levels may result in the generation of dangerous levels of hydrogen cyanide or hydrogen sulfide gas.

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Sample Preservation

When practical, sample preservation should be performed as soon as possible after collection. It is not appropriate to make arrangements with the laboratory to preserve samples unless specifically allowed by the applicable regulatory agency. Samples not immediately preserved upon collection require field documentation to be provided to the laboratory identifying the storage environment (cooler, trailer, etc.), storage temperature, date, and time preserved. Laboratory data from samples not immediately preserved upon collection may be qualified.

For composite samples, when possible, each aliquot used to make the composite should be separately preserved. When use of an automated sampler prevents preservation of each aliquot, the aliquots should be maintained at less than 6° C until composite samples can be preserved.

Documentation of Preservation, Dates, and Times

The samples collected, the preservation used, dates, and times must be documented in the field logbook, and on the sample containers. This documentation must be included as part of the project records and reported to the project manager. Samples collected along with date and time collected must be documented on the laboratory Analysis Request Form.

Unusual Sample Behavior

If a sample exhibits unusual behavior upon attempts to preserve, such as reacting vigorously when preservatives are added, discard the sample and obtain a new sample. Alternate preservation procedures may be used when allowed. If none are appropriate or available, the sample may be provided to the laboratory without preservation. Label the sample appropriately and advise the laboratory of any preservation used. Record the behavior of the sample in the field logbook and on the laboratory Analysis Request Form so that it is appropriately communicated to the laboratory. This information should be provided to the project manager as well.

Contamination from Sample Containers or Preservatives

Documentation must be maintained by the laboratory to uniquely identify the source of the material used to make each preservative. Data users should routinely review results for methanol blanks, trip and field blank samples for evidence of contamination from preservatives or sample containers. In the event that laboratory provided preservatives or sample containers cannot be ruled out as possible contamination sources, the laboratory should be immediately notified. If the laboratory determines that preservatives or sample containers are possible sources of contamination, the laboratory should then inform their clients as appropriate.

Delivery of Samples to Laboratories and Sample Processing

Sample collection and delivery to the laboratory must be accomplished with enough holding time left to ensure the analyses can be routinely conducted within the applicable holding times. If a sampling event is expected to occur over multiple days, the laboratory should be notified to determine the best approach for delivering samples to meet analytical holding times. If expedited analyses are required to prevent holding time violations, additional costs may be incurred. Laboratory sample schedules are contingent upon priorities of other samples and unforeseen events such as instrument malfunction. Schedules can change after samples have been delivered to the laboratory. To minimize the impact of schedule changes, it is important to provide instructions to the laboratory before or during sample receipt at the laboratory concerning actions to take when a schedule change affects holding times. Deliver appropriately collected and preserved

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samples to the MDEQ Lab along with a completed Analysis Request Form. When samples are delivered to the lab in person, MDEQ RRD field staff or contractors are responsible for setting up samples in the MDEQ Lab sample receiving area per MDEQ Lab procedure. Once samples have been verified against the completed Analysis Request Form, relinquish samples to the sample receiving personnel by completing the chain of custody portion of the Analysis Request Form. For samples that are shipped to the laboratory, complete the chain of custody portion of the Analysis Request Form, enclose in a waterproof container such as a sealed plastic bag and send with the samples. The sample receiving personnel will then complete the received by portion of the chain of custody along with received by date and time. A unique laboratory Work Order ID will be generated for the samples and indicated on the Analysis Request Form. A copy of the Analysis Request Form will be provided to the sample delivery agent if samples are delivered in person.

Processing of samples should begin as soon as possible after receipt. Appendix 1 contains the amount of time the sample and any sub-sample generated from the sample can be held prior to analysis. When holding times are exceeded, analytical data should be qualified to inform the data user that holding times were not met. Where more than one holding time is specified, all applicable holding times should be used to validate results. Upon discovery that the holding times may not be met, the laboratory should contact the project manager. Decisions whether sample processing should continue depends upon the use of the results.

Interpretation of Lab Results When Holding Times Are Exceeded

Results from samples analyzed past the holding times are not necessarily unusable. When holding times are exceeded, the usability of the data will depend on such factors as the relationship between sample levels and cleanup criteria or risk based screening levels, the type of decisions to be based on the data, the presence of other data from other samples, and other factors relative to whether the data establishes a reliable representative concentration of the hazardous substance. When holding times are exceeded, results should be interpreted as a minimum concentration.

Oxidants

Oxidants can alter the contaminant during storage and can interfere in some analyses. One common oxidant is chlorine. Test kits to measure or detect chlorine are available from several vendors. Most of these will respond to any oxidant in the sample. Water samples existing naturally in the environment usually do not contain chlorine, while tap water from a municipal water source is chlorinated. Appendix 1, Table 4, footnote 6 identifies instances when it is necessary to mitigate interferences due to oxidants (e.g., chlorine).

Preservation of Samples for Volatile Contaminants

The MDEQ implemented the use of methanol preservation of soil samples using procedures in SW-846 Method 5035 on April 30, 1998. Specifications for collecting soil samples using methanol preservation are provided in RRD Standard Operating Procedures for Methanol Preservation in the Field (RRD-35). Additional information on the application of U.S. EPA SW-846 Method 5035 is included in RRD Sampling and Analysis Reference Materials.

Preservation of Samples for Gasoline Oxygenates

Some laboratories may utilize high temperature purging (> 60° C) to improve separation of highly miscible contaminants from water, such as oxygenates, alcohols and ethers; however, high temperature purging during analysis of acid-preserved samples can cause ethers to convert into alcohols, which may result in under reporting of some ethers and over reporting of the

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corresponding alcohols. Laboratories which use high temperature purging should neutralize the samples prior to analysis. Alternately, separate samples can be collected and preserved with trisodium phosphate dodecahydrate (TSP) to pH > 11. These samples must be stored and shipped to the laboratory in separate containers. The laboratory must be advised of using TSP for preservation.

Preservation of Samples for Cyanide

Possible interferences for cyanide analysis are carbonates, oxidizing agents (e.g., chlorine), sulfides, and soluble aldehydes. Sample preservation and interference mitigation should start within 15 minutes of sampling.

For site investigations where water samples are collected from the same source (aquifer, stream, lake, etc.), and it is reasonable to conclude they all will exhibit the same characteristic, a reduced set of samples collected may be tested for interferences. All confirmation samples must be tested. The field logbook should indicate which samples were used for the tests, the test conducted, and indications whether the tests were positive or negative for the specific interferences.

Laboratories must provide the appropriate instructions for preserving samples for cyanide analysis. These instructions may vary depending upon the specific methods used and the preservatives provided by the laboratory used to mitigate interferences.

Field collection personnel should have the appropriate check lists that indicate to the laboratory what preservation steps were taken and the chemicals added to the samples.

Safety

Safety Data Sheets are available on the MDEQ Lab's web page and should accompany personnel in the field and be used to ensure safety. Preservatives should be stored in sealed containers with appropriate and sufficient absorbent materials to minimize dangers in case of breakage. Preservatives which are incompatible, such as acids and bases, must be separated in different locations to avoid mixing in case of breakage. Preservatives must be kept away from environmental and quality control samples. Use safety glasses and appropriate gloves to handle chemicals and properly place them into a closed chamber at the site until proper disposal can be arranged.

Applicability

The bottle specifications, codes, and preservatives are primarily those of the MDEQ Lab, intended to be used by MDEQ RRD staff and their contractors. Other specifications, codes, preservatives and their concentrations specific to the laboratory selected for the analysis, or the regulatory programs which will review the results, may be applied. Sample collectors should review analysis-specific containers and preservation recommendations with the laboratory to identify exceptions to the information in this document. Any exceptions in the professional judgment of the laboratory that may jeopardize the validity of the results should be resolved with the MDEQ RRD prior to collecting samples.

The information in this document is applicable to air, water, soil and sediment matrices and for contaminants regulated under Parts 201 and 213. These guidelines and specifications may not be applicable to other matrices or to cleanups conducted under other regulatory programs. When samples are required to meet the criteria of another regulatory program, the requirements for sample preservation, sample containers, and holding times of that program should be applied.

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APPENDICES

Table 1: Sample Containers, Preservation, Storage and Holding Times

REMEDATION AND REDEVELOPMENT DIVISION CHIEF APPROVAL:

Robert Wagner, Chief

March 10, 2016
Date

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APPENDIX 1: SAMPLE CONTAINERS, PRESERVATION, STORAGE, AND HOLDING TIMES

SAMPLE CONTAINER	INCLUDED ANALYSES	NOTES	PRESERVATION AND STORAGE	MAXIMUM HOLDING TIME
WATER				
GN – 500 mL Plastic	OP, NO ₂ , SS, TDS, Turb, DOC	1,9	Cool, ≤ 6° C	2, 7, 28 days
MN – 500 mL Plastic	Alk, Cl, F, SO ₄ , Cr+6, pH, Cond	2	Cool, ≤ 6° C	15 min, 24 hrs, 2, 14, 28 days
GA – 500 mL Plastic	COD, TOC, NH ₃ , NO ₃ +NO ₂ , KN, TP	3, 9	H ₂ SO ₄ to pH < 2 (10 drops / 500 mL), Cool, ≤ 6° C	28 days
MA / MAD – 500 mL Plastic	Total & Dissolved Solids	4, 9	1:1 HNO ₃ to PH <2 (5 mL / 500 mL)	180 days
GB – 250 mL Plastic	Total Cyanide	5	10N NaOH to pH 12 (10 drops / 250 mL) Cool, ≤ 6° C	14 days
CA – 500 mL Plastic Amber	Chlorophyll	6	MgCO ₃ (5 drops / 250 mL) Cool, ≤ 6° C	14 days
LHg – 500 mL Glass	Low Level Mercury	7	Lab Preserved	90 days
GCN – 50 mL Plastic Kit	Available Cyanide	8	PbCO ₃ Filter, NaOH to pH 12, Cool, ≤ 6° C	2 days
VOA – 40 mL Vial	Volatiles, BTEX/MTBE/TMB Chlorinated, GRO, 1,4-Dioxane	10	HCl to pH < 2 (5 drops / 40 mL), Cool, ≤ 6° C	14 days
METH – 40 mL Vial	Methane, Ethane, Ethene	11	HCl to pH < 2 (5 drops / 40 mL), Cool, ≤ 6° C	14 days
ON / DRO / BNA – 1 L Amber	Pesticides/PCBs, Toxaphene, Chlordane, DRO/ORO, BNA/PNA/Benzidines/Fingerprint	12	Cool, ≤ 6° C	7 days
SOIL / SEDIMENT				
MS / GS – 8 oz Jar	Metals, CN, COD, TOC, KN, TP	13	Cool, ≤ 6° C	14, 28, 180 days
OS / BNA – 8 oz Jar	Pesticides/PCBs, Toxaphene, DRO/ORO, BNA/PNA/Fingerprint	14	Cool, ≤ 6° C	14 days
VOA – Methanol Trip Blank	Volatiles, BTEX/MTBE/TMB Chlorinated, GRO, 1,4-Dioxane	15	MeOH (10 mL/10g), Cool, ≤ 6° C	14 days
AIR				
Bottlevac	Volatiles	16	Room Temperature	30 days
Suma Canister	Volatiles	17	Room Temperature	30 days

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- 1 - GN includes: Ortho-Phosphate, Nitrite, Turbidity (2 days), Suspended Solids, Dissolved Solids (7 days).
- 2 - MN includes: pH (<15 min), Chromium 6 (24 hrs), Alkalinity (14 days), Chloride, Fluoride, Sulfate, Conductivity (28 days).
- 3 - GA includes: COD, TOC, NH₃, NO₃+NO₂, KN, TP (28 days).
- 4 - MA/MAD includes: Mercury (28 days), All metals except Mercury (180 days). If field filtration for dissolved metals is not possible, send unpreserved sample to the lab within 24 hrs of collection for lab filtration and preservation.
- 5 - GB includes: Total Cyanide (14 days, 24 hrs if sulfides present). Chlorinated samples must be dechlorinated with ascorbic acid (0.6 g/L) upon collection followed by preservation with NaOH.
- 6 - CA includes: Chlorophyll (2 days). If sample is filtered upon collection and filter is added to 90% Acetone and refrigerated, hold time is one month. Store filtered sample in the dark on ice.
- 7 - LHg includes: Low Level Mercury (90 days if preserved with Bromine Chloride within 28 days of sample collection). Samples for Low Level Mercury should be preserved at the lab. Clean hands dirty hands technique should be used for sample collection.
- 8 - GCN includes: Available Cyanide (14 days). For samples containing sulfides, within 15 min of collection pour 50 mL of sample into PbCO₃ vial and mix. Filter using provided filter plunger. Decant sample filtrate into a new 50 mL tube and preserve with NaOH.
- 9 - Samples requiring Dissolved analyses must be filtered through a 0.45 um filter followed by preservation. If field filtration is not possible, send unpreserved sample to the lab within 24 hrs for lab filtration and preservation.
- 10 - VOA includes: Volatiles, BTEX/MTBE/TMB, Chlorinated, GRO, 1,4-Dioxane (14 days). Fill vial completely (No Air Bubbles) and ensure Teflon side of septum faces sample. 3 vials required VOAs, 2 vials required for GRO, and 2 vials required for 1,4-Dioxane.
- 11 - METH includes: Methane, Ethane, Ethene (Ethylene) (14 days). 2 vials required with red septa.
- 12 - ON / DRO / BNA Includes: Pesticides, PCB, BNA, PNA, BN, Acids, DRO, ORO, Benzidines (7 days). Collect 2 ambers if Pesticides/PCB **or** BNA/PNA/BN/Acids are requested. Collect 3 ambers if Pesticides/PCB and BNA/PNA/BN/Acids are requested. Collect 4 ambers if DRO/ORO are additionally requested.
- 13 - MS / GS includes: Total / Available Cyanide (14 days), COD, TOC, KN, TP, Mercury (28 days), All metals except Mercury (180 days)
- 14 - OS / BNA includes: Pesticides, PCB, BNA, PNA, BN, DRO, ORO (14 days)
- 15 - VOA MeOH includes: Volatiles, BTEX/MTBE/TMB, Chlorinated, GRO, 1,4-Dioxane in soil/sediment (14 days). Weigh 10 gm of soil and add to pre-weighed 40 mL vial. Add 10 mL methanol to the vial. Fill the syringe with soil/sediment sample, cap and label.
- 16 - Bottlevac includes: Volatiles (30 days)
- 17 - Suma Canister includes: Volatiles (30 days)