



October 22, 2004

## RRD OPERATIONAL MEMORANDUM NO. 2

**SUBJECT: SAMPLING AND ANALYSIS - ATTACHMENT 4  
SAMPLE PRESERVATION, SAMPLE HANDLING, AND HOLDING TIME  
SPECIFICATIONS**

### 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 211: Part 211, Underground Storage Tank Regulations, of NREPA  
Part 213: Part 213, Leaking Underground Storage Tanks, of NREPA  
MDEQ: Michigan Department of Environmental Quality  
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 and R 299.5706a(4)  
Facility: Includes "facility" as defined by Part 201 and "site" as defined by Part 213

### PURPOSE

This attachment to RRD Operational Memorandum No. 2 provides sampling handling, preservation, and holding time specifications. This attachment applies to site assessments, site investigation and response activities under Part 201, Part 211, and Part 213.

### SAMPLE CONTAINERS AND PRESERVATIVES

Containers and preservatives should be obtained from the laboratory performing the analysis whenever possible. When this is not possible, arrangements must be made with the selected laboratory to ensure the sample containers and preservatives to be used are appropriate. Preservatives must be provided with appropriate identification marks, safety information, instructions for use if necessary, and with expiration dates. The preservatives and expiration dates must be recorded into field logbooks as samples are collected so that each preserved sample is cross referenced with the added preservative(s).

The specific size, types of containers, and associated container codes used by the MDEQ laboratory are identified in Table 1. Preservatives normally used are listed in Table 2. Appropriate containers for each contaminant are specified with their respective bottle codes in Table 3.

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 or laboratory and whenever contamination is suspected. 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 wastes 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 could result in generation of dangerous quantities of cyanide or sulfide gas.

Sample preservation should be performed immediately upon sample collection or arrangements made with the laboratory to preserve samples within the specified time. For composite samples, when possible, each aliquot used to make the composite should be preserved at the time of collection. When use of an automated sampler prevents preservation of each aliquot, the aliquots should be maintained at about four degrees centigrade (4° C) until composite samples can be preserved.

If a sample reacts vigorously when preservatives are added, discard the sample and obtain a new sample without preservation. Label the sample appropriately to advise the laboratory that it is not preserved; record the behavior of the sample in the field logbook and on chain of custody or sample receipt forms so that it is appropriately communicated to the laboratory.

#### **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. The results of methanol blanks, trip, and field blank samples should be routinely reviewed for evidence of contamination from preservatives or sample containers. In the event preservative and sample containers cannot be ruled out as contamination sources, relevant information must immediately be provided to the laboratory, and suspect supplies not used until their suitability can be established. If the laboratory determines that preservative or sample containers are possible sources of contamination, the laboratory should then inform their clients as appropriate.

#### **HOLDING TIMES**

Samples should be processed and/or analyzed as soon as possible after collection. Table 3 specifies the maximum amount of time the sample and any sub-sample generated from the sample can be held. Samples not meeting these specifications must receive a holding time code or other data qualifier. Where more than one holding time is specified, all applicable holding times should be used to validate results. Samples may be held for longer periods only if the laboratory has data on file to show that the specific types of samples under study are stable for longer periods.

Sample collection and delivery to the laboratory must ensure holding times will not be exceeded. 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 the ability to meet holding times.

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, 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.



## VOLATILE CONTAMINANTS

Specifications for collecting soil samples using methanol preservation are provided in RRD Operational Memorandum No. 2, Attachment 6. The preservation of samples to be analyzed for volatile contaminants is dependent upon the requirements provided in SW-846, Method 5035A.

This method should be consulted for guidance. Table 3 below has the requirements taken from Method 5035A. Future revisions of Method 5035A may alter these requirements.

## DE-CHLORINATION

Water samples existing naturally in the environment should not need de-chlorination. De-chlorination procedures may be required for some samples taken from water sources where chlorination is used. De-chlorination is accomplished using the instructions provided in Table 3, footnote number 4, under De-chlorinate. Specific procedures for methods and contaminants may apply and should be used when possible. Applicable contaminants for which de-chlorination procedures may be required are provided below.

Acetonitrile	1,2-Dibromoethane (EDB)
Acrolein	Nitrosamines
Acrylonitrile	Organophosphorus Pesticides
Acrylamide	Phenolics
Benzidines	Polychlorinated biphenyls
Chlorinated Acids/Herbicides	1,2,3-Trichloropropane
Chlorinated Pesticides	Semivolatiles
1,2-Dibromo-3-Chloropropane	Volatiles

## ANALYSIS OF GASOLINE OXYGENATES

High temperature purging during analysis of acid preserved samples can cause ethers to degrade which may result in underreporting of some ethers. When a sample is collected and preserved with acid for the analysis of volatiles that include gasoline oxygenate compounds, methyl(tert)butylether, t-Butyl alcohol, Di-isopropyl ether, Ethyl(tert)butylether, Ethyl alcohol, Methyl alcohol, and Tertiaryamylmethylether, the acid-preserved samples should be neutralized prior to analysis. Trisodium phosphate dodecahydrate (TSP) has been determined by the U.S. EPA to be effective and safe for this purpose. Separate samples may be collected specifically for the analysis of oxygenates, and preserved using TSP to adjust the pH to > 11 rather than preserving them with acid.

## SAFETY

Be aware of dangers associated with chemical preservatives and their handling. Obtain Material Safety Data Sheets (MSDSs) from the laboratory providing the preservative prior to the sampling event to determine appropriate safety precautions and first aid. MSDSs should accompany personnel in the field. Preservatives must be stored in sealed containers away from other preservatives, and 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**

Many published methods include specifications for sample containers, preservation, and holding times that may be specific for certain contaminants analyzed using the specific method. Those specifications may be more detailed than the specifications provided in Table 3 or in similar generic tables. When samples are collected for analysis by a method not specifically listed in Table 3, the method-specific requirements for sample containers, preservation, and holding times must be followed.

There are additional sources of holding time and preservation guidance, including the Clean Water Act, the Resource Conservation Recovery Act, the Safe Drinking Water Act, and the U.S. EPA CLP. The guidelines and specifications in this document are applicable to water and soil matrices and for contaminants regulated under Parts 201, 211, 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 agency, the requirements for sample preservation, sample containers, and holding time of that agency should be applied.

Questions concerning this memorandum should be directed to Mr. A. Ralph Curtis, RRD, at 517-373-8389; or email to [curtisar@michigan.gov](mailto:curtisar@michigan.gov).

The following documents are rescinded with the issuance of this attachment:

- Environmental Response Division Operational Memorandum 16, Sample Preservation, Sample Handling, and Holding Time Guidelines for the Act 307 Program, dated January 4, 1995.
- Storage Tank Division Operational Memorandum 14, Analytical Parameters and Methods, Sample Handling, and Preservation for Petroleum Releases, Table 4, Container, Preservation, and Holding Time Requirements for Common Petroleum Product Sampling and Analysis, dated June 12, 1998.

**APPENDED TABLES:**

Table 1. Sample Containers and Container Codes

Table 2. Preservatives

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

This memorandum and its attachments are intended to provide direction and guidance to foster consistent application of Part 201, Part 211, and Part 213 and the associated administrative rules. This document is not intended to convey any rights to any parties or create any duties or responsibilities under the law. This document and matters addressed herein are subject to revision.

**Table 1. Sample Containers and Container Codes**

Container Code	Size ml	Bottle Type	Container Code	Size ml	Bottle Type
DO	250	Glass, glass stopper	BNA	1000	Glass, amber
GN	500	Plastic	MS	250	Glass, wide mouth
GA	500	Plastic	GS	250	Glass, wide mouth
GG	250	Glass, screw cap	OS/BNA	250	Glass, wide mouth
GB	500	Plastic	VOA	40	Glass, septum vial (soils require MeOH kit)
	250	Plastic	SCD	NA	Soil coring device <sup>1,2</sup>
S	250	Plastic	MO	250	Glass, wide mouth
MA	500	Plastic	OL	250	Glass, wide mouth
MAD	500	Plastic	HW	250	Glass, wide mouth
MD	500	Plastic	MX	250	Glass, wide mouth
MN	500	Plastic	OX	250	Glass septum jar
OG	250	Glass, wide mouth	L	500	Fluoropolymer <sup>1,3</sup>
VOA	40	Glass Septum vial	M	250	Glass or HDP <sup>1</sup>
ON	1000	Glass, amber	HDP	125	High Density Polyethylene <sup>1</sup>
Sealed Vial	Varies	Laboratory Specific			

1. SCD, L, M and HDP are not MDEQ Lab bottle codes.
2. The syringe type coring device, SCD, refers to the samplers listed in Method 5035A, or other validated samplers.
3. Contact the lab regarding availability and cleaning instructions.

**Table 2. Preservatives**

The following table represents the preservatives normally used for sampling and the approximate amounts to meet a targeted preservation.

Preservative	Concentration	Preservation	Approximate Amount
Sulfuric Acid (H <sub>2</sub> SO <sub>4</sub> )	Conc.	pH < 2	5 drops per 250 ml.
Nitric Acid (HNO <sub>3</sub> )	1:1	pH < 2	5 ml per 250 ml.
Hydrochloric Acid (HCl)	1:1	pH < 2	5 drops per 40 ml.
Sodium Hydroxide (NaOH)	10 N	pH > 9	2 drops per 250 ml.
		pH > 12	10 drops per 250 ml.
Chloroacetic Acid	0.1 N	pH 4-5	Varies with sample
Trisodium phosphate dodecahydrate (TSP)	Powder	pH > 10	Varies with sample
MeOH	Lab Grade	1:1	10 ml per 10 gr soil.
Ascorbic Acid	Powder	Oxidizing Agents	About 0.6 gr per L.
Sodium Arsenite	0.1 N	Oxidizing Agents	5 ml per L.
Zinc Acetate (ZnAc)	2 N	Interferences	10 drops per 250 ml.
Disodium EDTA	2.5 %	Interferences	1 ml per 100 ml.
Ethylenediamine	Powder	Interferences	50 mg per L.

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**

Contaminants <sup>2</sup>	Methods <sup>3</sup>	Container Codes <sup>1</sup>		Preservation <sup>4</sup>	
		Soil	Water		
<b>Specific Contaminants</b>					
Acidity	305.1		MN	4° C	1 <sup>+</sup>
Alkalinity	310.1		MN	4° C	1 <sup>+</sup>
<i>Anions by Ion Chromatography</i>	9056 300.1		MN	Contaminant Specific <sup>6</sup>	
Acetate			MN	4° C	2
Formate			MN	4° C	2
Bromide			MN	None Required	2 <sup>†</sup>
Chloride			MN	None Required	2 <sup>†</sup>
Fluoride			MN	None Required	2 <sup>†</sup>
Nitrate or Nitrite-N			MN	4° C	4 <sup>†</sup>
Nitrate and Nitrite-N			MN	pH < 2 H2SO4, 4° C	2 <sup>†</sup>
Ortho-Phosphate-P			MN	4° C	4 <sup>†</sup>
Sulfate			MN	4° C	2 <sup>†</sup>
Bromate			MN	None Required	2 <sup>†</sup>
Chlorate			MN	None Required	2 <sup>†</sup>
Chlorite			BNA	50 mg Ethylenediamine per L. 4° C	1 <sup>+</sup>
Asbestos	100.1		GN	4° C	4 <sup>†</sup>
Biochemical Oxygen Demand	405.1		GN	4° C	4 <sup>†</sup>
Bromide	320.1	GS	MN	None Required	2 <sup>†</sup>
Chemical Oxygen Demand	410		GA	pH < 2 H2SO4, 4° C	2 <sup>†</sup>
Chloride	325	GS	MN	None Required	2 <sup>†</sup>
Chlorine, Total Residual	330		GN	None Required	
Color	110		GN	4° C	4 <sup>†</sup>
Conductance, Specific	9050A	----	MN	4° C	2 <sup>†</sup>
Fluoride	340.1	----	MN	None Required	2 <sup>†</sup>
Hardness	130.2	----	MA	pH < 2 1:1 HNO3 / H2SO4, 4° C	6
Hydrogen Ion, pH	9040, 9045	GS	MN	None Required	2 <sup>+</sup>

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**

Contaminants	Methods	Containers		Preservation	
		Soil	Water		
<b>Specific Contaminants</b>					
Iodide	345.1	----	MN	4° C	2t
Odor	SM 2150B	----	GN	4° C	2t
Total Organic Carbon (TOC)	415.1	----	GA	pH < 2 H <sub>2</sub> SO <sub>4</sub> / HCl/NaHSO <sub>4</sub> , 4° C	2t
Fraction of Organic Carbon	Walkley-Black	GS	GN	4° C	2t
Fraction of Organic Matter	D2974	GS	GN	4° C	2t
Oxygen, Dissolved, Probe	360.1	----	DO	None Required	
Oxygen, Dissolved, Winkler	360.2	----	DO	Fix on site with DO Kit <sup>10</sup> , avoid aeration, store at 10-20° C in dark.	8
Perchlorate	340.1 9058	GS	MN	None Required	2t
Petroleum Hydrocarbon Material <sup>8</sup>	1664 9071B	2xOG	2xOG	pH < 2 HCL, 4° C. For dry soils cool to 4° C. For pourable sediments and soils add 2 ml 1:1 HCl per 100g, 4° C	
Phenolics	420.2	----	GG/GP	pH < 2 H <sub>2</sub> SO <sub>4</sub> , 4° C	2t
Phosphorus, Ortho, Dissolved	365	----	GN(D)	Filter on site immediately, 4° C	4t
Phosphorus, Elemental		----	GA	4° C	4t
Phosphorus, Total	365.4	----	GA	pH < 2 H <sub>2</sub> SO <sub>4</sub> , 4° C	2t
Residue, Total	160.3	----	GN	4° C	7
Residue, Filterable (TDS)	160.1	----	GN	4° C	7
Residue, Non-Filterable (TSS)	160.2	----	GN	4° C	7
Residue, Settleable	160.5	----	GN	4° C	4t
Residue, Volatile	160.4	----	GN	4° C	7
Silica	370.1	----	GN	4° C	2t
Sulfate	375.1	----	MN	4° C	2t

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**

Contaminants	Methods	Containers		Preservation	
		Soil	Water		
<b>Specific Contaminants</b>					
Sulfide	9030 376.1	GS		See Footnote 11	7
			S	Cover surface of collected soil with 2 M ZnAc until moistened. No headspace.	
Sulfite	377.1	----	HDP	Avoid contact with air, cool < 50° C and add 1 ml EDTA <sup>12</sup> per 100 ml., < 50° C	
Temperature	170.1	----	----	Not Applicable	
Total Recoverable Petroleum Hydrocarbons (TRPH)	8440 <sup>13</sup>	GS	----	4° C	
Turbidity	180.1	----	GN	4° C	48
<b>Biological Tests</b>					
Coliform, Fecal and Total	9131 9132	----	M	4° C	8
Fecal Streptococci	SM 9230	----	M	4° C	6
<b>Cyanides</b>					
Cyanide, Total	9010B	GS	----	See Footnote <sup>15</sup> Unpreserved	14 24
Cyanide, Available	OIA1677	GS	GB	See Footnote <sup>15</sup> Unpreserved	14 24
Cyanide, Amenable (Free)	D4298-02	----	GB	pH ≥ 12 NaOH, store in dark, 4° C	24
<b>Nitrogen Forms</b>					
Ammonia – N	350.1	GS	GA	pH < 2 H <sub>2</sub> SO <sub>4</sub> , 4° C	28
Kjeldahl – N	351.1	GS	GA	pH < 2 H <sub>2</sub> SO <sub>4</sub> , 4° C	28
(Nitrate + Nitrite) – N	353.2	GS	GA	pH < 2 H <sub>2</sub> SO <sub>4</sub> , 4° C	28
(Nitrate + Nitrite) – N	353.2	GS	GA	4° C	24
Nitrate – N or Nitrite – N	353.2	GS	GN	4° C	48



Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants	Methods	Containers		Preservation	
		Soil	Water		
<b>Mercury</b>					
Mercury, Total	7470 7471	MS	MA	pH < 2 1:1 HNO <sub>3</sub> , 4° C	28
Mercury, Low Level	1669/1631	MS	L	10 ml 1:1 Hg-free HNO <sub>3</sub> per L, 4° C	28
<b>Hexavalent Chromium</b>					
Chromium VI (waters)	7199	----	HDP	Use buffer solution <sup>16</sup> to adjust pH 9-9.5 (check with pH paper or pH meter) 4° C	24
	7196	----	MN	4° C	24
					C
					P <sub>1</sub>
Chromium VI (soils)	3060A <sup>17</sup>	MS	----	4° C, Store field-moist. Dry Soils: High moisture soils and sediments:	2
					30
Low Molecular Weight Acids	5560 C	GS	GN	None Required	
Glycols	8015C	GS	GN	None Required	
Phosphorus, White <sup>18</sup>	7580	OX	VOA	Limit contact with air. No headspace, 4° C, store in dark. Tightly seal extracts and refrigerate.	5
				Extracts:	
				Ether Extract	
				Iso-Octane Extract	

Table 3. Specifications for Sample Containers, Preservation, and Holding Times

Contaminants	Methods	Containers		Preservation	
		Soil	Water		
<b>Metals</b>					
Metals, Totals	6010/6020	MS <sup>19</sup>	MA	pH < 2 1:1 HNO <sub>3</sub> , 4° C	6
Metals, Dissolved	6010/6020	----	MD MA(D)	Filter and preserve < 24 Hours of sampling. pH < 2 1:1 HNO <sub>3</sub> , 4° C	6
<b>Specific Organic Compounds</b>					
Acetonitrile	8033	----	2 x VOA	pH < 2 H <sub>2</sub> SO <sub>4</sub> , 4° C	14
Acrolein	603 8316	----	2 x VOA	pH 4-5 HCl, 4° C	14
Acrolein	603	----	2 x VOA	4° C	3
Acrylonitrile	603	----	2 x VOA	4° C	14
Acrolein and Acrylonitrile	603	----	2 x VOA	pH 4-5 HCl, 4° C	14
Acrolein and Acrylonitrile	603	----	2 x VOA	4° C	3
Acrylamide	8032	----	2 x VOA	pH < 2 HCl/H <sub>2</sub> SO <sub>4</sub> , 4° C	14
<b>Specific Organic Compounds</b>					
Benzidines	605 8270C	OS BNA	BNA	Adjust pH 2-7 using H <sub>2</sub> SO <sub>4</sub> and 10 N NaOH. If 1,2-dephenylhydrazine is expected to be present, adjust pH to 3.8-4.2 H <sub>2</sub> SO <sub>4</sub> and 10 N NaOH 4° C, store extracts in inert atmosphere in dark	W
Carbamates	8318	OS BNA	BNA	Cool, pH 4-5 using 0.1 N Chloroacetic Acid, 4° C, store sample and extracts in dark	W S
Carbonyls	8315A	OS BNA	BNA	4° C	W S

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**

Contaminants	Methods	Containers		Preservation		
		Soil	Water		C	P
<b>Specific Organic Compounds</b>						
Chlorinated Acids/Herbicides	8151A	OS/B NA	BNA	4° C, store samples and extracts in dark	W: S:	
Dioxins and Furans	8290 1613	OS/B NA	ON	4° C, store in the dark		
1,2-Dibromoethane (EDB) 1,2-Dibromo-3-Chloropropane, 1,2,3-Trichloropropane	8011 504.1		VOA	4° C	W:	
Nitrosamines	8270C	OS/B NA	BNA	pH 7-10 with H <sub>2</sub> SO <sub>4</sub> and 10 N NaOH, store extracts in sealed vials, in dark at -10° C	W: S:	
Chlorinated Pesticides <sup>20</sup>	8081A	OS/B NA	2 x ON See 23 <sup>23</sup>	pH 5-9 with H <sub>2</sub> SO <sub>4</sub> and 10 N NaOH within 72 hours, 4°C, store extracts in dark.	W: S:	
Organophosphorus Pesticides <sup>21</sup>	8141A	OS/B NA	ON	4° C Store samples and extracts in dark	W: S:	
Polychlorinated biphenyls	8082	OS/B NA	2 x ON See 23 <sup>23</sup>	4° C Store extracts in dark	W: S:	
Semivolatiles <sup>22</sup>	8270C	OS/B NA	2 x BNA See 23	Store extracts in sealed vials, in dark at -10° C	W: S:	

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**

Contaminants	Methods	Containers	Preservation	
<b>Volatiles (waters)</b>				
Fuel Oxygenates	8260B	2 x VOA	no headspace, TSP to pH > 11, 4° C	18
Reactive compounds <sup>24</sup>	8260B	2 x VOA	no headspace, 4° C	
Other Compounds	8260B	2 x VOA	pH < 2 using 1:1 HCl or solid NaHSO <sub>4</sub> , no headspace, 4° C	14
<b>Volatiles (soils) <sup>25</sup></b>				
Reactive Compounds Examples include styrene, 2-Chloroethylvinylether	Low Concentration	Sealed Vial	Use reagent water (no acid preservative), freeze > -20° C , < -7° C on site	
		SCD	4° C or freeze > -20° C , < -7° C on site, extruded into sealed vial without acid preservative within 48 hours	
Volatile Compounds	Methanol	2 x VOA	Preserve on site using ratio 1:1 methanol to soil, 4° C	14
Volatile Compounds	Methanol	SCD	4° C or freeze > -20° C , < -7° C on site and extruded into sealed vial with methanol within 48 hours	14

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**

**Hazardous Waste Characterization Using Method 1312**

Contaminants	Containers	Field Collection To TCLP Extraction	TCLP Extraction To Preparative Extraction	Preparative Extraction To Determinative Analysis	
Volatiles	OX	14 Days	Not Applicable	14 Days	28
Semivolatiles	MX	14 Days	7 Days	40 Days	61
Mercury	MX	28 Days	Not Applicable	28 Days	56
Metals	MX	180 Days	Not Applicable	180 Days	36

**Radiochemistry Contaminants**

Radiochemistry Contaminant	Method	Containers Water	Preservation	Co
Gross Alpha, and Gross Beta	9310	1 L HDP or Glass	pH to 2 1 N HNO3	6 Months
Alpha Emitting Radium Isotopes	9315	1 L HDP or Glass	pH to 2 1 N HNO3	6 Months
Radium 228	9320	1 L HDP or Glass	pH to 2 1 N HNO3	6 Months

Unpreserved samples for analysis of radiochemistry contaminants must be received at the laboratory within five days o

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**
**Wisconsin GRO/DRO Guidelines**

Contaminants Organic Compounds	Methods	Containers		Preservation <sup>26</sup>	Colder Prep	
		Soil	Water			
Gasoline Range Organics Waters:  Carbonate aquifer waters: Carbonate aquifer waters: Soils:	8015-Wis		3 x VOA	0.5 ml 1:1 HCl to sample bottle first, no headspace, avoid agitation, 4° C	14 Da	
			3 x VOA	Preserved with Sodium Azide <sup>27</sup>	14 Da	
			3 x VOA	Without Sodium Azide <sup>27</sup>	2 Da	
		VOA		Preserve in field with MeOH, 4° C	21 Da	
		SCD		4° C, preserve with MeOH < 48 Hours	21 Da	
Diesel Range Organics Waters:  Carbonate aquifer waters: Carbonate aquifer waters: Soils:	8015-Wis		BNA <sup>28</sup>	5 ml 1:1 HCL to sample bottle first, no headspace, 4° C	7 Da	
			BNA <sup>28</sup>	Preserved with Sodium Azide <sup>27</sup>	7 Da	
			BNA <sup>28</sup>	Without Sodium Azide <sup>27</sup>	2 Da	
		VOA		4° C, preserve with MeOH 1:1 < 72 hours	47 Da	
		SCD				

**Table 3. Specifications for Sample Containers, Preservation, and Holding Times**
**For soils requiring leach tests to evaluate the mobility of non-volatile contaminants in soils <sup>29</sup>**

Contaminants <sup>31</sup>	Methods	Containers	Preservations (sample and leachate)		Holdir			
			Sample	Leachate <sup>32</sup>	Collection To Leaching	Leaching To Preparatio		
Mercury	7470	MX	4° C	pH < 2 1:1 HNO <sub>3</sub> , 4° C	28 Days			
Metals	6010B/6020	MX	4° C	pH < 2 1:1 HNO <sub>3</sub> , 4° C	180 Days			
Semivolatiles	8270C	MX	4° C	4° C, Store extracts from the leachates in dark at -10 ° C	14 Days	7 Days		
Pesticides	8081A	MX	4° C	pH 5-9 10 N NaOH and H <sub>2</sub> SO <sub>4</sub> , 4° C	14 Days	7 Days		
PCBs	8082	MX	4° C	4° C, Store extracts from the leachate in dark	14 Days	7 Days		

**For soils requiring leach tests to evaluate the mobility of volatile contaminants in soils**

Contaminants	Methods	Containers	Preservations (sample and leachate)		Holdir			
			Sample	Leachates	Collection To Leaching			
Volatiles <sup>33</sup>	8260B	2 x SCD	< 4° C	pH < 2 1:1 HCl, 4° C	48 Hrs			

**Table 3 Footnotes**

1. The container sizes and types specific for the MDEQ Environmental Laboratory (MDEQ Lab) are listed in this table when applicable. Other laboratories may specify other sizes and types. Letters in parentheses ( ) indicate that the included letter must be added to the prefix code on the bottle from the MDEQ Lab to indicate to the laboratory what process was used, if any, for preservation.
2. "Contaminants" refers to elements, individual compounds, groups of compounds, chemical or physical properties. Contaminant groups in Table 3 are underlined and are simply identified for convenience. These group names do not reflect any official or standardized groups used by other agencies. Italicized contaminant names indicates that the MDEQ Lab does not perform analysis for the contaminant.
3. Methods in the table are listed primarily to clarify the type of method routinely used for environmental samples and preservation used for associated contaminants. The methods listed are not the only methods acceptable. RRD Operational Memorandum No. 2, Attachment 1, TDLs and Available Methods lists the available analytical methods the MDEQ has determined capable of achieving the TDLs. When available methods are used, applicable sample preservation techniques within those methods must be used.
4. Abbreviations and terms used for preservation are as follows:

<b>Abbreviation</b>	<b>Meaning</b>	<b>Abbreviation</b>	<b>Meaning</b>
< - >	Less than - Greater than	HNO <sub>3</sub>	Nitric acid
M	Molar concentration	NaOH	Sodium hydroxide
N	Normal concentration	ZnAc	Zinc acetate
HCl	Hydrochloric acid	° C	Degrees centigrade
H <sub>2</sub> SO <sub>4</sub>	Sulfuric acid	In Situ	Measure in matrix
EDTA	Ethylenediamine,tetra,acetic acid		

**ASAP** – Make arrangements to deliver samples overnight and have laboratory analyze samples upon receipt.

**Immediately** - Transport samples to laboratory within 24 hours or overnight. Plans must be made in advance to have the laboratory analyze the samples upon receipt.

**4° C** – Store samples at about four degrees centigrade. Just above freezing up to six degrees C is acceptable. Ice is preferred to cool samples. If commercial ice packs are used, the bottom, walls, and top inside cover of the cooler must be lined with the packs so as to completely encapsulate the samples as much as possible. A temperature control sample should be included when blue ice packs are used.

**De-chlorinate** – Means that a portion of the sample should be separated and tested for residual chlorine. Diethyl-p-phenylenediamine (DPD) kits are commercially available to test for residual chlorine in the field. About 25 mg ascorbic acid powder per 40 ml sample, for each 5 mg/L of residual chlorine determined from the DPD kit, should be added to sample bottles testing positive that are to be used to analyze for volatile contaminants, prior to sampling. For non-volatile contaminants use 80 mg/L sodium thiosulfate per liter of sample for each 5 mg/L of residual chlorine found. If pH adjustment is necessary, perform pH adjustment after dechlorination. Do not mix dechlorination reagents with the preservatives used to adjust the pH. Treat the samples only if they contain free or combined chlorine. Most environmental samples are not chlorinated while tap water samples originating from a municipal water source usually are chlorinated.

**pH** – Indicates an estimated hydrogen ion measurement. Use only the specified chemicals to adjust pH. Do not add more than is needed to obtain the desired pH. If preservation using hydrochloric or sulfuric acids (HCl or H<sub>2</sub>SO<sub>4</sub> ) is needed, two drops of 1:1 HCl, or H<sub>2</sub>SO<sub>4</sub> for every 40 ml of sample, will lower the pH to less than two for most waters.

## Table 3 Footnotes

5. "Holding Time" refers to the maximum time that a sample or sub-sample can be held before the next step in the analysis is performed. Samples may be held for other specified times if the laboratory has supporting data to demonstrate stability. Exceptions to times specified in the heading of this column are explained within the table for each applicable contaminant.
6. The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. Note: The addition of EDA has no effect on bromate or chlorate, so they can also be determined in a sample preserved with EDA. Residual chlorine dioxide should be removed from the sample. Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample must be purged with an inert gas (helium, argon, or nitrogen) for approximately five minutes or until no chlorine dioxide remains. This sparging must be conducted prior to ethylenediamine preservation and at time of sample collection.
7. Limit compositing to less than 24 hours and then follow grab sample guideline of 24 hours after collection.
8. Several methods are available to measure TPH. Results are method dependent.
9. No hold time has been established. Samples should be analyzed as soon as possible.
10. The MDEQ Lab DO kit uses solutions designated as DO-1 (Manganese Sulfate ) and DO-2 (alkaline Iodide-Azide).
11. Prior to collection, add to sample bottle 8 drops 1 M ZnAc per 100 ml sample to be collected and enough 10 N NaOH expected to make pH > 9. Collect sample with minimum of aeration, add more NaOH as needed to increase pH > 9. Fill bottle without headspace. If the sulfide concentration is expected to exceed 64 mg/L, increase the amount of ZnAc proportionally.
12. Disodium EDTA. Prepare using 2.5 g per 100 ml distilled water.
13. Applicable to mineral oils. Not appropriate for analysis of soils for gasoline and other light petroleum fractions.
14. Under the Federal Safe Drinking Water Act guidance, a 30-hour holding time for coliform samples mailed from water treatment systems is acceptable. Water samples for coliform analysis should have 1-2 inches of headspace in the sample container.
15. Aqueous samples should be tested for sulfides, oxidizing agents, and soluble aldehydes within 15 minutes of sampling to determine and preserve as appropriate. Alternatively, all samples may be preserved with NaOH to a pH>12 and sent to the lab for analysis within 24 hours.

## A. Test for Oxidizing Agents

Test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment.

To samples testing positive add 0.1N Sodium Arsenite solution a few ml at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 ml of Sodium Arsenite solution for each liter of sample.

Ascorbic Acid can be used as an alternative although it is not as effective as Sodium Arsenite. Add a few crystals of Ascorbic Acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of Ascorbic Acid for each liter of sample volume.

## Table 3 Footnotes

B. Test for Sulfides (Note that samples are always treated with Lead Carbonate or Cadmium Nitrate.)

Samples with visible particulates must be filtered.

Keep this filter (#1).

Treat samples with solid Lead Carbonate or Cadmium Nitrate powder and immediately filter.

Discard this filter.

Test filtrate for sulfides using Lead Acetate paper and further treat samples showing positive results with Lead Carbonate or Cadmium Nitrate powder and filter.

Discard this filter.

Continue testing until samples show a negative result for sulfides using Lead Acetate paper.

C. Soluble Aldehydes Test

Use a separate solution of the sample to test for aldehydes.

Treat samples showing a positive result with 20 ml of 3.5% Ethylenediamine solution per liter of sample.

D. Preservation

Reconstitute the sample by adding the sediment collected on filter #1 back into the filtrate.

Add NaOH until the sample pH > 12 and cool to 4°C.

Maximum holding time is now 14 days. Equipment blanks must be handled the same as real samples.

16. Buffer Solution. Dissolve 33 g of ammonium sulfate in 75 ml of reagent water and add 6.5 ml of ammonium hydroxide. Dilute to 100 ml with reagent water. Degas the solution with helium gas for 5-10 minutes prior to use. Add the buffer solution, drop wise, to the sample and check after addition with pH paper, or continuously with a pH meter.

17. Method 3060A must be used for preparation of soils. Barium chromate is only partially soluble using Method 3060A. This method may not be appropriate for investigations involving this contaminant when high levels of barium are found at sites.

18. White phosphorus from munitions is released into the environment in the form of small, discrete particles. These particles persist in soils, sediments, and may occur as suspended or colloidal particles in anoxic waters. Therefore, some samples or sample aliquots from a given location may contain P4 particles while others do not. The nature and distribution of P4 contamination from other, non-military, sources has not been studied, but sample collection procedures should address the likelihood that P4 is present in discrete particles, and must be designed to ensure that multiple representative samples of the matrix of interest are collected. In addition, soil and sediment samples must be carefully homogenized and sub-sampled.

Aqueous samples should be poured gently into the sample container to minimize agitation which might drive off the volatile P4. If bubbling does occur while transferring the sample to the container, the sample should be discarded and another sample collected. Each container should be filled with sample until it overflows. Each container should be tightly sealed with a PTFE-lined cap. The container should then be inverted to check for air bubbles. If any air bubbles are present, a new sample must be collected.

**Table 3 Footnotes**

19. If boron is a chemical of concern at a site, use a wide mouth plastic container for collection of soil samples.
20. If analysis includes BHCs, cis, trans-Permethrin, or Trifluralin, samples should be extracted as soon as is practical. See requirements for specific pesticides, published under the Safe Drinking Water Act and applicable to drinking water samples.
21. If analysis includes Disulfoton Sulfoxide, Diazinon, Pronamide, or Terbufos, samples must be extracted as soon as is practical.
22. Includes groups referred to in other guidance as:  
Total Petroleum Hydrocarbons (TPH), Acid Extractables (Phenols), Chlorinated Hydrocarbons, Nitroaromatics and Isophorone, Nitrosoamines except Diphenylnitrosamine, Polynuclear Aromatics, Phthalate Esters, Haloethers, and Phenolics.
23. If samples are to be analyzed for semivolatiles and pesticides/PCBs, collect a total of three containers. For quality control purposes, collect an additional container for each contaminant group, for every 20 samples.
24. Reactive contaminants with cleanup criteria include 2-chloroethylvinyl ether and styrene. Contact the laboratory regarding other contaminants.
25. Preservation as provided in RRD Operational Memorandum No. 2, Attachment 6 is required for the collection of soils. The MDEQ Lab provides a sampling kit to collect soil samples using this procedure. Soils collected to determine volatiles leached from soils should be sampled with 25 gr syringe-type coring devices.

The sonication time used to extract the volatile compounds from the soil is important and must be standardized for analysis of volatile organic compounds in soil and comparison of results with the cleanup criteria. Soils should be sonicated as soon as possible after receipt, and a 20-minute sonication time must be used as specified in the MDEQ Lab SOP #501, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS).

26. Specifications must be followed from Modified DRO, Method for Determining Diesel Range Organics, Wisconsin DNR, September 1995 for DRO and Modified GRO, Method for Determining Gasoline Range Organics, Wisconsin DNR, September 1995, for GRO.
27. The pH of all water samples must be determined by the laboratory unless sample vials containing acid for field preservation were supplied by the lab. The pH measurement may be performed on left-over sample. If the pH is greater than two, the sample results must be flagged. Flagging is not required of samples collected from carbonate aquifers if preserved with sodium azide or extracted within 48 hours of collection.
28. The Wisconsin procedure requires a Teflon™ lined cap. The Teflon™ must be touching the sample.
29. The data in this table applies to soils to determine potential leaching of contaminants. See RRD Operational Memorandum No.2, Attachment 2, Soil Leaching Methods for applicable leaching tests.

Each soil type tested should have associated quality control as provided in the leaching procedures. This requires spiking the leaching solution with the contaminants of concern at levels above the TDIs listed in RRD Operational Memorandum No.2, Attachment 1. When relevant pathways have been evaluated for response activity under Part 201 or Part 213, spiking the leaching solution may be appropriate at approximately one-half of the cleanup criteria for the appropriate pathway whenever possible. Duplicate samples should be collected to facilitate the spiking of samples.

**Table 3 Footnotes**

The crushing, cutting, grinding, sieving, and filtering, or other procedures used in leaching procedures may alter the physical characteristics of soils. As the physical characteristics of soils may affect the mobility of contaminants, such procedures are not appropriate for soils for the purposes of this test. Such procedures may be appropriate for other types of material such as brick and concrete.

Samples collected and stored using a syringe-type coring device (SCD), as specified in Method 5035 of SW-846, should be extruded directly into the leaching solution by the laboratory to minimize exposure to the atmosphere.

After completion of the leaching procedure for soils, aliquots taken for analysis of specific contaminants must be immediately collected and preserved as specified in Table 3 for aqueous solutions of the respective contaminants.

30. Other holding times, specific for compounds within the contaminant groups, may be more appropriate. If the compounds of concern at a site have been established, use specifications in this table specific for these compounds, or specifications as may be provided in the analytical method itself.
31. Contact the MDEQ Lab concerning the use of leaching procedures for other contaminants.
32. Extracts from leaching tests should be preserved immediately after leaching, according to the guidance given in the individual analysis methods for the contaminants being measured.
33. Sample collection procedures using a syringe-type coring device, as provided in Method 5035, are appropriate when leaching is used to evaluate the mobility of volatile components leached from soils. Extrusion of the soil sample into the leaching solution by the laboratory is required within 48 hours. After completion of the leaching procedure, an aliquot of leaching solution must be immediately collected and preserved as specified in Table 3 for associated contaminants in aqueous solutions. If larger sample sizes are required, multiple devices must be used.