

US EPA ARCHIVE DOCUMENT

December 22, 1997

MEMORANDUM

SUBJECT: Determination of Volatiles in Soil - Directive for Change

FROM: Norman R. Niedergang, Director
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TO: Corrective Action Project Managers
QA Staff

I. INTRODUCTION/SUMMARY

Soil/Solids traditionally have been collected for volatile organic determinations using “low concentration volatiles in soil” techniques described in Update II to SW-846, or earlier editions. Update III to SW-846, published June 13, 1997, deleted the “low concentration volatiles in soil” sample collection/laboratory procedure. Update III mandates that analysis aliquots (field or off-site lab) be collected in the VOA vial (with TFE lined septa cap) used for laboratory analysis. Either a methanol extraction reagent or a matrix modifying reagent are to be added to a soil aliquot at time of sample collection. Separate soil samples are collected for percent moisture determinations for reporting volatile results on a dry weight basis.

Technical and QA staff of our Waste, Pesticides and Toxics Division (WPTD) have reviewed and disseminated published experimental data comparing Update II and Update III soil sample collection techniques for volatile organics. Our Division has supported some of this work through the UST program in Wisconsin. Update III sample collection techniques are more complicated and tedious for volatiles than those of Update II; however, the accuracy of the modern Update III soil collection techniques warrant their immediate use versus traditional methods. Previous methodology has been shown to significantly under-report the presence of volatiles in soil.

II. DIRECTIVE

1. Starting January 1, 1998, all RCRA Corrective Actions and Underground Storage Tank (UST) activities under the direct control of the Waste, Pesticides and Toxics Division will determine volatiles in soil using sample collection procedures consistent with Methods 5021 or 5035 of Update III to SW-846, “Test Methods

for Evaluating Solid Waste” as published in Federal Register of June 13, 1997, Vol. 62, No. 114, pp. 32452-463.

2. If Work Plan/Quality Assurance Project Plans (QAPPs) were approved prior to January 1, 1998 using the traditional “low-concentration volatiles in soil” procedures of Update II to SW-846, these documents are to be modified for future sampling, done after January 1, 1998 to reflect use of Update III techniques for soil/solids. Significant numbers of corrective action soil surveys are not expected to occur during first quarter of calendar year 1998. Time should be available to update sample collection/laboratory test procedures for soil volatiles. Updating these documents will be a high priority of the QA staff. Any exceptional circumstances that suggest use of the old procedure must be brought to the attention of the Corrective Action Process Manager and QA staff no later than January 15, 1998.
3. Although Update III to SW-846 was effective June 13, 1997, EPA’s Office of Solid Waste, in a policy memorandum, recommended Update III changes be cautiously implemented to allow laboratory and sampling organizations time to purchase new instrumentation/equipment. A six (6) month delay in implementing Update III was suggested, and this is equivalent to the above January 1, 1998 date.
4. Update III to SW-846 provides three (3) options for volatile determinations of soil, either at on-site field labs, or for off-site analytical support laboratories.
 - a. Soils will be collected and tested using only the methanol extract option of Method 5035.
 - b. Soils will be collected and tested using both the methanol extract option of Method 5035 for large volatile concentrations and either one of the low concentration procedures of Method 5021/5035.
 - c. Alternatively, soils can be collected using the En-Core (or equivalent) sampler for subsequent sample preparation by Methods 5021 or 5035 in a field or off-site laboratory.

The need and use of a low concentration option from Method 5021 or Method 5035 will be determined for each Corrective Action or UST activity based on Data Quality Objectives, risk, project needs, intended data use, etc. This directive does not apply to in-situ field determinations of volatiles in soil. Attached to this Directive is a table identifying EPA Region 9 Soil Preliminary Remedial Goals

and Superfund Soil Screening Levels whose values for volatiles are less than 200 ppb. The table identifies critical volatile compounds that may dictate use of low concentration options. The 200 ppb cutoff is taken from SW-846 guidance. This criteria may vary for specific lab instrumentation.

5. It is relatively easy to implement the methanol extraction for sample collection/laboratory analysis. Volatile soil determinations, using methanol, are done using the same instrumentation currently in place for waters. Many or most laboratories are now purchasing sample preparation instrumentation necessary for the low concentration option of Method 5035, or for Method 5021, hence the 6-month delay in implementation. Consistent use of Update III will provide a level playing field for sampling/lab organizations.
6. U.S. EPA contractor support (e.g.,-oversight activities) for RCRA Corrective Action or UST activities, will determine volatiles in soil/solids using Update III procedures.
7. Soils/samples tested at the Region 5 Central Regional Laboratory for the WPTD will determine soil volatiles consistent with Update III.

III. DETAILED BACKGROUND

The analysis of volatile organic compounds, or volatiles in soil commonly has utilized collection of a soil in a 40-60 ml VOA vial with TFE lined septa, refrigerated transport to a laboratory (field or off-site), and soil subaliquots (2-5) selected by the laboratory for heated purge and trap GC or GC/MS analysis. This process has been known as the “low concentration volatiles in soil” test procedure. For medium or high level volatile concentrations in soil, the laboratory could alternatively extract the soil with water-miscible methanol extraction solvent and then test the methanol extract (after dilution) as they would for water. Methanol extraction values were traditionally a very minor part of all volatile soil data reported.

A large body of state, federal, and private research, independent from operational EPA staff and programs, has demonstrated the above “low concentration volatiles in soil” methodology to be inaccurate and biased low versus sample collection in the specific VOA containers used for laboratory analysis (field or lab). Negative errors are commonly observed for the traditional technique and are caused by a variety of field/transport/lab volatile concentration losses.

Update III to SW-846, published in the June 13, 1997 Federal Register, deleted the “low concentration volatiles in soil” protocol from the manual and replaced it with the following three (3) alternatives:

1. Method 5021 - Heated Head Space. This is applicable to volatile concentration below 200 ppb.

2. Method 5035 - Heated Purge and Trap (Low Concentration Option in range of 5 to 200 ppb). Five (5) mls of a matrix modifying solution is added to 2-5g of soil at time of sample collection.
3. Method 5035 - Methanol Extract (High Concentration Option for volatiles exceeding 200 ppb). Methanol is added to 2-5g of soil at time of collection, then subsequently diluted with water and tested for volatiles by Method 5030.

All of the three alternatives require a tared VOA vial with matrix modifying solution or methanol, addition of 2-5g soil at time of collection to the vial, and then a final vial weight to determine soil aliquot weight by difference. Separate vials are used for the collection and determination of soil moisture content.

The above options can be implemented in several ways depending on field or off-site lab capability or based on Data Quality Objectives.

1. A separate VOA vial is always collected for a percent moisture value.
2. A single methanol extract VOA vial is collected for each soil site to provide for volatile concentrations exceeding 200 ppb. Analyses can be repeated, since the methanol extract is easily rediluted.
3. Two or more low concentration option VOA vials (Methods 5021 or 5035) are collected for each soil site. One is necessary for concentration measurements below 200 ppb - the other serves as a backup for any reanalyses. The heated headspace analysis (Method 5021) can be repeated using a different or smaller air volume.
4. The methanol extract VOA vial alone may suffice for many soil surveys. The low level options of Methods 5021 and 5035 may be unnecessary, depending on DQOs or risk assessment values. A unique aspect of methanol extracts is that soils can be composited for volatiles via their methanol extracts.
5. Method 5035 specifies/approves the use of the En-Core proprietary/patented soil sampler, as an alternative to use of methanol reagent in the field. This sampler can collect 5g soil cores with no loss in sample integrity if transported to a lab within two days of sample collection. Sample preparation can then be done by any of the above techniques.

The above procedures and alternatives are more complicated and tedious than the traditional "low-concentration volatiles in soil," however, their accuracy warrants and justifies their use versus the traditional techniques. The new procedures require careful coordination between

field and lab personnel and use of VOA vials that are compatible with specific laboratory instrumentation. For more information, or assistance in choosing the new option best suited to project objectives, please consult with QA staff members.

Attachment

ATTACHMENT

Volatile Contaminants, whose EPA Region 9 Soil Preliminary Remedial Goals (PRGs) or Superfund Soil Screening Levels:

1. Are less than 200 ppb (ug/kg) threshold/detection of methanol extraction for method 8260; or
2. Between 200 and 1,000 ppb (0.2 - 1.0 ppm), where quantitation is uncertain for method 8260 after methanol extraction of soil.

Tap Water PRGs which are less than 1 ug/L (ppb) (threshold of Method 8260) are listed for comparison.

(If Soil PRG is greater than 1,000 ppb or 1.0 ppm, it is not listed and methanol extraction should be successful for risk assessment.)

Volatile Contaminant Group	Soil Residential PRG (ug/kg or ppb) (<200) (200-1000)	Soil Industrial PRG (ug/kg or ppb) (<200) (200-1000)	Superfund Soil Screening level-DAF 20 (ug/kg or ppb) (<200) (200-1000)	Tap Water PRG (ug/L) (<1)
<u>Appendix IX Hydrocarbon:</u>				
benzene (ca)	630		30	0.39
<u>Non Appendix IX Hydrocarbon:</u>				
1,3 butadiene (ca)	6.5	14	Not Available	.011
<u>Common Appendix IX Halogenated Hydrocarbons:</u>				
bromomethane (nc)			800	
carbon tetrachloride (ca)	230	500	70	.17
1,2 dichloroethane (ca)	250	550	20	.12
1,1 dichloroethene (ca)	37	80	60	.046
cis-1,2 dichloroethene (nc)			400	
trans-1,2 dichloroethene (nc)			700	
1,2 dichloropropane (ca)	310	680	30	.16
1,3 dichloropropene (ca)	250	550	4	.081
methylene chloride (ca)			20	4.3 (lab cont.)
Volatile Contaminant Group	Soil Residential (ug/kg or ppb) (<200) (200-1000)	Soil Industrial PRG (ug/kg or ppb) (<200) (200-1000)	Superfund Soil Screening level -DAF 20 (ug/kg or ppb) (<200) (200-1000)	Tap Water PRG (ug/L) (<1)

1,1,2,2 tetrachloroethane (ca)	450		3	.055
1,1,1,2 tetrachloroethane (ca)				.43
tetrachloroethene (PCE) (ca)			60	1.1
1,1,2 trichloroethene (ca)	650		20	.20
Vinyl chloride	16	35	10	.02
1,4 dichlorobenzene (ca)				.47
<u>Non Appendix IX Halogenated Hydrocarbons:</u>				
vinyl bromide (ca)	190		410	.10
<u>Appendix IX Trihalomethanes:</u>				
chloroform (ca)	250	530	600	.16
bromodichloromethane (ca)	630		600	.18
Dibromochloromethan e (ca)			400	1.0
Bromoform (ca)			800	
<u>Specialized Appendix IX Halogenated Hydrocarbons:</u>				
1,2 dibromo-3- chloropropane (DBCP) (ca)	320		Not Available	.048
1,2 dibromoethane (EDB) (ca)	4.9	20	Not Available	.00076
1,4 dichloro-2-butene (ca)	7.5	100	Not Available	.0012
1,2,3 trichloropropane (ca)	1.4	3.1	Not Available	.0016
Volatile Contaminant Group	Soil Residential PRG (ug/kg or ppb) (<200) (200-1000)	Soil Industrial PRG (ug/kg or ppb) (<200) (200-1000)	Superfund Soil Screening Level- DAF 20 (ug/kg or ppb) (<200) (200-1000)	Tap Water PRG (Ug/L) (<1)
<u>Appendix IX Water -- Miscible Volatiles:</u>				
acrolein (nc)	100	340*	Not Available	.042

acrylonitrile	190	470*	Not Available	3.7*
1,4 dioxane			Not Available	1.0*
methacrylonitrile (nc)	2,000*		Not available	
acetonitrile (nc)			Not Available	71*
<u>non Appendix IX Water Miscible Volatiles:</u>				
acrylamide (ca)	980		Not Available	.015
ethyl acrylate (ca)	210	450	Not Available	.23
ethylene oxide (ca)	130	320	Not Available	.024
malonitrile (nc)	1,300*		Not Available	.73
propylene oxide (ca)	Not Available	Not Available	Not Available	.22

Ca) - Cancer PRG

(Nca) - noncancer PRG

*All water miscible volatiles have poor purging efficiencies by method 8260. Detection limits are elevated for method 8260 for these types of volatiles. Asterisked volatile criteria are adjusted for purging efficiency. 1,4 dioxane has less than 1% purging efficiency at room temperature.

