METHOD 3570

MICROSCALE SOLVENT EXTRACTION (MSE)

1.0 SCOPE AND APPLICATION

1.1 Method 3570 is a procedure for extracting volatile, semivolatile, and nonvolatile organic compounds from solids such as soils, sludges, and wastes. The microscale approach minimizes sample size and solvent usage, thereby reducing the supply costs, health and safety issues, and waste generated.

1.2 This method has been validated for several mono- and poly-cyclic aromatic hydrocarbons (MAHs and PAHs) and can be applied to any combination of these compounds.

1.3 This method also may be used to extract any volatile organic compounds (VOCs) or semivolatile organic compounds (SVOCs) once their extraction performance has been demonstrated to be satisfactory using an appropriate analytical technique. Method 3570 is not amenable to samples that have been preserved in the field using methanol.

1.4 Prior to employing this method, analysts are advised to consult the base method for each type of procedure that may be employed in the overall analysis (e.g., Methods 3500, 3600, 5000, and 8000) for additional information on quality control procedures, development of QC acceptance criteria, calculations, and general guidance. Analysts also should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly required in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, appropriately experienced and trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Samples are prepared by shake extraction with an organic solvent in sealed extraction tubes. Careful manipulation of the sample, solvent, drying agent, and spiking solutions during the procedure minimizes loss of volatile compounds while maximizing extraction of volatile, semivolatile, and nonvolatile compounds.

2.2 Sample extracts are collected, dried, and concentrated using a modification of the Kuderna-Danish concentration method. By increasing the number of theoretical plates and reducing the distillation temperature, extracts are concentrated without loss of volatile constituents.

2.3 Since volatile compounds are included in the method, their extraction from solids

requires special handling and particular attention to detail. All solid samples are kept cold during the extraction procedure by storing them in a small cooler with blue ice or other appropriate cooling device. Samples are removed from the cooler only for as long as necessary to remove the sample aliquot. As much as possible, the sample container is kept tightly capped.

2.4 Samples should be prepared one at a time to the point of solvent addition (i.e., do not pre-weigh a number of samples then add the solvent). Pay particular attention to minimizing the exposure of the sample and/or extract to air.

2.5 Samples should be extracted as soon after collection as possible. Do not weigh out aliquots for percent solids before the samples are extracted. Do not homogenize the samples unless they appear to be heterogeneous. If so, thoroughly chill the sample and spatula before proceeding. Homogenize quickly and gently, then re-cap and re-chill the sample before proceeding.

3.0 DEFINITIONS

Refer to the SW-846 chapter of terms and acronyms for potentially applicable definitions.

4.0 INTERFERENCES

4.1 Solvents, reagents, glassware, and other sample processing hardware may yield artifacts and/or interferences to sample analysis. All these materials must be demonstrated to be free from interferences under the conditions of the analysis by analyzing method blanks. Specific selection of reagents and purification of solvents by distillation in all-glass systems may be necessary. Refer to each method for specific guidance on quality control procedures and to Chapter Four for guidance on the cleaning of glassware.

4.2 Refer to Method 3500 for additional information on interferences.

4.3 If necessary, florisil or silica gel cleanup procedures may be employed.

5.0 SAFETY

There are no significant safety issues specific to this method. However, SW-846 methods do not purport to address all safety issues associated with their use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

6.0 EQUIPMENT AND SUPPLIES

6.1 The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated

and documented.

6.2 Polytetrafluoroethylene (PTFE) tubes and caps.

6.3 Glass powder funnel with glass wool plugging the bottom.

6.4 Kuderna-Danish concentrator tube – 25-mL, graduated. A ground glass stopper is used to prevent evaporation of extracts.

6.5 Snyder columns – three-ball micro and two-ball micro

6.6 Rotator – Glas-Col or equivalent.

6.7 Boiling sticks – solvent-extracted.

6.8 Water bath – heated, capable of temperature control (+/- 5 °C). The bath should be used in a hood.

6.9 Vials – amber glass, 2-mL capacity, with PTFE-lined screw or crimp top.

6.10 Syringes - gastight, contaminant-free. 500 µL, 25 µL.

6.11 Apparatus for determining percent dry weight.

6.11.1 Drying oven – capable of maintaining 105 °C.

6.11.2 Desiccator.

6.11.3 Crucibles – disposable aluminum.

6.12 Analytical balance – capable of weighing to 0.01 g.

6.13 Glass beads – solvent-rinsed, bake in 400 °C oven for approximately one hour.

6.14 Pasteur glass pipettes – 1mL, disposable.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water as defined in Chapter One.

7.3 Sodium sulfate (granular, anhydrous), Na_2SO_4. Purify by heating at 400 °C for four hours in a shallow porcelain bowl. Store unused portion of sodium sulfate in a desiccator.

7.4 Extraction and exchange solvents.

The choice of solvent will depend on the analytes of interest and no single solvent is universally applicable to all analyte groups. Whatever solvent system is employed *including* those specifically listed in this method, the analyst *must* demonstrate adequate performance for the analytes of interest, at the levels of interest. At a minimum, such a demonstration will encompass the initial demonstration of proficiency described in Method 3500, using a clean reference matrix. Method 8000 describes procedures that may be used to develop performance criteria for such demonstrations as well as for matrix spike and laboratory control sample results.

All solvents should be pesticide quality or equivalent. Solvents may be degassed prior to use.

7.4.1 Methylene Chloride, CH_2Cl_2.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

9.0 QUALITY CONTROL

9.1 Refer to Chapter One for guidance on quality assurance (QA) and quality control (QC) protocols. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated. All data sheets and quality control data should be maintained for reference or inspection. When inconsistencies exist between QC guidelines, method-specific QC criteria take precedence over both technical-specific criteria and those criteria given in Chapter One, and technique-specific QC criteria take precedence over the criteria in Chapter One.

9.2 Refer to Method 3500 for additional quality control procedures.

9.3 Before processing any samples, the analyst should demonstrate that all parts of the equipment in contact with the sample and reagents are interference-free. This is accomplished through the analysis of a method blank. Each time samples are extracted, cleaned up, and analyzed, and when there is a change in reagents, a method blank should be prepared and analyzed for the compounds of interest as a safeguard against chronic laboratory contamination.

9.4 Any method blanks, matrix spike samples, or replicate samples should be subjected to the same analytical procedures (Sec. 11.0) as those used on actual samples.

9.5 Each extraction batch of twenty or fewer samples should include an extraction blank, a laboratory control sample (LCS), a matrix spike sample, and a matrix spike duplicate or laboratory duplicate sample.

9.6 All field and QC samples should be spiked with an appropriate mix of surrogate compounds in order to track extraction efficiency.

9.7 Any reagent blanks, matrix spike, and replicate samples should be subjected to exactly the same analytical procedures as those used on field samples.

10.0 CALIBRATION AND STANDARDIZATION

There are no calibration or standardization steps directly associated with this procedure.

11.0 PROCEDURE

11.1 Add approximately 2.5 grams of anhydrous sodium sulfate to a pre-cleaned PTFE extraction tube which has a PTFE screw cap. Also add 5 to 10 pre-cleaned glass beads.

11.2 Weigh 2 to 3 grams of solids or waste into the tared extraction tube. Do not mix the sample and sodium sulfate at this time. Wipe the lip and threads of the tube with a Kimwipe, or equivalent. Tightly cap, then record the weight to the nearest 0.01 g.

11.3 Add 50 µg of the surrogate standard compounds in methylene chloride (DCM) directly to the soil. The surrogates recommended are fluorobenzene, 2-fluorobiphenyl, and 5-a-androstane. Other compounds may be used as surrogates, depending upon the desired target analytes and project requirements. If the sample is a matrix spike sample, add 50 µg of the appropriate matrix spike compounds.

The surrogate and matrix spike compounds should be at a concentration of 100 µg/mL in the spiking solution.

11.4 Add 12 mL of DCM to the tube, and cap tightly.

11.5 Shake the tubes vigorously until the slurry is free-flowing. Break up any chunks with a metal spatula, working quickly but gently. Cap immediately when finished.

Add more sodium sulfate and manually mix as necessary to produce a free-flowing, finely divided slurry.

11.6 Extract the samples by rotating end-over-end for at least 4 hours.

11.7 Allow the solids to settle or centrifuge for one to two minutes. Decant or pipet the solvent layer into a small glass funnel containing a layer of anhydrous sodium sulfate over a plug of glass wool. The sodium sulfate should be thoroughly pre-wetted with DCM. Filter the extract into a 25mL Kuderna-Danish (K-D) concentrator tube. Rinse the sodium sulfate with 2 to 3 mL of DCM as soon as the surface is exposed. Do not allow the top of the sodium sulfate layer to go dry.

11.8 Extract the soil twice more by adding approximately 5 mL of DCM to the sample, capping the extraction tube tightly, and shaking vigorously by hand for 2 minutes. Be certain to wipe the lip and threads of the extraction tube with a Kimwipe, or equivalent, before capping each time.

More sodium sulfate can be added at this point as necessary to dry the extract and break up any clumps that may have formed.

11.9 After each extraction step, follow step 11.7.

11.10 Add a Teflon boiling stick to the K-D concentrator tube, and attach one, three-ball micro-Snyder column and one, two-ball micro-Snyder column in series.

11.11 Pre-wet the Snyder columns by adding 0.5 mL of DCM to the top of the column.

11.12 Place the K-D apparatus in a constant temperature hot water bath so that the concentrator tube is partially, but not completely, immersed. Adjust the temperature of the bath and the position of the apparatus so that the solvent boils evenly, and the micro-Snyder column balls chatter but the chambers do not flood with condensed solvent (approximately 60 to 65 °C).

11.13 Reduce sample volume to approximately 1.0 mL. Remove and allow to cool and drain for several minutes.

11.14 Remove the Snyder columns and the boiling stick.

11.15 Record the exact final volume of the extract.

If the volume of the extract does not fall exactly on one of the calibration lines of the concentrator tube, then add enough DCM so that it does, then record that volume.

11.16 Add an appropriate amount of the internal standard compounds to give a concentration of 50 µg/mL in the extract. Add the internal standard directly to the K-D tube. Transfer the extract to a 2 mL vial fitted with a PTFE lined screw cap. Cap the vial and store in the freezer or over ice until analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

There are no data analysis and calculation steps directly associated with this procedure. Follow the directions given in the determinative method.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance goals for users of the methods. Instead, performance goals should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method.

13.2 Single-laboratory precision data were obtained for MAHs and PAHs at two different spiking concentrations in clean sand. Spiked samples were extracted in triplicate. Extracts were analyzed by Method 8100 modified to include the MAHs. Data summary tables are included in this method. For guidance purposes, the data are reported in detail in Reference 1.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, (202) 872-4477.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. “Simultaneous Analysis of Monocyclic Aromatic Hydrocarbons in Soil by Microscale Solvent Extraction (MSE).” EPRI Report TR-Research Project 9137-01, October 1996.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain the tables and figures referenced by this method.

TABLE 1

EXAMPLE MSE GC/FID RECOVERY DATA AND STANDARD DEVIATIONS FOR MAHs AND PAHs IN CLEAN MEDIUM SAND SPIKED AT 0.050 mg/kg[1]

Compound	Sample A		Sample B		Sample C		Std. Dev.
	Conc.[2]	% Rec.	Conc.[2]	% Rec.	Conc.[2]	% Rec.	
Benzene	NA	NC	NA	NC	NA	NC	NC
Toluene[3]	0.074	150	0.077	150	0.109	220	0.019
Ethylbenzene	0.045	89	0.046	93	0.046	92	0.0009
m/p-Xylene	0.094	94	0.093	93	0.098	98	0.0026
Styrene	0.045	90	0.026	52	0.046	91	0.011
o-Xylene	0.046	92	0.056	112	0.048	96	0.0054
1,2,4-Trimethylbenzene	0.047	93	0.048	96	0.050	100	0.0018
Naphthalene	0.044	89	0.035	69	0.045	90	0.0057
2-Methylnaphthalene	0.047	95	0.049	98	0.051	102	0.0017
1-Methylnaphthalene	0.042	84	0.046	93	0.045	90	0.0023
Acenaphthylene	0.050	99	0.049	98	0.050	100	0.0007
Acenaphthene	0.055	110	0.054	109	0.063	125	0.0046
Dibenzofuran	0.046	91	0.046	91	0.047	94	0.0007
Fluorene	0.041	82	0.043	86	0.045	89	0.0018
Phenanthrene	0.053	106	0.044	87	0.050	101	0.0047
Anthracene	0.051	102	0.056	112	0.047	94	0.0045
Fluoranthene	0.045	90	0.052	104	0.045	90	0.0040
Pyrene	0.050	100	0.047	94	0.048	96	0.0014
Benz(a)anthracene	0.047	95	0.046	93	0.037	74	0.0056
Chrysene[3]	0.061	122	0.065	131	0.035	69	0.017
Benzo(b)fluoranthene[3]	1.33	2660	1.93	3860	1.66	3310	0.30
Benzo(k)fluoranthene	0.051	102	0.039	78	0.033	65	0.0093
Benzo(a)pyrene	0.042	85	0.016	31	0.047	94	0.017
Indeno(1,2,3-cd)pyrene	0.035	69	0.033	66	0.039	77	0.0029
Dibenz(a,h)anthracene	0.038	76	0.037	74	0.040	80	0.0015
Benzo(g,h,i)perylene	0.042	84	0.041	82	0.044	88	0.0014

NA = Not available
NC = Not calculated

1 Three clean medium sand samples were spiked at 0.050 mg/kg with all target compounds (in acetone), and then extracted and analyzed by the method. A small spiking volume at high analyte concentration was used to maximize the analyte/soil interaction prior to the extraction step.

2 Concentration units are mg/kg.

3 High compound recovery was caused by an unidentified interference, possibly a silicone compound.

TABLE 2

EXAMPLE MSE GC/FID RECOVERY DATA AND STANDARD DEVIATIONS FOR MAHs AND PAHs IN CLEAN MEDIUM SAND SPIKED AT 0.075 mg/kg[1]

Compound	Sample A		Sample B		Sample C		Std. Dev.
	Conc.[2]	% Rec.	Conc.[2]	% Rec.	Conc.[2]	% Rec.	
Benzene[4]	0.329	88	0.373	99	0.395	105	0.034
Toluene[3]	0.095	126	0.095	126	0.094	125	0.0003
Ethylbenzene	0.070	93	0.068	91	0.074	99	0.0032
m/p-Xylene	0.146	97	0.142	95	0.145	97	0.0021
Styrene	0.070	93	0.068	91	0.070	93	0.0010
o-Xylene	0.072	96	0.071	95	0.073	98	0.0009
1,2,4-Trimethylbenzene	0.078	104	0.074	98	0.078	103	0.0025
Naphthalene	0.068	91	0.068	91	0.069	92	0.0004
2-Methylnaphthalene	0.075	99	0.075	100	0.073	98	0.0009
1-Methylnaphthalene	0.068	91	0.068	91	0.068	90	0.0003
Acenaphthylene	0.075	99	0.074	99	0.073	98	0.0007
Acenaphthene	0.078	103	0.081	107	0.076	101	0.0023
Dibenzofuran	0.069	92	0.070	93	0.069	92	0.0004
Fluorene	0.071	94	0.071	94	0.068	91	0.0014
Phenanthrene	0.076	101	0.075	100	0.076	102	0.0008
Anthracene	0.071	94	0.069	92	0.069	92	0.0009
Fluoranthene	0.070	93	0.074	98	0.070	94	0.0019
Pyrene	0.071	95	0.075	100	0.070	94	0.0024
Benz(a)anthracene	0.068	91	0.055	73	0.068	91	0.0078
Chrysene[3]	0.056	74	0.055	73	0.091	121	0.020
Benzo(b)fluoranthene[3]	1.11	1480	0.907	1210	1.15	1530	0.13
Benzo(k)fluoranthene	0.061	81	0.048	64	0.070	93	0.011
Benzo(a)pyrene	0.065	87	0.066	88	0.065	87	0.0007
Indeno(1,2,3-cd)pyrene	0.062	82	0.063	83	0.054	72	0.0048
Dibenz(a,h)anthracene	0.062	82	0.058	77	0.061	81	0.0018
Benzo(g,h,i)perylene	0.066	88	0.064	86	0.067	89	0.0010

NA = Not available
NC = Not calculated

1 Three clean medium sand samples were spiked at 0.075 mg/kg with all target compounds (in acetone), and then extracted and analyzed by the method. A small spiking volume at high analyte concentration was used to maximize the analyte/soil interaction prior to the extraction step.
2 Concentration units are mg/kg.
3 High compound recovery was caused by an unidentified interference.
4 Benzene was spiked at 0.375 mg/kg.