United States
Environmental Protection
Agency

Office of Water and
Waste Management
Washington, DC 20460

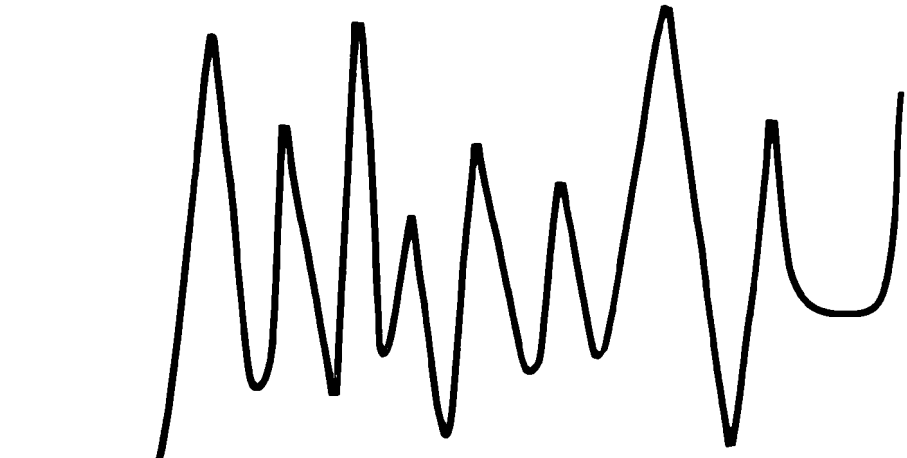
SW - 846
Revision A
August 8, 1980

Solid Waste

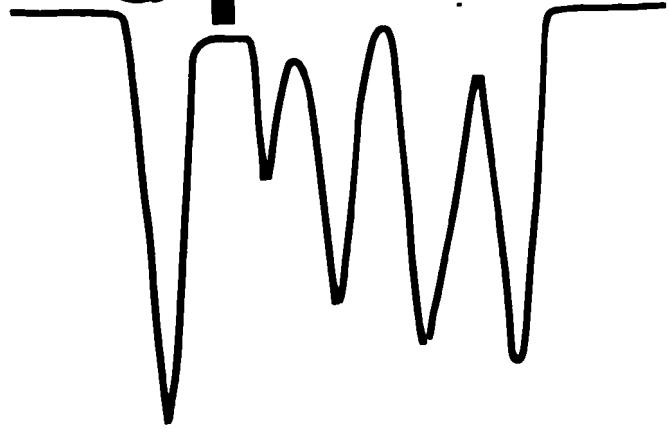
EPA

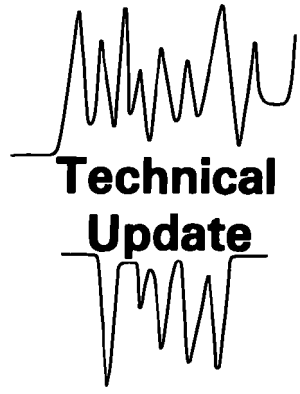
Test Methods for Evaluating Solid Waste

Physical/Chemical Methods



Technical Update





The enclosed material, SW-846.a, updates the manual "Test Methods for Evaluating Solid Waste" (SW-846). It is the first in a continuing series of "Technical Updates" to be issued as corrections, or additional methodologies and procedures become available.

Insert these pages in your manual to replace like-numbered pages or add as new pages where appropriate. The date of issue is printed in the upper righthand corner. Changes made on a page in that revision (but not those made in past revisions) are double-underlined. For easy and precise reference, the sequential number of each change is given in a footnote.

The Office of Solid Waste thanks those in both the public and private sectors who have made suggestions for improvement of this manual. We encourage additional comments and suggestions, which may be made by telephone or in writing. Comments should be sent to:

Manager, Waste Analysis Program
Office of Solid Waste
U.S. EPA (WH-565)
Washington, D.C. 20460
(202-755-9187)

U,S. Environmental Protection Agency

seal, a thermowell and temperature regulating device , a heating device (mantle, hot plate, or bath), and a specimen support system. A typical resin flask set up for this type test is shown in figure 1.

2. The supporting device and container should not be affected by or cause contamination of the waste under test.
3. The method of supporting the coupons will vary with the apparatus used for conducting the test but should be designed to insulate the coupons from each other physically and electrically and to insulate the coupons from any metallic container or other device used in the test. Some common support materials include: glass, fluorocarbon or coated metal.
4. The shape and form of the coupon support should assure free contact with the waste.

Test Procedure

1. Assemble the test apparatus as described the "Equipment" section above.
2. Fill the container with the appropriate amount of waste. (See #5 under the "Precautions and Comments" section.)
3. Begin agitation at a rate sufficient to insure that the liquid is kept well mixed and homogeneous.
4. Using the heating device bring the temperature of the waste to 55° C (130° F).
5. If the anticipated corrosion rate is moderate (i.e., <.254 mmpy)*, the test should be run for at leat 200 hours to insure adequate weight loss to permit accurate results to be obtained. If the corrosion rate is low (i.e., <.0254 mmpy)**,

* Change #1
** Change #2

then the test duration should be on the order of 2000 hours. in cases where the anticipated corrosion rate is completely unknown, initial testing should be performed using a 200 hour duration.

6. In order to accurately determine the amount of material lost to corrosion, the coupons have to be cleaned after immersion and prior to weighing. The cleaning procedure should remove all products of corrosion while removing a minimum of sound metal. Cleaning methods can be divided into three general categories: mechanical, chemical and electrolytic.

Mechanical cleaning includes scrubbing, scraping, brushing and ultrasonic procedures. Scrubbing with a bristle brush and mild abrasive is the most popular of these methods; the others are used in cases of heavy corrosion as a first step in removing heavily encrusted corrosion products prior to scrubbing. Care should be taken to avoid removing sound metal.

Chemical cleaning implies the removal of material from the surface of the coupon by dissolution in an appropriate solvent. Solvents such as acetone, dichloromethane, and alcohol are used to remove oil, grease or resinous materials, and are used prior to immersion to remove the products of corrosion. Solutions suitable for removing corrosion from the steel coupon are:

Solution	Soaking Time	Temperature
20% NaOH + 200g/l zinc dust	5 min	Boiling
or		
Conc. HCl + 50g/l $SnCl_2$ + 20g/l $SB^{-1}3$	Until clean	Cold

Electrolytic cleaning should be preceeded by scrubbing to remove loosely adhering corrosion products. One method of electrolytic cleaning that can be employed is:

Solution	50 g/l H_2SO_4
Anode	Carbon or lead
Cathode	Steel coupon
Cathode current density	20 amp/cm^2 (129 amp/in^2)
Inhibitor	2 cc organic inhibitor/liter
Temperature	74°C (165°F)
Exposure Period	3 minutes

Note: Precautions must be taken to insure good electrical contact with the coupon, to avoid contamination of the cleaning solution with easily reducible metal ions, and to insure that inhibitor decomposition has not occurred. Instead of using a proprietary inhibitor, 0.5 g/l or either diorthotolyl thiourea or quinolin ethiodide can be used.

Whatever treatment is employed to clean the coupons, its effect in removing sound metal should be determined using a blank (i.e., a coupon that has not been exposed to the waste). The blank should be cleaned along with the test coupon and its waste loss subtracted from that calculated for the test coupons.

7. After corroded specimens have been cleaned and dried, they are reweighed. The weight loss is employed as the principal measure of corrosion. Use of weight loss as a

measure of corrosion required making the assumption that all weight loss has been due to generalized corrosion and not localized pitting. In order to determine the corrosion rate for purpose of this requlation, the following formula is used:

$$\text{Corrosion Rate (mmpy)} = \frac{(\text{weight loss})\ (11.145)}{(\text{area})\ (\text{time})}*$$

where weight loss is in milligrams, area in square centimeters, time in hours, and corrosion rate in millimters per year (mmpy).

* Change #3

Table 7.2-1

APPROVED FILTER HOLDERS

Vacuum Filters

Manufacturer	Size	Model No.	Comments
Nalgene	500 ml	45-0045	Disposable plastic unit, includes prefilter and filter pads, and reservoir Should only be used when solution is to be analyzed for inorganic constituents
Nuclepore	47 mm	410400	
Millipore	47 mm	XX10 047 00	

Pressure Filters

Nuclepore	142 mm	420800	
Micro Filtration Systems	142 mm	302300	
Millipore	142 mm	YT30 142 HW	

Table 7.2-2

APPROVED FILTRATION MEDIA

Filter Type	Supplier	Filter To Be Used For Aqueous Systems*	Filter To Be Used For Organic Systems*
Coarse Prefilter	Gelman	†	†
	Nuclepore	210907 211707	210907 211707
	Millipore	AP25 042 00 AP25 127 50	AP25 042 00 AP25 127 00
Medium Prefilters	Nuclepore	210905†† 211705	210905†† 211705
	Millipore	AP20 042 00 AP20 124 50	AP20 042 00 AP20 124 50
Fine Prefilters	Nuclepore	210903 211703	210903 211703
	Millipore	AP15 042 00††† AP15 124 50	AP15 042 00††† AP15 124 50
Fine Filters (0.45um)	Gelman	60173 60177	60540 60544
	Pall	NX04750†††† NX14225	
	Nuclepore	111107 112007	181107 182007
	Millipore	HAWP 047 00 HAWP 142 50	FHLP 047 00 FHLP 142 00
	Selas	83485-02 83486-02	83485-02 83486-02

† Change #4
†† Change #5
††† Chenge #6
†††† Change #7

3. Stock standards - prepare stock standard solutions in methyl alcohol using assayed liquids or gas cylinders as appropriate. Because of the toxicity of many of the compounds being analyzed, primary dilutions of these materials should be prepared in a hood . A NIOSH/MESA approved toxic gas respirator should be used when the analyst handles high concentrations of such materials.

   a. Place about 9.8 ml of methyl alcohol into a 10 ml ground glass stoppered volumetric flask. Allow about 10 minutes or until all alcohol wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

   b. Add the assayed reference material:

      i. Liquids

         Using a 100 ul syringe, immediately add 2 drops of assayed reference material to the flask, then reweigh. Be sure that the 2 drops fall directly into the alcohol without contacting the neck of the flask.

      ii. Gases

         To prepare standards from any of the organic compounds that boil below 30°C, fill a 5 ml valved gas-tight syringe with the reference standard to the 5 ml mark. Lower the needle to 5 mm above the methyl alcohol meniscus. Slowly inject the reference standard above the surface of the liquid (the heavy gas will rapidly dissolve into the methyl alcohol).

c. Reweigh, dilute to volume, stopper, then mix by by inverting the flask several times. Transfer the standard solution to a 15 ml screw cap bottle with a teflon cap liner.

d. Calculate the concentration in mg/l from the net gain in weight.

e. Store stock standards at 4.0°C.* Prepare fresh standards weekly for the 4 compounds whose BP $\leq$ 30° C. All other standards must be replaced with fresh standards each month.

Calibration

1. Using stock standards, prepare secondary dilution standards in methyl alcohol that contains the compounds of interest, eitner singly or mixed together.
2. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those indicated in the Procedure section. By injecting secondary standards, adjust the sensitivity of the analytical system for each compound being analyzed so as detect $\leq$ 1 ug.

Quality Controls

1. Before processing any samples, the analyst should daily demonstrate through the analysis of an organic-free water or solvent blank that the entire analytical system is interference free.
2. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique.

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* Change #8

4. Gas chromatograph - Analytical system complete with programmable gas chromatograph suitable for on-column injection and all required accessories, including FID or HSD, column supplies, recorder and gases. A data system for measuring peak area is recommended.
5. Supelcoport 80/100 mesh coated with 1% SP-1240 DA in 1.8 meter long 2 mm ID glass column (Column 1) or Chromosorb W-AWDMCS 80/100 mesh coated with 5% OV-17 packed in a 1.8 meter long X mm ID glass column (Column 2).
6. Syringes - 5 ml glass hypodermic with Luerlok tip (2each).
7. Micro syringe - 10, 25, 100 ul.
8. 2-way syringe valve with Luer ends (3 each).
9. Syringe - 5 ml gas tight with shut-off valve.
10. Bottle - 15 ml screw-cap, with teflon cap liner.
11. Kuderna-Danish apparatus (K-D) [Kontes K-570000 or equivalent] with 3 ball Snyder column.
12. Water bath - heated with concentric ring cover capable of temperature control (± 2°C). The bath should be used in a hood.
13. Chromatographic column - 10mm ID by 100mm length with teflon stopcock.
14. Reaction vial - 20 ml with teflon - lined cap.

Reagents

1. 2 - propanol - pesticide quality or equivalent
2. Stock standards - prepare stock standard solutions at a concentration of 1.0 ug/ul by dissolving 0.100 grams

of assayed reference material in pesticide quality 2-propanol and diluting to volume in a 100 ml ground glass stopped volumetric flask. The stock solution is transferred to ground glass stoppered reagent bottles, stored in a refrigerator, and checked frequently for signs of degradation or evaporation, especially just prior to preparing working standards from them.

3. PFB derivative reagents:

   a. Hexane and toluene - pesticide quality or equivalent

   b. Sodium sulfate - (ACS) granular, anhydrous (purified by heating at 400°C for 4 hours in a shallow tray).

   c. Potassium carbonate - (ACS) powdered.

   d. Silica gel - (ACS) 100/200 mesh, grade 923; activated at 130°C and stored in a dessicator.

   e. Pentafluorobenzyl bromide - 97% minimum purity.

   f. 1,4,7,10,13,16-Hexaoxacyclooctadecane (18 crown 6) - 98% minimum purity.

   g. Preparation of derivitizing reagent: Add 1 ml pentafluorobenzil bromide and 1 gm of the 18 crown 6 ether to a 50 ml volumetric flask and dilute to volume with 2-propanol. Prepare fresh weekly.*

Calibration

1. Using stock standards, prepare secondary dilution standards in 2-propanol that contain the compounds of interest, either singly or mixed together.
2. Assemble necessary gas chromatographic apparatus and establish operating parameters equivalent to those in the

* Change #9

"procedure section." By injecting secondary standards adjust the sensitivity limit and the linear range of the analytical system for each compound being analyzed for to a sensitivity of $\leq$ 1 ug (2X background).

Quality Control

1. Before processing any samples the analyst should demonstrate through the analysis of an organic - free water or solvent blank that the entire analytical system is interference free.
2. Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the accuracy of the analysis. Where doubt exists over the identification of a peak on the gas chromatogram confirmatory techniques such as mass spectroscopy should be used.
3. The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of this method in dealing with each sample matrix by spiking each sample with known amounts of the compounds the waste is being analyzed for and using these spiked samples readjust the sensitivity of the instrument such that 1 ug/gm of sample can be readily detected (see Quality Control).

Flame Ionization Gas Chromatography Procedure

1. Assemble gas chromatograph with column 1 and Flame Ionization Detector (apparatus section).
2. Set nitrogen carrier gas at 30 ml/min flow rate.

3. Set column temperature at 80°C at injection and program to immediately rise at 8°C/min to 150°C.

Derivatization and Electron Capture Gas Chromatography Procedure

1. Pipet a 1.0 ml aliquot of the 2-propanol solution of standard or sample extract into a glass reaction vial. Add 1.0 ml derivatization reagent. This is a sufficient amount of reagent to derivatize a solution whose total phenolic content does not exceed 0.3 mg/ml.
2. Add about 3 mg of potassium carbonate to the solution and shake gently.
3. Cap the mixture and heat for 4 hours at 80°C in a hot water bath.
4. Remove the solution from the hot water bath and allow it to cool.
5. Add 10 ml hexane to the reaction vial and shake vigorously for one minute. Add 3.0 ml of distilled deionized water to the reaction vial and shake for two minutes.
6. Decant organic layer into a concentrator tube and cap with a glass stopper.
7. Pack a 10mm ID chromatographic column with 4.0 grams of activated silica gel. After settling the silica gel by tapping the column, add about two grams of anhydrous sodium sulfate to the top.
8. Pre-elute the column with 6 ml hexane. Discard the eluate and just prior to exposure of the sulfate layer to air pipet onto the column 2.0 ml of the hexane solution that contains the derivatized sample or standard. Elute the

column with 10.0 ml of hexane (Fraction 1) and discard this fraction. Elute the column, in order with 10.0 ml 15% toluene in hexane (Fraction 2), 10.0 ml 40% toluene in hexane (Fraction 3), 10.0 ml 75% toluene in hexane (Fraction 4), and 10.0 ml 15% 2-propanol in toluene (Fraction 5). Elution patterns for the phenolic derivatives are shown in Table 8.04-2 Fractions may be combined as desired depending upon the specific phenols of interest or level of interferences. Collect the fractions in appropriate sized K-D apparatus and concentrate each fraction to 10 ml.

9. Assemble gas chromatograph with column 2 and HSD (apparatus section).
10. Using 5% methane/95% argon as the carrier gas adjust flow to 30 ml/min.
11. Set column temperature at 200°C.
12. Inject 2-5ml of the appropriate fraction using the solvent - flush technique. Smaller (1.0 ml) volumes can be injected if automatic devices are employed. Record volume injected to the nearest 0.05 ml and the resulting peak size in area units. If the peak area exceeds the linear range of the system dilute the extract and reanalyze.

Calibrate the system immediately prior to conducting any analyses and recheck as in Quality Control for each type of waste. Calibration should be done no less frequently than at the beginning and end of each session.

Calculations

1. If a response for the contaminant being analyzed for is greater than 2X background is noted, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using spiked samples, that the instrument sensitivity is $\leq$ 1 ug/gm.
2. When duplicate and spiked samples are analyzed, all data obtained should be reported.
3. If one desires to determine the actual concentration of the compound in the waste, the method of standard addition should be used.

d. Just prior to exposure of the sodium sulfate layer to the air add 40 ml hexane and continue the elution at the rate of 2 ml/minute. This eluate is Fraction 1. Concentrate the fraction by standard K-D technque. No solvent exchange is necessary. After concentration and cooling, transfer to a* 10 ml volumetric flask, dilute to 10 ml and analyze by gas chromatography.

e. Next elute the Florisil with 100 ml of 5 percent ethyl ether/95% hexane (v/v) and concentrate as in step d. [Fraction 2].

f. Next, elute with 100 ml of 15% ethyl ether/85% hexane (v/v) and concentrate Fraction 3 as in step d.

g. Elute with 100 ml of 50% ethyl ether/50% hexane (v/v), and concentrate, Fraction 4 as in step d.

h. Finally, elute with 100 ml of ethyl ether, and concentrate, Fraction 5 as in step d.

Gas Chromatography

1. Assemble gas chromatograph with either Column 1 or 2 (see Apparatus).

Column 1 (Supelcoport 100/120 with 1.5% SP 2250 + 1.95% SP 2401)

a. Set carrier gas at 60 ml/minute flow rate.

b. Column temperatures will vary from 180°C to 220°C depending on the compound.

Column 2 (Supelcoport 100/120 with 3% OV-1)

a. Set carrier gas at 60 ml/min flow rate.

b. Column temperature will vary from 200°C to 220°C depending on the compound.

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* Change #10

2. Calibrate the system at the beginning and end of an analytical session by spiking aliquots of the extract with calibration standards.
3. Inject 2-5 ul of the sample extract or appropriate Florisil eluate using the solvent-flush technique. Smaller (1.0 ul) volumes can be injected if automatic devices are employed. Record the volume injected to the nearest 0.05 ul, and the resulting peak size, in area units.
4. If a response for the contaminant being analyzed for is greater than 2x background, then the waste does not meet the criteria for delisting of being fundamentally different than the listed waste. If a response is not noted, then prior to concluding that the sample does not contain the specific contaminant, the analyst must demonstrate, using the spiked samples, that the method sensitivity is $\leq$ 1 ug of compound per gm of sample.
5. If the peak area measurement is prevented by the presence of interferences, further cleanup is required.

preparation and measurement steps. Where doubt exists over the identification of a peak on the chromatogram, confirmatory techniques such as mass spectroscopy should be used.

Cleanup and Separation

Cleanup procedures are used to extend the sensitivity of a method by minimizing or eliminating interferences that mask or otherwise disfigure the gas chromatographic response to the pesticides and PCB's. The Florisil column allows for a select fractionation of the compounds and will eliminate polar materials. Elemental sulfur interferes with the electron capture gas chromatography of certain pesticides but can be removed by the techniques described below.

Florisil Column Cleanup:

1. Add a weight of Florisil, (nominally 21g,) predetermined by calibration to a chromatographic column. Settle the Florisil by tapping the column. Add sodium sulfate to the top of the Florisil to form a layer 1-2 cm deep. Add 60 ml of hexane to wet and rinse the sodium sulfate and Florisil. Just prior to exposure of the sodium sulfate to air, stop the elution of the hexane by closing the stopcock on the chromatography column. Discard the eluate.
2. Adjust the sample extract volume to 10 ml and transfer it from the K-D concentrator tube to the Florisil column. Rinse the tube twice with 1-2 ml hexane, adding each rinse to the column.
3. Place a 500 ml K-D flask and clean concentrator tube under the chromatography column. Drain the column into the flask until the sodium sulfate layer is nearly exposed. Elute the column

with 200 ml of 6% ethyl ether in hexane (Fraction 1) using a drip rate of about 5 ml/min. Remove the K-D flask and set aside for later concentration.

4. Elute the column again, using 200 ml of 15% ethyl ether in hexane (Fraction 2), into a second K-D flask. Perform the third elution using 200 ml of 50% ethyl ether/hexane (V/V),* (Fraction 3). The elution patterns for the pesticides and PCB's are shown in Table 8.08-2.
5. Concentrate the eluates by standard K-D techniques, substituting hexane for the glassware rinses and using the water bath at about 85°C. Adjust final volume to 10 ml with hexane. Analyze by gas chromatography.
6. Elemental sulfur will usually elute entirely in Fraction 1. To remove sulfur interference from this fraction or the original extract, pipet 1.00 ml of the concentrated extract into a clean concentrator tube or Teflon-sealed vial. Add 1-3 drops of mercury and seal. Agitate the contents of the vial for 15-30 seconds. Place the vial in an upright position on a reciprocal laboratory shaker for 2 hours. Analyze by gas chromatography.

Gas Chromatography

Table 8.08.1 summarizes some recommended gas chromatographic column materials, operating conditions for the instrument, and some estimated retention times. Examples of the separations achieved by these columns are shown in Figures 8.08-1 through

* Change #11

Method of Standard Additions

In this method, equal volumes of sample are added to a deionized distilled water blank and to three standards containing different known amounts of the test element. The final volume of the blank and of the standards must be the same so that the interfering substance is present in the same amount. The absorbance of each solution is determined and then plotted on the vertical axis of a graph with the concentrations of the standard plotted on the horizontal axis. When the resulting line is extrapolated back to zero absorbance, the point of interception of the abscissa is the concentration of the unknown. The abscissa on the left of the ordinate is scaled the same as on right side, but in the opposite direction from the ordinate. An example of a plot so obtained is shown below:

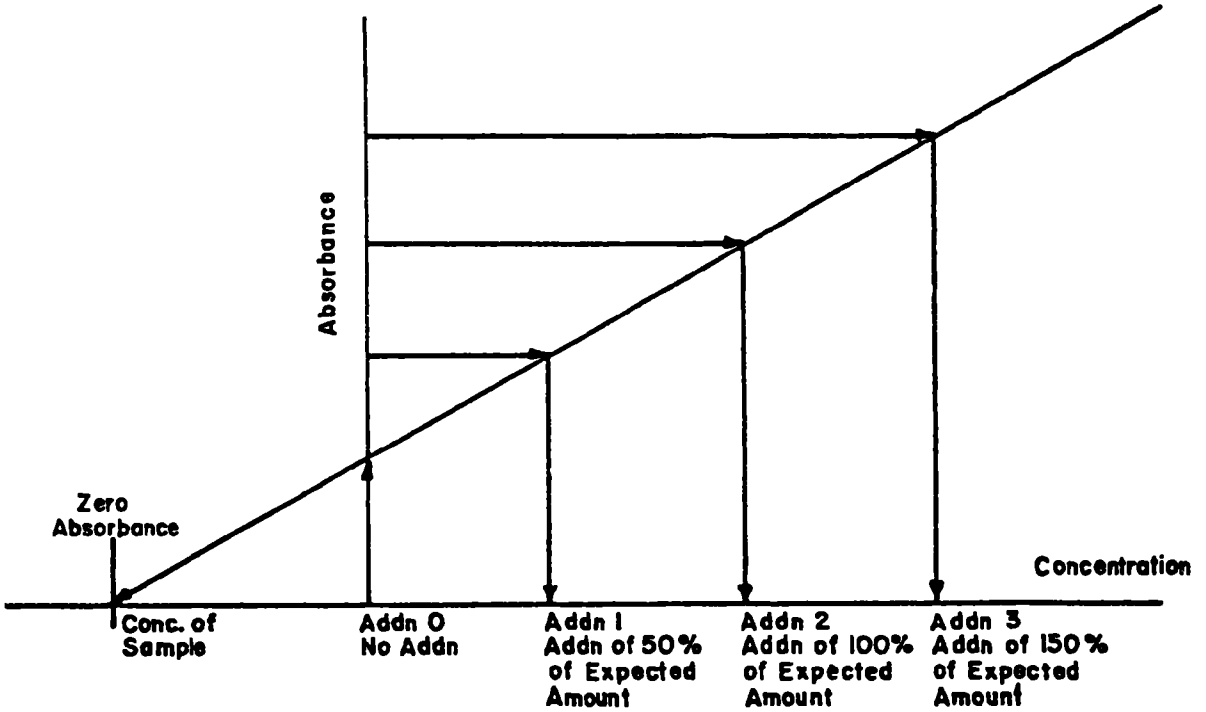

Figure 8.49-1
PLOT OF METHOD OF STANDARD ADDITIONS

Note: For this method to be valid, the plot must be linear. The slope of this line should not differ by more than 20% from the slope of the standard solutions. The effect of the assumed interference must not change as the proportion of sample to standard changes.

Solids, Sludges and Slurries

Solids, sludges and slurries may be analyzed by these methods by weighing out suitable portions and digesting as described for each metal. The material is then filtered through a 0.45 micron filter while washing down the sides of the beaker and rinsing the filter with distilled deionized water. The filtrate is then made up to a suitable volume and analyzed in the ususal manner. Results can be related back to the original sample weight and reported as mg/kg.

Samples Containing oils, greases, or waxes*

Samples of listed and non-listed wastes may contain substantial amounts of organic materials. These organics can be in the form of oils, greases, or waxes. The general HNO_3 digestion, as given in this manual, will not be vigorous enough to remove organics when analyzing for metals. In order to overcome this deficiency, the metals analysis may be performed in groups, when organics are present.

The first group: (Direct Aspiration Method)

Ba, Cd, Cr, Pb, and Ag

The second group: (Wet Digestion Method)

As, Hg, (Se), Cd, Cr, Ag, (Pb), and (Ba)

* Change # 15

Scope

Elements of the first group can be determined directly by by dissolving the organic portion of the waste in an apporpriate organic solvent and proceeding with atomic absorption using a direct aspiration technique. To determine the elements of the second group the waste is subjected to a wet digestion procedure, followed by subsequent analysis as specified in this manual.

There is some overlap between these two groups of metals and the analyst may chose either method for determining those elements common to both groups.

To analyze for metals in oil, grease, or wax containing wastes, the following methods apply:

I. Analysis of wastes containing oil, grease, or wax of the elemets Ba, Cd, Cr, Pb, and Ag.

A. Reagents

1. Cyclohexane — ultra high purity grade
2. Mthylisobutylketone — " "
3. p-Xylene — " "

B. Procedure

1. Weigh out a 100 gm representative sample of the waste or extract. Separate the phases, if more than one phase is present, and weigh eacn phase.
2. The metals in the organioc phase can be determined by diluting with a solvent (specified in the reagents section or other appropriate solvent) and proceding with atomic absorption by direct aspiration as given in this manual. Record metal concentrations taking any dilutions into account.

3. Metals in the aqueous phase are determined by the procedures in this manual. (Sections 8.50 thru 8.60)
4. Report concentrations for the metals as the weighted average for both the organic and aqueous phases.

II. Analysis of oil, grease or wax containing wastes for the elements As, Hg, (Se), Cd, Cr, Ag, (Pb), and (Ba)

A. Reagents

1. Concentrated Nitric Acid	ultra high purity
2. Concentrated Sulfuric Acid	" "
3. Hydrogen Peroxide (30%)	" "
4. Cnecentrated Hydrochloric Acid	" "

B. Apparatus

Digestion flask, 250 ml flat bottom boiling flask with ₹ 24/40 joint, 300 mm Allihin condenser filled to 50 mm with Rashing rings and glass beads, and heating mantle. Kjeldahl flask 300 ml, ground glass stoppered.

C. Procedure

1. weigh out a 100 gm representative sample of the waste or extract. Separate the phases, if more than one is present, and weigh each phase.
2. Weigh 2.0 gms of the organic phase into the digestion or Kjeldahl flask. Add 10 ml H_2SO_4 and a 6 mm glass bead. Swirl flask to mix the contents.
3. If using a Kjeldahl flask approximately 3/4 of the neck of the flask should be cooled by air by directing an air stream against the neck of the flask. If using the flask and condenser apparatus, connect the Allihin condenser and circulate cooling water.

4. Heat flask gently and continue heating until dense white fumes appear. While boiling, cousiously add 1 ml HNO_3 dropwise to oxidize the organic material. This may be done through the condenser. When the HNO_3 has boiled off and dense white fumes reappear repeat the treatment with an additional 1 ml of HNO_3. Continue the addition of HNO_3 in 1 ml incerments until the digestion mixture is no darker than a straw color, indicating that almost all the organic matter has been oxidized.
5. Cool the flask slightly and add 0.5 ml (dropwise) of H_2O_2. Heat until dense white fumes appear, and while boiling coutiously add 1 ml of HNO_3 dropwise. When the HNO_3 has boiled off and dense white fumes reappear repeat the treatment with H_2O_2 and HNO_3 until the digestion mixture is colorless, at which time the organic material will be completely oxidized. Four treatments will usually suffice. The total amount of H_2O_2 used should be noted.
6. When oxidation is complete, allow the flask to cool, wash down the mouth, neck/condenser with a small volume of distilled water (5 ml) and mix the contents. Continue heating to the appearence of dense white fumes.
7. Cool and dilute to a total volume of 25 ml. Procede with determination of metals as given in this manual.

Note: If a percipitate forms add 2ml of concentrated HCL before diluting to remove the precipitate. If the precipitate pesists filter or centrifuge the solution to remove the precipitate, and procede to determine As, Se, Hg, Cr, and Cd. Ba, Pb, and Ag may be determined either by the direct aspiration method or by digestion of a smaller sample.

8. Metals in the aqueous phase, if an aqueous phase was present, are determined by the procedures in this manual, sections 8.50 thru 8.60.
9. Report concentration for metals as the weighted average for both organic and aqueous phases.

Conclusion

The details of the following approved methods are examples of acceptable techniques. Dilutions and concentrations may have to be varied to suit the instrument being used. It is important not to overwhelm the instrument with very high concentrations above the optimum recommended range. Contamination can result which is difficult to remove. At the same time, many dilutions introduce error which can be avoided by some knowledge of the waste beforehand. If nothing is known, caution is advised.

For additional information the applicable sections of "Methods for Chemical Analysis of Water and Wastes", EPA 600/4-79-020 (Appendix II of this manual) may be consulted.

Graphite Furnace*

Comments:

1. It has been reported that the addition of cyanogen iodide in this procedure does not interfere in the silver determination.
2. Samples should be analyzed immediately after collection.

Procedure

1. Standards are prepared by making dilutions to cover the range 1 - 25ug Ag/liter as described in the direct aspiration method.
2. Samples are prepared, standard additions made and analyses are performed as in the direct aspiration method.

Instrument Operation

Wavelength: 328.1 nanometers

Optimum Concentration Range: 1-25 ug/liter.

Lower detection limit: 0.2 ug/liter

Purge gas: Argon

Drying time and temp: 30 sec - 125°C

Ashing time and temp: 30 sec - 400°C

Atomizing time and temp: 10 sec - 2700°C

The conditions listed above are based on a 20 ul injection; continuous flow purge gas and non-pyrolytic graphite on a Perkin Elmer model HGA 2100 furnace. Other equipment will have different requirements. Follow the manufacturer's manual.

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* Change #12

Method 8.82

HEADSPACE METHOD

Scope and Application

This method provides a procedure for the extraction of volatile organic compounds in pastes and solids. The static headspace technique is a simple method which allows large numbers of samples to be analyzed in a relatively short period of time. Because of the large variability and complicated matrices of waste samples in the solid and paste forms, detection limits for this method may vary widely among samples. The method works best for compounds with boiling points less than 125°C. Due to their low solubility, low molecular weight compounds can only be detected at high concentrations or at reduced pressure.

The sensitivity of this method will depend on the equilibria of the various compounds between the vapor and dissolved phases.

Static Headspace Technique

Summary of Method

The waste is collected in sealed glass containers and allowed to equilibrate at 90°C. A sample of the headspace gas is withdrawn with a gas tight syringe for analysis by the appropriate gas chromatographic method.

Apparatus

1. Gas-tight syringe - 5-cc.
2. Head space standard solutions - Prepare two standard solutions of the compounds being determined at the 50-ng/ul and

250-ng/ul concentrations. Standard solutions should be prepared using methanol, methane, or other appropriate solvent. The standard solutions should be stored at less than 0°C, then allowed to warm to room temperature before dosing. Fresh standards should be prepared weekly. Procedures for preparing standards are outlined in the Purge and Trap Procedure of this manual (Method 8.83).

3. Vials, 125 ml "Hypo-Vials" (Pierce Chemical Co., #12995), or equivalent.
4. Septa, "Tuf-Bond" (Pierce #12720), or equivalent.
5. Seals, aluminum, (Pierce #13214), or equivalent.
6. Crimper, hand, (Pierce #13212), or equivalent.

Procedure*

1. Place 10.0-g each of the well-mixed waste sample into three separate 125-ml septum seal vials.
2. Dose one sample vial through the septum with 200-ul of the 50-ng/ul standard methanol solution. Label this 1 ppm spike.
3. Dose a separate (empty) 125 ml septum seal vial with 200 ul of the 50 ng/ul standard methanol solution. Label this 1 ppm standard.
4. Place the sample, 1 ppm spike, and the 1 ppm standard vials into a 90°C water bath for 1 hour. Store the remaining sample vial at 4.0°C for possible future analysis.
5. While maintaining the vials at 90°C withdraw 2 ml of the headspace gas with a gas tight syringe and analyze by injecting into a GC, operating under the appropriate conditions for the GC measurement used. Analyze all three samples in exactly the same manner.

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* Change #13

6. Analyze the 1 ppm standard and adjust instrument sensitivity to give a responce of at least 2x the background. Record retention time and peak area.
7. Analyze the 1 ppm spiked sample in the same manner. Record RT and peak area.
8. Analyze the undosed sample as in item 7.
9. If a positive responce is noted for the undosed sample, then the waste has not been demonstrated to be free of the contaminat of interest and is thus not fundamentally different than the listed waste. If no response is noted, reinject the 1 ppm standard to verify the required sensitivity.

Note: Standard quality assurance protocols should be employed, including blanks, duplicates, and dosed samples, as described in Section 10.

Bibliography

1. "Interim Methods for the Sampling and Analyses of Priority Pollutants in Sediments and Fish Tissue," U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, Ohio 45268 [1980].
2. "Master Scheme for the Analysis of Organic Compounds in Water, Part I: State-of-the-Art Review of Analytical Operations," U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, Georgia 30605.
3. "An EPA Manual for Organic Analysis Using Gas Chromatography - Mass Spectrometry," W.L. Budde and J.W. Eichelberger, U.S. Environmental Protection Agency, Environmental Monitoring Support Laboratory, Cincinnati, Ohio, 1979, EPA/600/8-79/006, Order Number PB-297164.

Method 8.83

PURGE AND TRAP METHOD

Scope and Application

This method covers a procedure for the extraction of purgeable organic compounds from aqueous liquids and free flowing paste samples prior to gas chromatographic analysis.

The success of the extraction depends on partitioning the compounds between the sample phase and gaseous headspace phases. This partitioning is a function of temperature, interfacial area, the volatility of the species being analyzed for, its solubility in the liquid being purged, and the volatility of the waste matrix. For highly volatile matrices, direct injection preceded by dilution, if necessary, should be used. For pastes, dilution of the sample until it becomes free flowing is used to insure adequate interfacial area. The success of this method also depends on the level of interferences in the sample; results may vary due to the large variability and complicated matrices of solid waste samples.

Summary of Method

An inert gas is bubbled through the sample contained in a specially-designed purging chamber. This purging transfers the volatile compounds from the liquid phase to the vapor phase. The gaseous effluent is then swept through a short sorbent tube where the organic compounds are trapped. After purging is completed, the trap is heated and backflushed to

EXTRACTION CONDITIONS cont. (4)

Compound	Extraction pH	Extraction Solvent
Tetrachloroethene	NA	NA
Tetrachlorophenol	12	Methylene Chloride
Toluene	NA	NA
Toluenediamine	> 11	Methylene Chloride
Toluene diisocyanate(s)	NA*	Methylene Chloride
Toxaphene	5-9 or > 11	Methylene Chloride
Trichloroethane	NA	NA
Trichloroethene(s)	NA	NA
Trichlorofluoromethane	NA	NA
Trichlorophenol(s)	12	Methylene Chloride
2,4,5-TP(Silvex)	<7 or > 11	Ethyl Ether or Methylene Chloride
Trichloropropane	NA	NA
Vinyl chloride	NA	NA
Vinylidene chloride	NA	NA
Xylene	NA	NA

* Change # 14

Method 8.85

SONICATION METHOD

Scope and Application

This method covers a procedure for the extraction of non-volatile and semi-volatile organic compounds from solids. The sonication produces solid disruption to ensure intimate contact of the sample matrix with the extraction solvent.[1]

Summary of Method

A weighed sample of the solid waste is ground, mixed with the extraction medium, then dispersed into the solvent using sonication. The resulting solution may then be cleaned up further or analyzed directly using the appropriate technique (Methods 8.24 through 8.25).

Apparatus

1. Apparatus for Grinding.*†

   The necessity for grinding and the choice of grinding apparatus will depend on the physical and chemical characteristics of the solid waste material in question. Any of

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[1] The high energy vibrations produced by this method may produce artifacts and may drive off some semi-volatile compounds.

* Grinding is only necessary if the waste cannot either pass through a 1-mm standard seive or be extracted through a 1-mm diameter hole.

† Specific equipment listed in this method are for descriptive purposes only. Equivalent equipment is available from other manufactures and laboratory supply companies.