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Solid Waste

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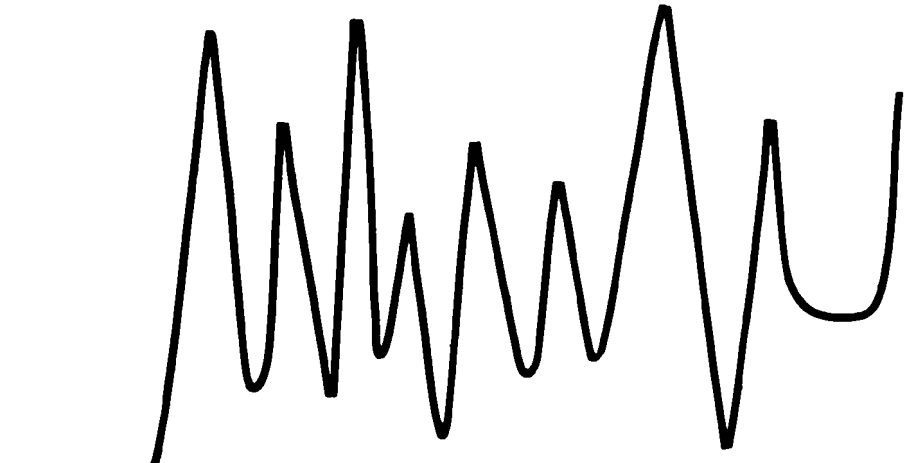
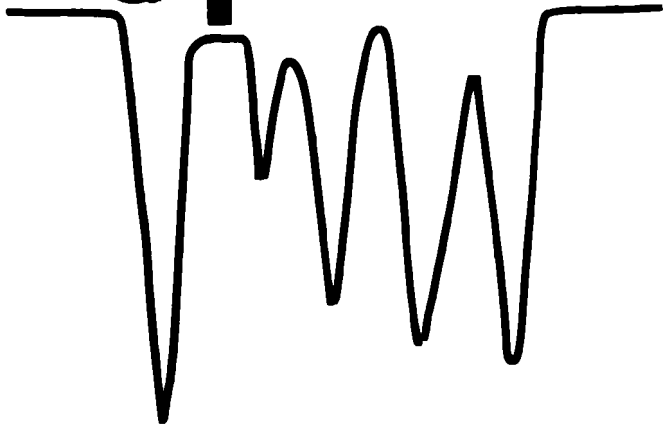
Test Methods for Evaluating Solid Waste

Physical/Chemical Methods



Technical Update



U.S. Environmental Protection Agency

TEST METHODS FOR EVALUATING SOLID WASTE

PHYSICAL/CHEMICAL METHODS

Technical Update

This manual (SW-846B) updates the Test Methods for Evaluating Solid Waste (SW-846), and was written by the Hazardous and Industrial Waste Division of the Office of Solid Waste.

U.S. ENVIRONMENTAL PROTECTION AGENCY
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This publication (SW-846B) is the second revision to Test Methods for Evaluating Solid Waste (SW-846). Any mention of commercial products in the manual or this revision does not constitute endorsement by the U.S. Government. Editing and technical content were the responsibilities of the Hazardous and Industrial Waste Division, Office of Solid Waste.

PREFACE

Attached is the second revision, dated April 15,1981, to the Environmental Protection Agency's manual, Test Methods for Evaluating Solid Waste (SW-846).

These attached pages should be inserted in the manual in place of like-numbered pages or as entirely new pages, where appropriate. The date on which the page was issued is printed in the upper right-hand corner. Modified sections are indicated in the contents by double underscores.

The Office of Solid Waste encourages comments and suggestions for improving the utility or content of this manual. Comments may be made by telephoning 202-755-9187 or writing:

Manager, Waste Analysis Program
Office of Solid Waste
U.S. EPA (WH-562)
Washington, DC 20460

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Method 8.27

Capillary Column GC/MS method for the analysis of Wastes

Scope and Application

This method may be used to determine the presence and concentration of the volatile and extractable organic compounds which are listed in Appendix VIII, 40 CFR 261.33 in wastes. The method employs capillary column gas chromatography-mass spectrometry. Quantitation can be performed in two ways depending on the level of information required.

Summary of Method

The waste is categorized by its physical makeup into one of the following three classes.

- Liquid (either single or multi-phase systems)
- Solid
- Combination of Liquid and Solid

Liquids are analyzed in their "as received" form except that if more than one phase is present the organic and aqueous phases are separated and the two phases analyzed separately. The organic phases are analyzed by direct injection onto the capillary column using either the split or splitless technique. Aqueous phases are determined by a combination of the purge and trap technique for volitiles and a series of extractions for the base/neutrals and acids. The extracted fractions are then combined and analyzed as a single solution using the splitless technique.

Solids are analyzed using purge and trap technique for volatiles and a soxhlet extraction for the extractables.

Samples containing both liquid and solid phases are first separated into their component liquid and solid phases using centrifugation. The separated phases are then analyzed as either liquids or solids as described above.

The components of the sample are quantitated in either of two ways, depending on the degree of quantitation necessary. The first way estimates concentration and assigns these estimated concentrations into ranges. Since this is not a rigorous quantitative procedure it may only be used for order of magnitude type estimates of concentration. These ranges are:

- Greater than 50%
- Between 10 and 50%
- Between 1 and 10%
- Between 100 ppm and 1%
- Between 1 and 100 ppm

For determining the precise concentration of a component in a sample the method of standard additions is employed.

Procedure

The analyst must first determine which category the sample belongs to.

- If the sample is a liquid go to the section labled "Liquids" (I) of this procedure.
- If the sample is a solid go to the section labled "Solids" (II) of this procedure.
- If the sample contains both liquid and solid go to the section labled "Mixtures of Liquids and Solids" (III) of this procedure.

I. Liquids

The analyst should determine if more than one liquid phase is present in the sample. If more than one phase is present the sample should be separated into its organic and aqueous phases respectively. This separation can be achieved by using either gravity or cenrifugation. The separated phases should be weighed. 10.0 gm of well mixed sample should be used.

A. Organic Liquids

1. Summary
   Organic Liquids are injected directly onto the capillary column using either the split or splitless mode. The liquid may be diluted if necessary to facilitate sample handling or to accomodate the linear range of the mass spectrometer.

2. Apparatus and Materials
   a. Sample Vials - 10 dram vials with teflon lined caps
   b. Gas Chromatograph - Analytical system capable of split and splitless injections and all required accessories including column supplies, gases, etc.
   c. Column - 30m SE-30, SE-52, SE-54, or equivalent, .2 to .25mm internal diameter with a film thickness between .15 to .40u.
   d. Mass Spectrometer - Capable of scanning from 35 to 450 daltons every 1 second or less. The mass-spectrometer must be able to operate at 70 volts for electron ionization and must produce a recognizable mass spectrum for 50 ng or less of DFTPP when the sample is introduced through the GC column. The GC column should be directly interfaced (i.e. no separator) to the mass spectrometer through either an all glass or all glass lined system. If a fused silica capillary column is used, the analyst is required to complete the interface by placing the end of

the column in the ion source.

e. Computer System - The computer system interfaced to the mass spectrometer should be capable of continuously acquiring mass spectra for the duration of the gas chromatographic program. (about 1 hr.) All data must be stored either within the data system or on line mass storage devices such as disk or tape. The system must have software available capable of searching GC/MS runs for the following:

   1) selected ion chromatograms
   2) total ion chromatograms
   3) reverse and forward search for any compound from the EPA/NIH Mass Spectral Data Base.

3. Reagents
   a. Methylene chloride - Pesticide quality
   b. Ethyl Ether - " "
   c. Ethylacetate - " "
   d. Methanol - " "
   e. Standards - Standards can be made up as necessary if appropriate reagents are available. Naphthalene-d_8 or phenanthrene-d_{10} may be used as internal standards.

4. Calibration
   a. The mass spectrometer is calibrated with either PFK or FC-43 over the scan range. The mass spectrometer should be scaned from 35 to 450 daltons in 2 sec or less. 50ng or less of DFTPP should be injected in the splitless mode using the conditions given in Table 8.27-1.
   b. The DFTPP spectrum obtained from the top of the chromatographic peak (backgroud subtracted) should meet the criteria listed in Table 8.24-2.

5. Sample Preparation
   a. If the liquid can be convieniently drawn into a 10 ul syringe, then no sample preparation is necessary. Weigh 1 gm of the liquid into a a pre-tared 10 dram vial. Add the internal standard at a level that would give 50 ng on column when injected. (The amount added will vary with split ratio)
   b. If it is necessary to dilute the sample, a weighed portion of the organic phase should be transfered to an appropriate volumetric flask and diluted to volume with one of the solvents listed in the reagent section. The internal standard is added at a level that would give 50 ng on column when injected prior to dilution. Record the dilution volume.

6. Gas Chromatography/Mass spectrometry
   a. Establish the chromatographic conditions given in table 8.27-1.
   b. Set the Gas Chromatograph for either split or splitless injection depending on estimated concentration. For example, an organic liquid that can be conveniently drawn up in a syringe can be analyzed using the split mode. An oily sample that needs to be diluted to 1:100 might best be handled using the splitless mode. If using the split mode, record the split ratio. Record both linear and volume column flow.
   c. Inject sample, start the chromatographic program, and acquire data. Record amount of sample injected. (1 to 5 ul when using split mode and 1 to 2 ul when the splitless mode is employed).
   d. Inject appropriate standards and acquire data using sample conditions as employed in c.

7. Qualitative and Quantitative Determination
   a. A compound will be judged to have been identified if either three or more characteristic ions of the compound maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within $\pm$ 20%; or, a reverse search yields a numerical value equivalent to the criteria stated above.
   b. Samples can be quantitated in two ways. The first is by the method of standard additions. This method is always acceptable and must be used when the actual concentration is needed. The second method is used when order of magnitude estimates of concentration are needed. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 integrated area counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts, this condition should be met in the sample +20%
   c. Example Calculation
      5 ul of a 5 mg/ml solution of benzene was injected with a split ratio of 100:1 to produce the

chromatogram in figure 8.27-1. The integrated area of the benzene peak from the total ion chromatogram was 7840 counts. 10 gm of an organic liquid sample was disolved in methylene chloride in a volumetric flask to a final volume of 100 ml. 5 ul of this solution was injected with the same split ratio to produce the chromatogram in figure 8.27-2. The integrated area for benzene in this sample was 4235 counts. The peak for toluene gave an area of 4827 counts. The estimated concentration of benzene and toluene in this sample are:

Benzene Standard

5 mg/ml = 5 ug/ul

5 ug/ul x 5 ul = 25 ug injected

7840 counts/25 ug = 313.6 counts/ug

Benzene in Sample

4235 counts/5 ul injected x 1 ug/ 313.6 counts =

13.5 ug/5 ul

13.5 ug/5 ul x 1000 ul/ml =

2700 ug/ml

2700 ug/ml x 100 ml/10 gm dilution = 27000 ug/gm

27000 ug/gm = 27 mg/gm

27 mg/gm x 1 gm/1000 mg = .027 = 2.7%

The sample is 2.7% benzene

Toluene in sample

By an analogus method the sample is calculated to

be 3.1% toluene.

8. Report
   a. Report the results of each analysis giving the method used to quantify each comound. Report the scan number of each compound.
   b. Example:

Compound	Quantitation Method	Scan #	Amount	Range
Benzene	Estimate/Benzene	500	2%	1-10%
Toluene	Estimate/Benzene	622	3%	1-10%

B. Aqueous Liquid

1. Summary
   Aqueous liquids are analyzed by purge and trap and extraction methods given in Methods 8.83 and 8.84. After the aqueous sample is purged and traped and extracted by Methods 8.83 and 8.84 the traped material and the extracts (which have been combined) are analyzed by capillary column gas chromatography-mass spectrometry.

2. Apparatus and Materials
   See the appropriate sections in Methods 8.83, 8.84, and the apparatus and materials section for organic liquids in this method

3. Reagents
   See the appropriate sections in Methods 8.83, 8.84, and the reagents section for organic liquids in this method.

4. Calibration
   a. The mass spectrometer is calibrated with PFK or FC-43 over the scan range of interest. For the volatiles scan over the range 20 to 260 daltons, and scan over the range 35 to 450 daltons for the base/neutrals and acid extractables. The scan rates should be 2 sec. or less. 50 ng or less of bromoflurobenzene or DFTPP should be injected for the volitiles and extractables respectively. Chromatographic conditions are given in Tables 8.27-2 and 8.27-3.
   b. The specta obtained from the top of the chromatographic peak (background subtracted) should meet the criteia listed in Tables 8.24-2 and 8.24-3.

5. Sample Preparation
   a. Follow the purge and trap and extraction methods given in Methods 8.83 and 8.84 of this manual for preparation of the sample.
   b. Base/neutral and acid extractable fractions may be combined and analyzed in a single GC/MS analysis.

6. Gas Chromatography/Mass Spectrometry
   a. Establish the chromatographic conditions described in Tables 8.27-2 or 8.27-3, whichever is appropriate.
   b. Set gas chromatograph in either the split or

splitless mode. If using the split mode record the split ratio. Record both the linear and volume column flow.

c. When analyzing volatiles it may be necessary to adjust desorption time or cool the first few cm of the column with a flurocarbon spray in order to maintain chromatographic resolution.

d. Inject sample and acquire data, recording the amount injected. Follow the same procedure for any standards.

7. Quantitative and Qualitative Determination

a. A compound can be qualitativly identified in either of two ways. At least three characteristic ions of the compound must maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within ± 20%; or, a reverse search yeilds a numerical value equivalent to the criteria stated above.

b. Samples can be quantitated in two ways. The first is by the method of standard additions. This method is always acceptable and should be used when the exact concentration is needed. The second method is to be used only for order of magnitude estimates of concentartion. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 integrated area counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts, this condition should be met in the sample ±20%

c. Example Calculation

A 10 gm sample contained 3.5 gm of organic liquid with a volume of 3.9 ml. 5 ul of the organic liquid was injected with a split ratio of 100 to 1. The integrated area of benzene gave 3582 counts. Benzene in the organic phase is calculated:

3582 counts/5 ul x 1 ug/313.6 counts = 11.4 ug/5 ul

11.4 ug/5 ul x 1000 ul/ml = 2280 ug/ml

the density is 3.5gm/3.9ml = .9 gm/ml

2280 ug/ml = 2.28mg/ml

2.28mg/ml x 1gm/1000mg x 1 ml/.9gm = .0025 = .25%

The purge and trap analysis of the aqueous phase was performed on 6.5 gm of liquid. Benzene gave 12562 counts. The benzene in the aqueous phase is:

12562 counts/6.5 gm x 1 ug/313.6 counts =

40.0 ug/6.5 gm = 6.2 ppm

This is insignificant compared to .25%

The total amount of benzene in the sample is calculated:

.25% x .35 of total = .0875% or 875 ppm

8. Report
   a. Report the results of each analysis giving each compound identified, the scan number, the quantity of the compound, and the method used to calculate that quantity.
   b. Example

Compound	Quantitation Method	Scan #	Amount	Range
Benzene	Estimate/Benzene	687	875ppm	100ppm-1%

II. Solids

Two samples of well mixed solid should be used in this analysis. One sample is used for the purge and trap analysis of volatiles and one for soxhlet extraction analysis.

A. Purge and Trap Determination of Volatiles in Solids

1. Summary
An appropriate weight of sample (1-10 gm) is diluted with 10 ml of organic-free water. The diluted sample is purged for 12 min. with inert gas at room temperature. The gaseous phase is passed through a sorbent trap where the organic compounds are concentrated. The contents of the trap are desorbed into the GC/MS by heating and backflushing the trap.

2. Apparatus and Materials
a. See the apparatus section of Method 8.83 of this manual.
b. Gas Chromatograph - Analytical system capable of split and splitless injections and all required accessories including column supplies, gases, etc.
c. Column - 30m SE-30, SE-52, SE-54, or equivalent, .2 to .25mm internal diameter with a film thickness between .15 to .40u.
d. Mass Spectrometer - Capable of scanning from 20 to 260 daltons every 1 second or less. The MS must be able to operate at 70 volts for electron ionization and must produce a recognizable mass spectrum for 50 ng or less of BFB when the sample is introduced through the GC column. The GC column should be directly interfaced (i.e. no separator) to the mass spectrometer through an all glass or all glass lined system. If a fused silica capillary column is used, the analyst is required to complete the interface by directly connecting the end of the column to the ion source.
e. Computer System - The computer system interfaced to the mass spectrometer should be capable of continuously acquiring mass spectra for the duration of the gas chromatographic program. (about 1 hr.) All data must be stored either within the data system or on line mass storage devices such as disk or tape. The system must have software available capable of searching GC/MS runs for the following:

1) selected ion chromatograms
2) total ion chromatograms

3) reverse and forward search for any compound from the EPA/NIH Mass Spectral Data Base

3. Reagents - Standards as necessary (See Methods 8.24, 8.83, and I-A-3e of this Method)

4. Calibration
   a. The mass spectrometer is calibrated with either PFK or FC-43 over the scan range. 50ng or less of BFB should be injected in the splitless mode using the conditions given in table 8.27-3.
   b. The spectrum obtained from the top of the chromatographic peak (backgroud subtracted) should meet the criteria listed in table 8.24-2.

5. Sample Preparation
   a. Weigh an appropriate sample into a pretared 10 to 15 ml Teflon lined, screw-capped vial.
   b. Dilute the sample with 10 ml distilled water. Disperse the sample into the water. Transfer the total sample to the purging device using a syringe with an 1/8 in. gauge Teflon needle. Seal the sample in the purging device. Add the internal standard and purge with 40 ml/min (He or N_2) for 12 min. at room temperature.

6. Gas Chromatography/Mass spectrometry
   a. Establish the chromatographic conditions given in table 8.27-1.
   b. Set up the Gas Chromatograph for either split or splitless injection. If using the split mode, record the split ratio, linear and volume column flow.
   c. The first few inches of the column should be cooled using flurocarbon spray. Heat the trap to 200°C. Backflush it for 4 min in the desorb mode into the gas chromatograph.

7. Qualitative and Quantitative Determination
   a. A compound can be qualitativly identified in either of two ways. At least three characteristic ions of the compound must maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within $\pm$ 20%; or, a reverse search yeilds a value equivalent to the criteria stated above.
   b. Samples can be quantitated in two ways. The first is by the method of standard additions. This

method is always acceptable and should be used when the exact concentration is needed. The second method is to be used only for order of magnitude estimates of concentration as given on page 1 of this method. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 integrated area counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts this condition should be met in the sample $\pm$20%.

c. Example Calculation

5.0 gm of a solid sample was mixed with 10 ml water and purged and traped by the procedure specified. A splitless injection gave 29,043 integrated area counts for toluene. 1 ul of a standard solution of Toluene 100 ug/ml gave 16,290 integrated counts.

16290 counts/ 1 ul x 1000 ul/100 ug = 162900 counts/ug

29043 counts/5 gm x 1 ug/162900 counts = .18 ug/5 gm

.18 ug/5 gm = .036 ug/gm = .036 ppm

8. Report
   a. Report the results of each analysis giving each compound identified, the scan number, the quantity of the compound, and the method used to calculate that quantity.
   b. Example

      The level of toluene in the sample is very low and for the purpose of this analysis is reported at less than 1 ppm

B. Soxhlet Extraction for Solids

1. Summary
The sample is mixed with anhydrous sodium sulfate, placed in an extraction thimble or between two plugs of glass wool and extracted using methylene chloride. The extract is reserved. The remaining contents of the thimble are mixed with distilled water and the pH is adjusted to 2 or less. This aqueous mixture is extracted with ethyl ether. The two extracts are dried, combined, and anaylzed in one GC/MS analysis.

2. Apparatus and Materials
   a. Soxhlet extractor - 40 mm id, with 500 ml round-bottom flask.
   b. Kuderna-Danish Apparatus [Kontes K-570000 or equivalent] with 3-ball snyder column
   c. Gas Chromatograph - Analytical system capable of split and splitless injections and all required accessories including column supplies, gases, etc.
   d. Column - 30m SE-30, SE-52, SE-54, or equivalent, .2 to .25mm internal diameter with a film thickness between .15 to .40u.
   e. Mass Spectrometer - Capable of scanning from 35 to 450 daltons every 1 second or less. The MS must be able to operate at 70 volts for electron ionization and must produce a recognizable mass spectrum for 50 ng or less of DFTPP when the sample is introduced through the GC column. The GC column should be directly interfaced (i.e. no separator) to the mass spectrometer through an all glass or all glass lined system. If a fused silica capillary column is used, the analyst is required to complete the interface by directly connecting the end of the column to the ion source.
   f. Computer System - The computer system interfaced to the mass spectrometer should be capable of continuously acquiring mass spectra for the duration of the gas chromatographic program. (about 1 hr.) All data must be stored within the data system. Mass storage devices such as disk or tape are accepable. The system must have software available to allow searching GC/MS runs for the following:
      1) selected ion chromatograms
      2) total ion chromatograms
      3) reverse and forward search for any compound from the EPA/NIH Mass Spectral Data Base

3. Reagents
   a. Methylene chloride - Pesticide grade
   b. Ethyl Ether - Pesticide grade

c. Anhydrous Sodium Sulfate, ACS grade, purified by heating at 400°C for 4 hr. in a shallow tray.

4. Calibration
   a. The mass spectrometer is calibrated with either PFK or FC-43 over the scan range. 50ng or less of DFTPP should be injected in the splitless mode using the conditions given in table 8.27-1.
   b. The DFTPP spectrum obtained from the top of the chromatographic peak (backgroud subtracted) should meet the criteria listed in table 8.24-2.

5. Sample Preparation
   a. Blend 10.0 gm of the solid sample with 10.0 gm of anhydrous sodium sulfate. Weigh this mixture to the nearest 0.1 gm. Place in either a paper (pre-washed with methylene chloride and dried) or glass extraction thimble.
   b. Place the thimble in the extractor. (If any problems arise when using the thimble, i.e. if the sample clogs the thimble, an alternative would be to place a plug of glass wool in the extraction chamber, transfer the sample into the chamber, then cover the sample with another plug of glass wool.)
   c. Place 250 ml of methylene chloride into the 500 ml roundbottom flask, add a boiling chip and attach the flask to the extractor. Extract the sample for 16 hours.
   d. After the extraction is complete, cool the extract; rinse extractor flask and thimble with fresh solvent. Combine the extract and rinse. Dry the extract by passing it through a 4 inch column of sodium sulfate that has been washed with solvent. Collect the dried extract in a 500 ml Kuderna-Danish (KD) flask fitted with a 10 ml graduated concentartor tube. Empty the contents of the thimble into a pre-weighed 250 ml Erlinmeyer flask. Add 100 ml distilled water to the flask.
   e. Adjust the pH to 2 or less with sulfuric acid solution. Extract three times with fresh 60 ml portions of ethyl ether. Combine the three extracts and dry by passing through a 4 inch column of sodium sulfate. Rinse column with fresh solvent. The dried extract is added to the KD.
   f. Evaporate the aqueous solution in the erlinmeyer flask to dryness; cool the flask and weigh the residue. Determine the weight difference between

the residue in the erlinmeyer flask and the original sample.

g. Concentrate the dried extracts in the KD. A level that would give a final concentration of about 1 mg/ml is generally appropriate for GC/MS.

h. The concentrated extract should be placed in a volumetric flask and made up to the appropriate volume.

6. Gas Chromatography/Mass spectrometry

a. Establish the chromatographic conditions given in table 8.27-1.

b. Set the Gas Chromatograph for either split or splitless injection. If using the split mode, record the split ratio. Record both liniar and volume column flow.

c. Inject sample and acquire data. Record amount of sample injected. (2 to 5 ul for split and 1 to 2ul for splitless)

d. Inject appropriate standards and acquire data as in c.

7. Qualitative and Quantitative Determination

a. A compound can be qualitativly identified in either of two ways. At least three characteristic ions of the compound must maximize within one scan of the apex of the peak and the integrated ion areas agree with a library or standard mass spectrum within $\pm$ 20%; or, a reverse search yeilds a value equivalent to the criteria stated above.

b. Samples can be quantitated in two ways. The first is by the method of standard additions. This method is always acceptable and should be used when the exact concentration is needed. The second method is to be used only for order of magnitude estimates of concentartion. This is done by comparing the Total Ion Chromatogram of the compound in the sample with a standard. For example, if 100 ng of benzene gives a total of 10,000 counts then a peak corresponding to toluene with 25,000 counts would be expected to correspond to about 250 ng. When using this method the analyst should try to use standards which resemble the compounds in question as closely as possible. The internal standard is used as a method check. For example, if 50 ng of the internal standard normally gives 5000 integrated area counts this condition should be met in the sample $\pm$20%.

c. Example Calculation
10 gm of solid sample was extracted with methylene chloride and ethyl ether as in the procedure. The

sample lost about 4 gm during the extraction. The combined extracts were diluted to 500 ml with methylene chloride. 5 ul was injected with a split ratio of 100 to 1. Hexachlorobenzene was found in the extract with a total of 7,121 total area counts.

Dichlorobenzene was used as a standard

5 ul x 1 mg/ml x 1 ml/1000 ul = 5 ug

Total counts for Dichlorobenzene was 3760

3760 counts/5 ug = 752 counts/ug

Hexachlorobenzene in sample

7121 counts/5 ul x 1 ug/752 counts = 9.47 ug/5 ul

9.47 ug/5 ul x 1000 ul/1 ml x 500 ml = 947000ug

947000 ug = .947 gm

.947 gm/10 gm = .0947 = 9.5% hexachlorobenzene

8. Report
   a. Report the results of each analysis giving each compound identified, the scan number, the quantity of the compound, and the method used to calculate that quantity.
   b. Example

Compound	Quantitation Method	Scan #	Amount	Range
Hexachloro benzene	Estimate/dichloro benzene	693	9.5 %	1-10%

III. Mixtures of Liquids and Solids

A 10 to 20 gm sample of well mixed waste is used. The sample is divided into its component phases and the procedures oulined in sections I and II of this Method are employed for analysis.

A. Separation Procedure for Liquids and Solids

1. Summary
   A 10 to 20 gm sample of the waste is separated into its component phases by centrifugation. The Liquid Phases are either decanted or pipeted for analysis using section I and the solid residue is analyzed using section II.

2. Apparatus and Materials
   a. Centrifuge tubes - 10-20 ml pyrex glass or equivalent with ground glass stopper.
   b. Centrifuge - Capable of 2400 RPM

3. Reagents - Reserved

4. Calibration - See calibration sections in parts I and II of this method

5. Sample Preparation
   a. Alliquot a 10 to 20 gm sample of well mixed waste into a pre weighed cenrifuge tube. Weigh.
   b. Place tube into centrifuge and spin at 2400 RPM for 15 min. or until the solids and liquid phases are separated.
   c. Pour off liquid phase and weigh. Proceed to section I of this method.
   d. Weigh remaining solids and proceed to section II of this method. The purge and trap method for the determination of volatiles in solids may be omitted since the volatiles are determined in the liquid phase of the sample.

B. Report

1. Report the results as a weighted average of the liquid phases and solid phase.
2. Example calculation
   See sections I and II

Table 8.27-1 (Liquids)

Column: SE-30, SE-52, SE-54 (30 m)
Linear Flow Rate: 50 cm/sec H_2 or 30 cm/sec He
Temperature Program: Inject at 25°C then 50°C
Program 50° to 280° C at 8°/min
Hold at 280°C for 15 min.

Table 8.27-2 (Extractables)

Column: SE-30, SE-52, SE-54 (30 m)
Linear Flow Rate: 50 cm/sec H_2 or 30 cm/sec He
Temperature Program: Inject at 50°C hold 2 min.
Program to 280°C at 8°C/min
Hold at 280°C for 15 min

Table 8.27-3 (Volatiles)

Column: Same as 8.27-2
Linear Flow Rate: Same as 8.27-2
Temperature Program: Inject at 25°C (cool head of column with flurocarbon spray) then to 50°C
Program 50°C to 200°C at 4°C/mir
Hold at 200°C for 10 min

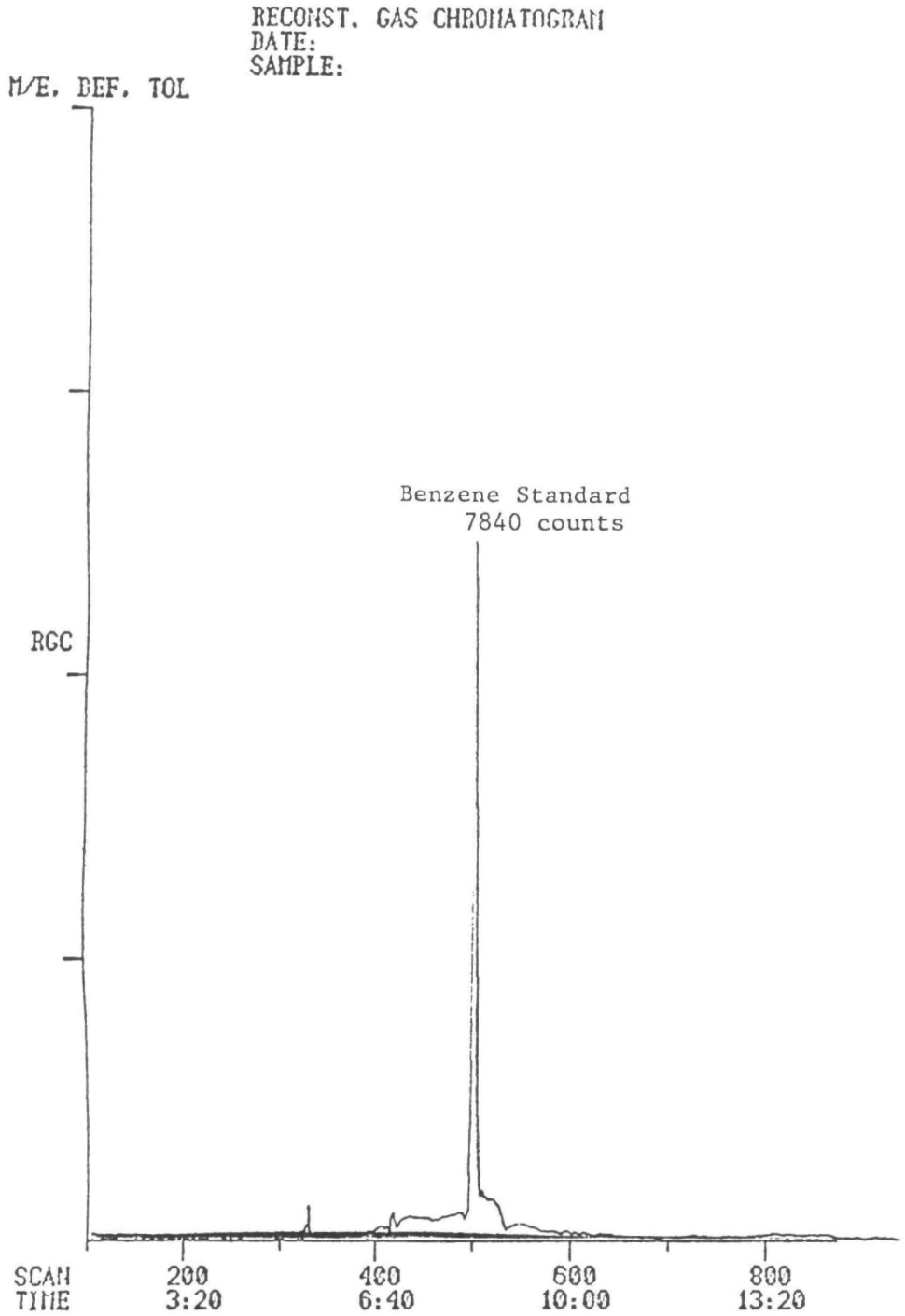
RECONST. GAS CHROMATOGRAM
DATE:
SAMPLE:
M/E. BEF. TOL
Benzene Standard
7840 counts
RGC
SCAN
TIME
200
3:20
400
6:40
600
10:00
800
13:20

Figure 8.27-1

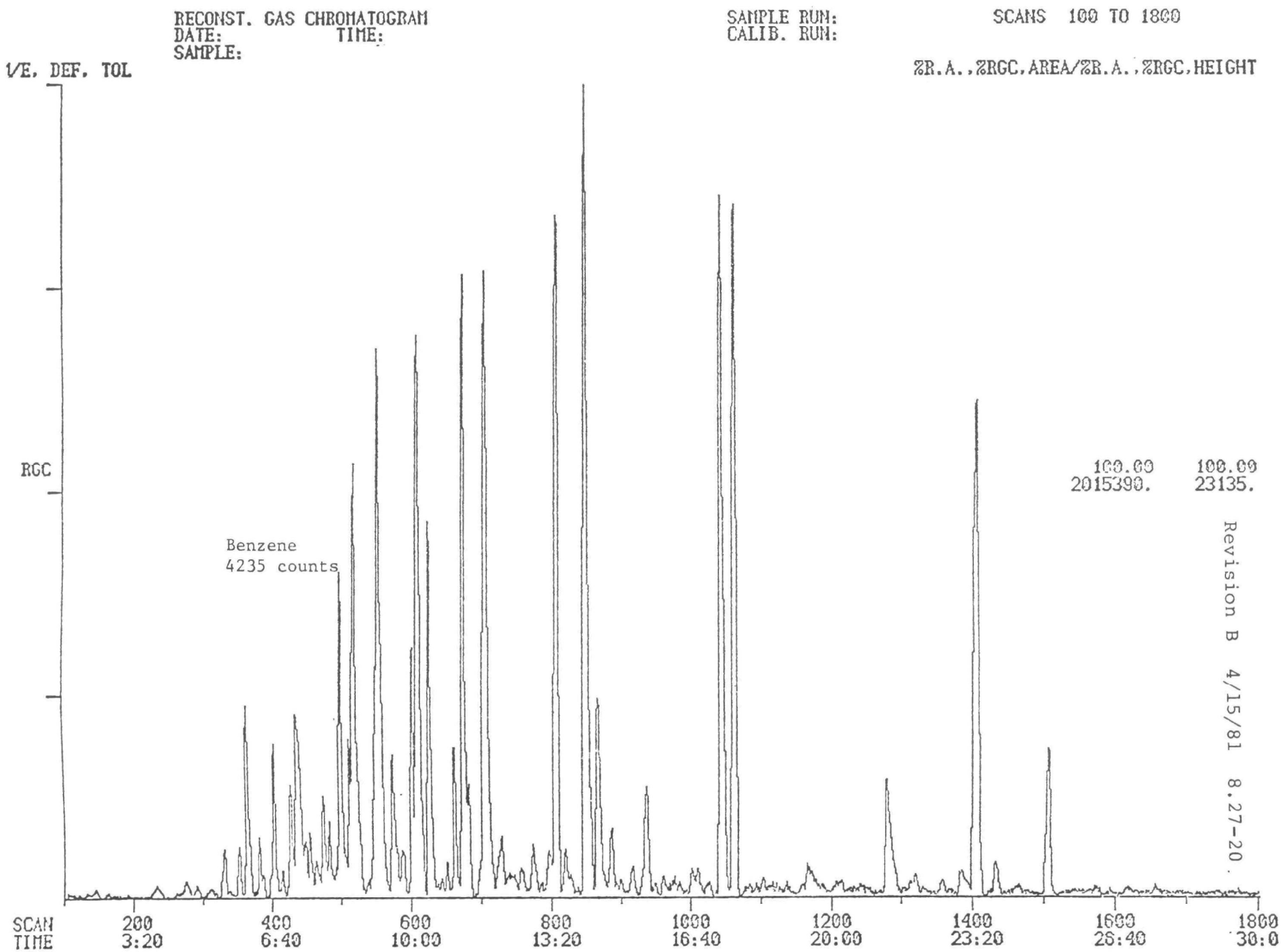
RECONST. GAS CHROMATOGRAM
DATE: TIME:
SAMPLE:
SAMPLE RUN:
CALIB. RUN:
SCANS 100 TO 1800
V/E, DEF, TOL
%R.A.,%RGC,AREA/%R.A.,%RGC,HEIGHT
RGC
100.00 100.00
2015390. 23135.
Benzene
4235 counts
Revision B 4/15/81 8.27-20
SCAN 200 400 600 800 1000 1200 1400 1600 1800
TIME 3:20 6:40 10:00 13:20 16:40 20:00 23:20 26:40 30:0

Figure 8.27-2

Method 8.56
TOTAL ORGANIC HALIDE

1. Scope and Application

   1.1 This method is to be used for the determination of Total Organic Halides as Cl^- by carbon adsorption, and requires that all samples be run in duplicate. Under conditions of duplicate analysis, the reliable limit of sensitivity is 5 µg/L. Organic halides as used in this method are defined as all organic species containing chlorine, bromine and iodine that are adsorbed by granular activated carbon under the conditions of the method. Fluorine containing species are not determined by this method.

   1.2 This is a microcoulometric-titration detection method applicable to the determination of the compound class listed above in drinking and ground waters, as provided under 40 CFR 265.92.

   1.3 Any modification of this method, beyond those expressly permitted, shall be considered as major modifications subject to application and approval of alternate test procedures under 40 CFR 260.21.

   1.4 This method is restricted to use by, or under the supervision of, analysts experienced in the operation of a pyrolysis/microcolumeter and in the interpretation of the results.

2. Summary of Method

   2.1 A sample of water that has been protected against the loss of volatiles by the elimination of headspace in the sampling container, and is free of undissolved solids, is passed through a column containing 40 mg of activated carbon. The column is washed

to remove any trapped inorganic halides, and is then pyrolyzed to convert the adsorbed organohalides to a titratable species that can be measured by a microcoulometric detector.

3. Interferences

3.1 Method interferences may be caused by contaminants, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under the conditions of the analysis by running method blanks.

3.1.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by treating with chromate cleaning solution. This should be followed by detergent washing in hot water. Rinse with tap water and distilled water, drain dry, and heat in a muffle furnace at 400°C for 15 to 30 minutes. Volumetric ware should not be heated in a muffle furnace. Glassware should be sealed and stored in a clean environment after drying and cooling, to prevent any accumulation of dust or other contaminants.

3.1.2 The use of high purity reagents and gases help to minimize interference problems.

3.2 Purity of the activated carbon must be verified before use. Only carbon samples which register less than 1000 ng/40 mg should be used. The stock of activated carbon should be stored in its granular form in a glass container with a Teflon seal. Exposure to the air must be minimized, especially during and after milling and sieving the activated carbon. No more than a two-week supply

should be prepared in advance. Protect carbon at all times from all sources of halogenated organic vapors. Store prepared carbon and packed columns in glass containers with Teflon seals.

3.3 This method is applicable to samples whose inorganic-halide concentration does not exceed the organic-halide concentration by more than 20,000 times.

4. Safety

The toxicity or carcinogenicity of each reagent in this method has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current-awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material-handling data sheets should also be made available to all personnel involved in the chemical analysis.

5. Apparatus and Materials (All specifications are suggested. Catalog numbers are included for illustration only).

5.1 Sampling equipment, for discrete or composite sampling

5.1.1 Grab-sample bottle - Amber glass, 250-mL, fitted with Teflon-lined caps. Foil may be substituted for Teflon if the sample is not corrosive. If amber bottles are not available, protect samples from light. The container must be washed and muffled at 400°C before use, to minimize contamination.

5.2 Adsorption System

5.2.1 Dohrmann Adsorption Module (AD-2), or equivalent, pressurized, sample and nitrate-wash reservoirs.

5.2.2 Adsorption columns - pyrex, 5 cm long X 6-mm OD X 2-mm ID.

5.2.3 Granular Activated Carbon (GAC) - Filtrasorb-400, Calgon-APC, or equivalent, ground or milled, and screened to a 100/200 mesh range. Upon combustion of 40 mg of GAC, the apparent-halide background should be 1000-mg Cl^- equivalent or less.

5.2.4 Cerafelt (available from Johns-Manville), or equivalent - Form this material into plugs using a 2-mm ID stainless-steel borer with ejection rod (available from Dohrmann) to hold 40 mg of GAC in the adsorption columns. CAUTION: Do not touch this material with your fingers.

5.2.5 Column holders (available from Dohrman).

5.2.6 Volumetric flasks - 100-mL, 50-mL.

A general schematic of the adsorption system is shown in Figure 1.

5.3 Dohrmann microcoulometric-titration system (MCTS-20 or DX-20), or equivalent, containing the following components:

5.3.1 Boat sampler.

5.3.2 Pyrolysis furnace.

5.3.3 Microcoulometer with integrator.

5.3.4 Titration cell.

A general description of the analytical system is shown in Figure 2.

5.4 Strip-Chart Recorder.

6. Reagents

6.1 Sodium sulfite - 0.1 M, ACS reagent grade (12.6 g/L).

6.2 Nitric acid - concentrated.

6.3 Nitrate-Wash Solution (5000 mg NO_3^-/L) - Prepare a nitrate-wash solution by transferring approximately 8.2 gm of potassium nitrate into a 1-litre volumetric flask and diluting to volume with reagent water.

6.4 Carbon dioxide - gas, 99.9% purity.

6.5 Oxygen - 99.9% purity.

6.6 Nitrogen - prepurified.

6.7 70% Acetic acid in water - Dilute 7 volumes of acetic acid with 3 volumes of water.

6.8 Trichlorophenol solution, stock (1 µL = 10 µg Cl^-) - Prepare a stock solution by weighing accurately 1.856 gm of trichlorophenol into a 100-mL volumetric flask. Dilute to volume with methanol.

6.9 Trichlorophenol solution, calibration (1 µL = 500 ng Cl^-) - Dilute 5 mL of the trichlorophenol stock solution to 100 mL with methanol.

6.10 Trichlorophenol standard, instrument-calibration - First, nitrate wash a single column packed with 40 mg of activated carbon as instructed for sample analysis, and then inject the column with 10 µL of the calibration solution.

6.11 Trichlorophenol standard, adsorption-efficiency (100 µg Cl^-/L) - Prepare a adsorption-efficiency standard by injecting 10 µL of stock solution into 1 liter of reagent water.

6.12 Reagent water - Reagent water is defined as a water in which an

interferent is not observed at the method detection limit of each parameter of interest.

6.13 Blank standard - The reagent water used to prepare the calibration standard should be used as the blank standard.

7. Calibration

7.1 Check the adsorption efficiency of each newly-prepared batch of carbon by analyzing 100 mL of the adsorption-efficiency standard, in duplicate, along with duplicates of the blank standard. The net recovery should be within 5% of the standard value.

7.2 Nitrate-wash blanks (Method Blanks) - Establish the repeatability of the method background each day by first analyzing several nitrate-wash blanks. Monitor this background by spacing nitrate-wash blanks between each group of eight pyrolysis determinations.

7.2.1 The nitrate-wash blank values are obtained on single columns packed with 40 mg of activated carbon. Wash with the nitrate solution as instructed for sample analysis, and then pyrolyze the carbon.

7.3 Pyrolyze duplicate instrument-calibration standards and the blank standard each day before beginning sample analysis. The net response to the calibration-standard should be within 3% of the calibration-standard value. Repeat analysis of the instrument-calibration standard after each group of eight pyrolysis determinations, and before resuming sample analysis after cleaning or reconditioning the titration cell or pyrolysis system.

8. Sample Preparation

8.1 Special care should be taken in the handling of the sample to

minimize the loss of volatile organohalides. The adsorption procedure should be performed simultaneously on duplicates.

8.2 Reduce residual chlorine by the addition of sulfite (1 mL of 0.1 M per liter of sample). Addition of sulfite should be done at the time of sampling if the analysis is meant to determine the TOX concentration at the time of sampling. It should be recognized that TOX may increase on storage of the sample. Samples should be stored at $4^{o}C$ without headspace.

8.3 Adjust pH of the sample to approximately 2 with concentrated HNO_3 just prior to adding the sample to the reservoir.

9. Adsorption Procedure

9.1 Connect two columns in series, each containing 40 mg of 100/200-mesh activated carbon.

9.2 Fill the sample reservoir, and pass a metered amount of sample through the activated-carbon columns at a rate of approximately 3 mL/min. NOTE: 100 mL of sample is the preferred volume for concentrations of TOX between 5 and 500 µg/L; 50 mL for 501 to 1000 µg/L, and 25 mL for 1001 to 2000 µg/L.

9.3 Wash the columns-in-series with 2 mL of the 5000-mg/L nitrate solution at a rate of approximately 2 mL/min to displace inorganic chloride ions.

10. Pyrolysis Procedure

10.1 The contents of each column is pyrolyzed separately. After rinsing with the nitrate solution, the columns should be protected from the atmosphere and other sources of contamination until ready for further analysis.

10.2 Pyrolysis of the sample is accomplished in two stages. The volatile components are pyrolyzed in a CO_2-rich atmosphere at a low temperature to assure the conversion of brominated trihalomethanes to a titratable species. The less volatile components are then pyrolyzed at a high temperature in an O_2-rich atmosphere.

NOTE: The quartz sampling boat should have been previously muffled at 800°C for at least 2 to 4 minutes as in a previous analysis, and should be cleaned of any residue by vacuuming.

10.3 Transfer the contents of each column to the quartz boat for individual analysis.

10.4 If the Dohrmann MC-1 is used for pyrolysis, manual instructions are followed for gas flow regulation. If the MCT-20 is used, the information on the diagram in Figure 3 is used for gas flow regulation.

10.5 Position the sample for 2 minutes in the 200°C zone of the pyrolysis tube. For the MCTS-20, the boat is positioned just outside the furnace entrance.

10.6 After 2 minutes, advance the boat into the 800°C zone (center) of the pyrolysis furnace. This second and final stage of pyrolysis may require from 6 to 10 minutes to complete.

11. Detection

The effluent gases are directly analyzed in the microcoulometric-titration cell. Carefully follow manual instructions for optimizing cell performance.

12. Breakthrough

Because the background bias can be of such an unpredictable nature, it can be especially difficult to recognize the extent of breakthrough of organohalides from one column to another. All second-column measurements for a properly operating system should not exceed 10-percent of the two-column total measurement. If the 10-percent figure is exceeded, one of three events can have happened. Either the first column was overloaded and a legitimate measure of breakthrough was obtained - in which case taking a smaller sample may be necessary; or channeling or some other failure occurred - in which case the sample may need to be rerun; or a high, random, bias occurred and the result should be rejected and the sample rerun. Because knowing which event has occurred may not be possible, a sample analysis should be repeated often enough to gain confidence in results. As a general rule, any analyses that is rejected should be repeated whenever sample is available. In the event that the second-column measurement is equal to or less than the nitrate-wash blank value, the second-column value should be disregarded.

13. Quality Control

13.1 Before performing any analyses. the analyst must demonstrate the ability to generate acceptable accuracy and precision with this procedure by the analysis of appropriate quality-control check samples.

13.2 The laboratory must develop and maintain a statement of method accuracy for their laboratory. The laboratory should update the accuracy statement regularly as new recovery measurements are made.

13.3 It is recommended that the laboratory adopt additional quality-assurance practices for use with this method. The specific practices that would be most productive will depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. Whenever possible, the laboratory should perform analysis of standard reference materials and participate in relevant performance-evaluation studies.

14. Calculations

OX as Cl^- is calculated using the following formula:

$$\frac{(C_1 - C_3) + (C_2 - C_3)}{V} = \mu g/L \text{ Total Organic Halide}$$

where:

C_1 = µg Cl^- on the first column in series

C_2 = µg Cl^- on the second column in series

C_3 = predetermined, daily, average, method-blank value (nitrate-wash blank for a 40-mg carbon column)

V = the sample volume in L

15. Accuracy and Precision

These procedures have been applied to a large number of drinking-water samples. The results of these analysis are summarized in Tables I and II.

16. Reference

Dressman, R., Najar, G., Redzikowski, R., paper presented at the Proceedings of the American Water Works Association Water Quality Technology Conference, Philadelphia, Dec. 1979.

TABLE I

PRECISION AND ACCURACY DATA FOR MODEL COMPOUNDS

Model Compound	Dose µg/L	Dose as µg/L Cl	Average % Recovery	Standard Deviation	No. of Replicates
$CHCl_3$	98	88	89	14	10
$CHBrCl_2$	160	106	98	9	11
$CHBr_2Cl$	155	79	86	11	13
$CHBr_3$	160	67	111	8	11
Pentachlorophenol	120	80	93	9	7

TABLE II

PRECISION DATA ON TAP WATER ANALYSIS

Sample	Avg. halide ug Cl/L	Standard Deviation	No. of Replicates
A	71	4.3	8
B	94	7.0	6
C	191	6.1	4

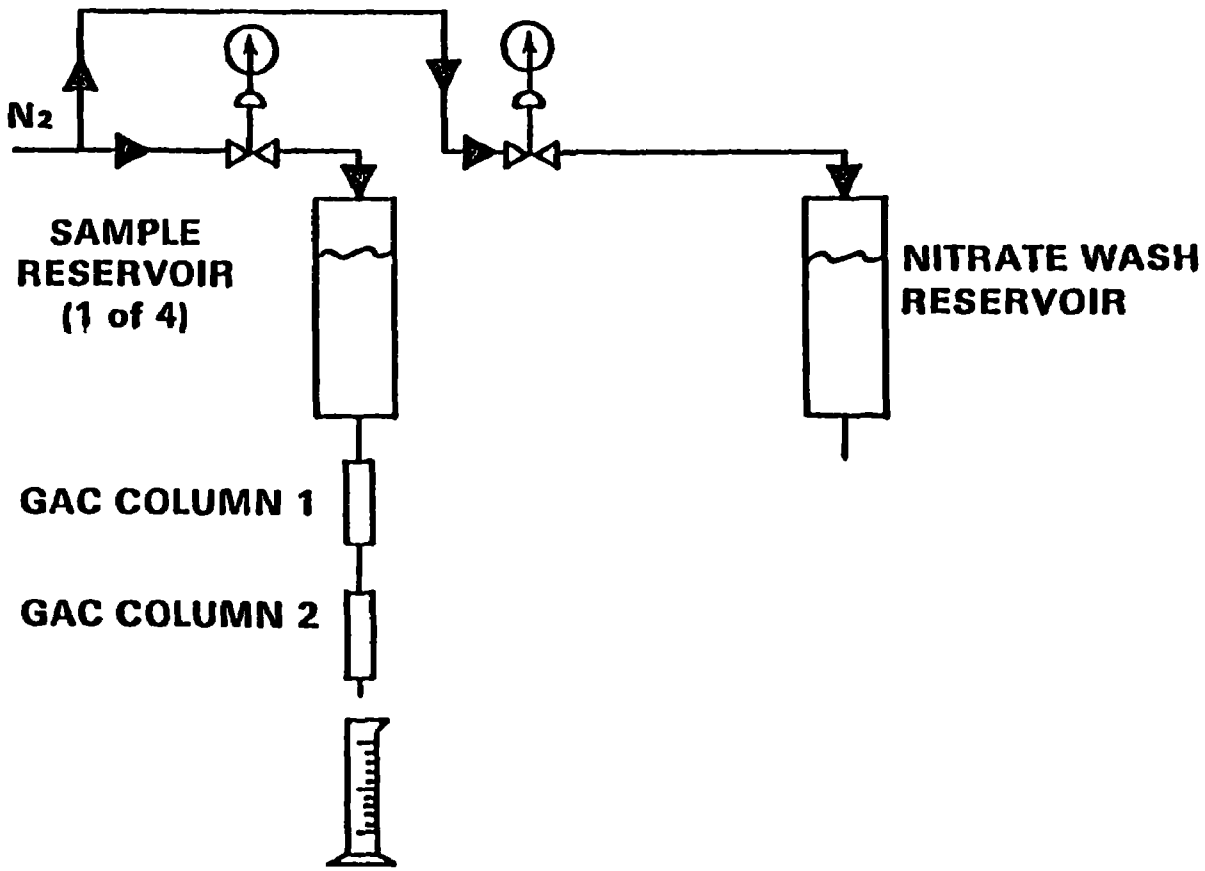

Figure 1. Adsorption Schematic

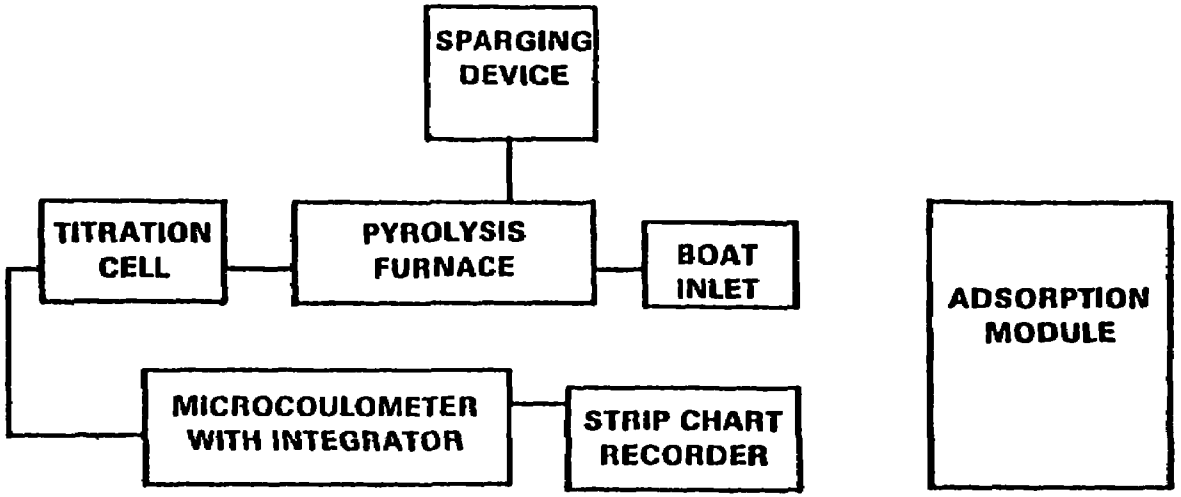

Figure 2. CAOX Analysis System Schematic

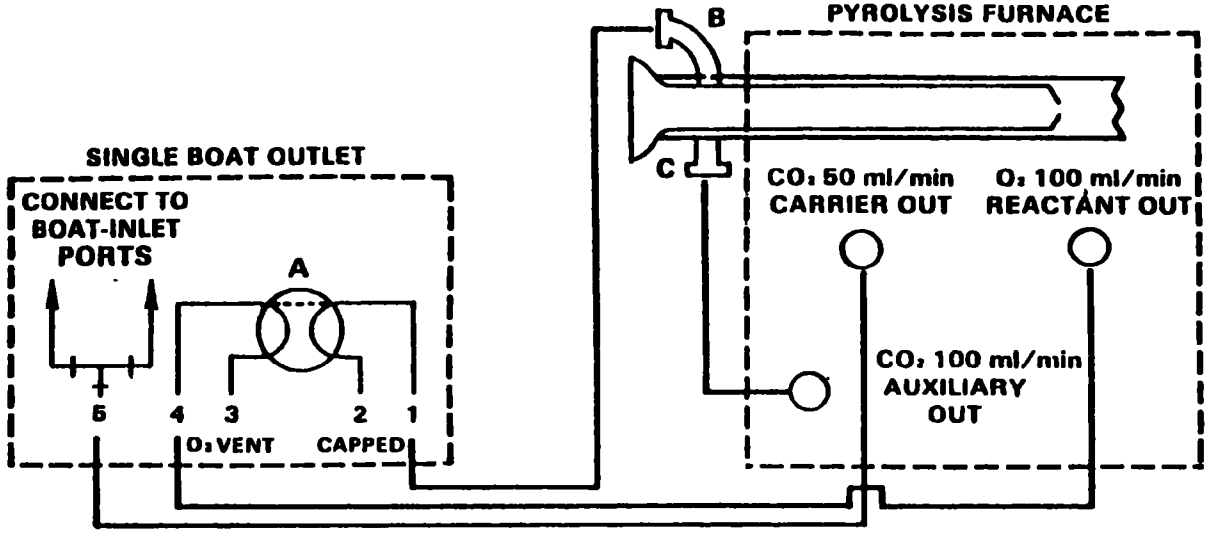

Figure 3. Rear view plumbing schematic for MCTS-20 system. Valve A is set for first-stage combustion, O_2 venting (push/pull valve out). Port B enters inner combustion tube; Port C enters outer combustion tube.

Method 8.57

Sulfides

1. Scope and Application
   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.
   1.3 This method is suitable for the measurement of sulfide in concentrations above 1 mg/l
2. Summary of Method
   2.1 Excess iodine is added to a sample which may or may not have been treated with zinc acetate to produce zinc sulfide. The iodine oxidizes the sulfide to sulfur under acidic conditions. The excess iodine is back titrated with sodium thiosulfate or phenylarsine oxide.
3. Comments
   3.1 Reduced sulfur compounds, such as sulfite, thiosulfate and hydrosulfite, which decompose in acid may yield erratic results. Also, volatile iodine-consuming substances will give high results.
   3.2 Samples must be taken with a minimum of aeration. Sulfide may be volitilized by aeration and any ozygen inadvertently added to the sample may convert sulfide to an unmeasurable form.
   3.3 If the sample is not preserved with zinc acetate, the analysis must start immediately. Similarly, the measurement of dissolved sulfides must also be commenced immediately.
4. Apparatus: Ordinary laboratory glassware
5. Reagents
   5.1 Hydrochloric acid, HCl, 6N
   5.2 Standard iodine solution, 0.0250 N: Dissolve 20 to 25 g KI in a little water in a liter volumetric flask and add 3.2 g iodine. Allow to dissolve. Dilute to 1 liter and standardize against 0.0250 N sodium thiosulfate or phenylarsine oxide using a starch indicator.
   5.3 Phenylarsine oxide 0.0250 N: commercially available.
   5.4 Starch indicator: commercially available.
   5.5 Procedure for standardization (see Residual Chlorine-iodometric titration)
6. Procedure
   6.1 Unprecipitated sample
      6.1.1 Place a known amount of standard iodine solution (5.2) into a 500 ml flask. The amount should be estimated to be in excess of the amount of sulfide expected.
      6.1.2 Add distilled water, if necessary, to bring the volume to approximately 20 ml.
      6.1.3 Add 2 ml of 6N HCl (5.1)
      6.1.4 Pipet 200 ml of sample into the flask, keeping the tip of the pipet below the surface of the sample.
      6.1.5 If the iodine color disappears, add more iodine

until the color remains. Record the total number of milliliters of the standard iodine used in performing steps 6.1.1 and 6.1.5.

6.1.6 Titrate with reducing solution (0.0250 N sodium thiosulfate or 0.0250 N phenylarsine oxide solution (5.3)) using the starch indicator (5.4) until the blue color disappears. Record the number of milliliters used.

6.2 Precipitated samples

6.2.1 Add the reagents to the sample in the original bottle. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3 Dewatered samples

6.3.1 Return the glass fibre filter paper which contains the sample to the original bottle. Add 200 ml of distilled water. Perform steps 6.1.1, 6.1.3, 6.1.5, and 6.1.6.

6.3.2 The calculations (7) should be based on the original sample put throug the filter.

7. Calculations

7.1 One ml of 0.0250 N standard iodine solution (5.2) reacts with 0.4 mg of sulfide present in the titration vessel.

7.2 Use the formula

mg/l sulfide = 400(A-B)/ml sample

where:

A=ml of 0.0250 N standard iodine solution (5.2)
B=ml of 0.0250 N standard reducing sodium thiosulfate or phenylarsine oxide solution (5.3)

8. Precision and Accuracy

8.1 Precision and accuracy for this method have not been determined.

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