2445
7-29-75

Q-1496

SAND75-0014
Unlimited Release

Manual of Analytical Methods for the Environmental Health Laboratory

C. E. Gray, Editor

SF 2900 Q(7-73)

Issued by Sandia Laboratories, operated for the United States Energy Research and Development Administration by Sandia Corporation.

Printed in the United States of America

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy $4.00; Microfiche $2.25

SAND75-0014
Unlimited Release
Printed June 1975

MANUAL OF ANALYTICAL METHODS FOR THE ENVIRONMENTAL HEALTH LABORATORY

Compiled and Edited by: Charles E. Gray
Environmental Health Laboratory-3311

Environmental Health Department, 3310
Sandia Laboratories
Albuquerque, New Mexico 87115

FORWARD

This manual was compiled from techniques used in the Environmental Health Laboratory of Sandia Laboratories at Albuquerque, New Mexico, and is a revision of an earlier publication (SC-M-67-3044) edited by Lial W. Brewer. The procedures are similar to those used in other laboratories devoted to Environmental Health practices. Some of the methods are standard and others are modified to suit our needs; others were developed at Sandia. The author has attempted to present all methods in a simple and concise manner, but in sufficient detail to make them readily usable. It is not inferred that the methods are universal for any type of sample, but they have been found very reliable for the types of samples mentioned. The author will welcome inquiry for clarification of any part of this manual. It is the desire of the author that this manual will be of use and service to others. New and revised procedures will be issued as supplements to this document.

CONTENTS

CONTENTS (cont)

FIGURES

CONTENTS (cont)

TABLES

SECTION A
ABSORPTION SPECTROPHOTOMETRY

The application of absorption spectrophotometry to the analysis of various materials is presented in this section. Analysis by optical absorption has two aspects, colorimetric and spectrophotometric.

Colorimetric analysis is the determination of the concentration of colored substances by their color intensity in a specific spectral region.

Spectrophotometric analysis is the determination of the concentration of a substance according to its absorption of a specific monochromatic radiation. In this method a special solution must be prepared for the determination of each material; the method is suitable for the routine determination of a given element in a given medium, but not for routine qualitative analysis.

The general principles and characteristics of the method, including the apparatus, measurement techniques, etc., are given in the following section.

ARSENIC IN AIR, URINE, AND WATER

Abstract

Ashed samples are reduced to trivalent arsenic, evolved as arsine gas and collected in silver diethyldithiocarbamate which is then determined colorimetrically at 560 nm.

APPARATUS

Spectrophotometer, Beckman DU or equivalent with 1-cm cells.

Arsine generator (Figure 1)

A Generator flask

B Scrubber with glass wool plug of lead acetate

C Evolution tube

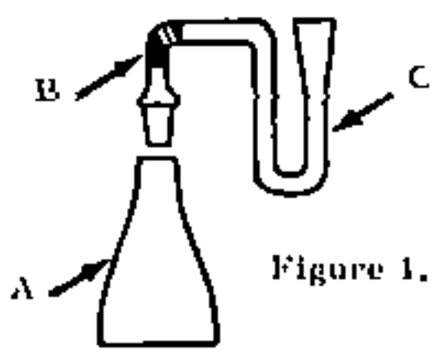

Figure 1. Arsine Generator

REAGENTS

Sulfuric acid, conc. (95% H_2SO_4)

Nitric acid, conc. (70% HNO_3)

Hydrochloric acid, conc. (36% HCl)

Perchloric acid, conc. (70% $HClO_4$)

Acid digestion mixture II, 3:1:1 conc. HNO_3; conc. H_2SO_4; conc. $HClO_4$

Arsenic Standard solution (1 mg/ml) - Dissolve 0.660 g As_2O_3 in 10 ml of 20% NaOH, then dilute to 1000 ml.

Ammonium oxalate, saturated solution

Stannous chloride solution, 40 g stannous chloride dihydrate dissolved in 100 ml conc. HCl

Potassium iodide solution - Dissolve 15 g KI in 100 ml water.

Lead acetate solution - Dissolve 10 g lead acetate in 100 ml water. Glass wool in the scrubber is soaked in this solution, drained, and dried.

Silver diethyldithiocarbamate

Zinc, granular 20 mesh

Pyridine, A.R.

Arsine absorbing solution - 1 g of silver diethyldithiocarbamate dissolved in 200 ml of A.R. pyridine. Solution is then filtered before use.

CALCULATIONS

$$\text{mg As/l urine} = \frac{\mu\text{g As (from curve)}}{\text{ml of urine}}$$

$$\text{mg As/l water} = \frac{\mu\text{g As}}{\text{ml of water}}$$

$$\text{mg As/m}^3 = \frac{\text{mg As}}{\text{m}^3 \text{ of air sampled at STP}} \quad \text{or}$$

$$\frac{\mu\text{g As}}{\text{liters of air sampled at STP}}$$

References

1. "Determination of Arsenic in Air," Manual of Analytical Methods, ACGIH (1958).

Abstract

A yellow color is developed when o-tolidine is reacted with chlorine in acid solution. The maximum absorption is at 416 nm and also at 438 nm at a pH of 1.6.

APPLICATIONS AND LIMITATIONS

This method registers the total available chlorine and is rapid and simple. Iron, manganese, and nitrite will interfere even in small quantities. The range is 0-1 PPM. Higher concentration can be analyzed by diluting the sample.

APPARATUS

Hach colorimeter

Fritted bubbler or midget impinger, all glass

Assorted laboratory glassware

REAGENTS

Hach O-TolVer Cat. No. 141

Sodium hydroxide (0.01N) - Dissolve 0.4 g NaOH in 1 liter of distilled water.

Hydrochloric acid (1N) - Add 8 ml of conc. HCl to 92 ml of water.

ANALYTICAL PROCEDURE

1. Pass a known volume of air through a fritted bubbler or a midget impinger containing 0.01N NaOH. After sampling, neutralize to pH 7.0 with 1N HCl.
2. Fill a 25-ml graduated cylinder with air sampling solution or water to be analyzed.
3. Add 1 ml O-TolVer and mix well.
4. If chlorine is present, a yellow color will develop. Allow 5 minutes for color development at 20°C.
5. Fill a colorimeter bottle with untreated water sample and place it in the light cell.
6. Insert the chlorine meter scale in the meter and use the Hach 5-45 color filter. Press the light switch and adjust the light control for a meter reading of zero PPM.

7. Add the prepared sample to a colorimeter bottle and place in the light cell. Press the light switch and read the PPM chlorine.

8. If the meter reads higher than 1 PPM, the sample must be diluted.

References

1. Hach Chemical Co. Engineers Laboratory Methods Manual, 1st Ed., 1969.

2. Boltz, D. F., Colorimetric Determination of Nonmetals, Interscience Publishers, Inc., N.Y. (1958), p. 163.

CHROMIC ACID MIST IN AIR

Abstract

Chromates react with sym-diphenylcarbazide in acid solution to produce a pink-violet color at 540 nm, which conforms to Beer's law.

APPLICATIONS AND LIMITATIONS

The range for this method is from 0.2 µg Cr (+6) up to about 10 µg Cr (+6). The main interferences are iron, copper, nickel, and vanadium.

APPARATUS

Midget impingers, all glass

Graduated cylinders, 25 ml

Spectrophotometer, Beckman DU or equivalent with 1-cm cells.

REAGENTS

Sodium hydroxide (1N) - Dissolve 40 g NaOH in 1 liter of distilled water.

Sulfuric acid (10% solution) - Add 100 ml concentrated H_2SO_4 to 800 ml distilled water. When cool, dilute to 1 liter.

Potassium dichromate (Cr + 6), 100 PPM or 0.1 µg/µl - Dissolve 0.2829 g $K_2Cr_2O_7$ in 1 liter of distilled water.

Sym-diphenylcarbazide reagent - Dissolve 0.4 g sym-diphenylcarbazide in 30 ml glacial acetic acid and dilute to 400 ml with distilled water.

ANALYTICAL PROCEDURE

1. Collect samples in two midget impingers in series, using 15 ml of 1N NaOH for collecting media in each impinger.
2. Transfer the samples to 25-ml graduated cylinders with distilled water.
3. Acidify with 10% sulfuric acid, check with litmus, and dilute to volume.
4. Place 5-ml aliquot into 25-ml graduated cylinders, add 5 ml 10% sulfuric acid and 1 ml sym-diphenylcarbazide reagent, and mix by inverting several times.
5. Dilute to 25 ml with distilled water.

6. Prepare standards from the 100-PPM standard $K_2Cr_2O_7$ by pipetting 0, 5, 10, 20, 50, and 100 µl into 25-ml graduated cylinders and treating the same as samples starting with step 4. These standards are, respectively, the 0 µg, 0.5 µg, 1.0 µg, 2.0 µg, 5.0 µg, and 10 µg of Cr (+6). The 0-µg standard is used to set the zero absorbance reading of the spectrophotometer at 540 nm.

7. Read standards and samples at 540 nm.

8. A calibration curve is drawn by plotting the µg of Cr (+6) against the absorbance of the standard.

CALCULATIONS

1. Blank absorbance values, if any, should be substracted from each sample absorbance value.

2. $$mg\ CrO_3/m^3 = \frac{\mu g\ Cr\ (+6)\ from\ curve}{\text{Vol. of air samples in liters}} \times \frac{\text{M.W. } (CrO_3)}{\text{M.W. (Cr)}}$$

$$= \frac{\mu g\ Cr\ (+6)}{(V)_{sample}} \times \frac{100}{52},$$

References

1. Jacobs, M. B., The Analytical Chemistry of Industrial Poisons, Hazards and Solvents, Interscience Publishers, 1949.

2. Snell and Snell, Colorimetric Methods of Analysis, Vol. II, D. Van Nostrand Co., 1949, pp. 274-275.

CYANIDES AND HYDROCYANIC ACID IN AIR AND WATER

Abstract

Cyanide is neutralized and converted to cyanogen chloride by reaction with chloramine-T. This reacts with pyridine-pyrazolone reagent to form a blue color which can be read at 630 nm.

APPLICATION AND LIMITATIONS

Sensitivity and precision can be improved by extracting the aqueous solution with n-butyl alcohol and then reading the absorbance at 630 nm. For aqueous color readings, the effective range is 1-5 µg and sensitivity is 0.5 µg. For the extracted color, the range is 0.2-2.0 µg, while the sensitivity is 0.1 µg. Only minor limitations occur with this method. The salt content of sample and standards should be the same to obtain colors of comparable intensity. Thiocyanates and cyanogen will give the same reaction as cyanides.

APPARATUS

Spectrophotometer, for use with 1-cm cells at 620-630 nm.

Assorted laboratory glassware

Fritted bubbler

REAGENTS

Sodium hydroxide (1N) - Dissolve 40 g NaOH in 1 liter of distilled water.

Sodium hydroxide (0.2N) - Dissolve 8 g NaOH in 1 liter of distilled water.

Acetic acid, conc.

Acetic acid, 1:1

Pyridine

n-butyl alcohol

Chloramine-T solution - Dissolve 1 g in 100 ml distilled water. PREPARE FRESH DAILY.

3-methyl-1-phenyl-5-pyrazolone solution, Eastman 1397 or equivalent - Prepare a saturated aqueous solution (= 0.5 g/100 ml water) in warm water.

Bis-pyrazolone, Eastman 6969 or equivalent - Can be prepared by dissolving 17.4 g of 3-methyl-1 phenyl-5-pyrazolone in 100 ml ethyl alcohol. Add 25 g phenyl hydrazine, freshly distilled, under reduced pressure. Reflux in an all-glass still. Ten to twelve hours of refluxing are necessary to produce the bis-pyrazolone. Filter while hot, wash with 95% ethyl alcohol, and air-dry.

Mixed pyridine-pyrazolone reagent - Mix 125 ml of saturated pyrazolone with a solution containing 0.025 g bis-pyrazolone dissolved in 25 ml pyridine. The mixed reagent develops a pink color on standing. PREPARE FRESH DAILY.

Disodium hydrogen phosphate solution - Dissolve 5 g anhydrous Na_2HPO_4 in 100 ml of distilled water.

Stock standard, 1 mg CN/ml - Dissolve 2.510 g KCN in 1 liter distilled water.

Working standard, 1 µg CN/ml - Dilute 10-ml stock standard to 1000 ml with distilled water, mix, and make a second dilution by pipetting 10 ml into a 100-ml volumetric flask. PREPARE FRESH DAILY.

ANALYTICAL PROCEDURE

1. For air samples, pass a known volume of air through a fritted bubbler containing 1N NaOH. Use two bubblers in a series. Sample at 1 liter/min.
2. Pipet one or more aliquots of the air sample absorption solution of water sample into a 25-ml graduated cylinder. Dilute to 15 ml with 0.2N NaOH and neutralize each with 1:4 acetic acid to pH of 6-7.
3. Add 0.2 ml chloramine-T solution, stopper, and mix. Allow 2 min for the reaction to occur.
4. Add 5 ml of mixed pyridine-pyrazolone reagent, stopper, and mix. Allow 20 minutes for color to develop. Make up to 25-ml volume by adding distilled water. Read absorbance at 620 nm.
5. If greater sensitivity is needed, add 1 ml of disodium hydrogen phosphate and 10 ml butyl alcohol, mix, and read absorbance at 630 nm.
6. Prepare a blank from 15 ml 0.2N NaOH and standards in the range 0.2-1 µg CN^-. Neutralize to pH of 6-7 with 1:4 acetic acid and proceed as in step 3. A calibration curve is drawn by plotting µg CN^- against the absorbance of the standard.

CALCULATIONS

$$\mu g\ CN^- / l = \frac{\mu g\ CN^-\ in\ sample\ from\ curve \times 1000}{ml\ sample}$$

References

1. Epstein, J., "Estimation of Microquantities of Cyanide," Anal. Chem. 19 (1947) p.272.

2. Lambach, F. J., Moore, W. A. and Ruehlen, C. C. "Determination of Cyanides in Water and Waste Samples," Anal. Chem. 26 (1954), p. 1784.

FLUORIDES AND HYDROGEN FLUORIDE IN AIR AND WATER

Abstract

Fluoride is determined colorimetrically by the reaction between fluoride and a zirconium-dye lake. As the amount of fluoride increases, the color of the dye lake becomes progressively lighter and can be measured at 570 nm.

APPLICATIONS AND LIMITATIONS

The SPADNS method is subject to errors where interfering ions may be present. They are:

	Conc. (PPM)	Type of error*
Alkalinity (as $CaCO_3$)	5000	-0.1
Al^{+3}	0.1	-0.1
Cl^{-1}	7000	+0.1
Fe^{+3}	10	-0.1
Hexametaphosphate $(NaPO_3)_6$	1.0	+0.1
PO_4^{-3}	16	+0.1
SO_4^{-2}	200	+0.1

*Error at 1.0 mg/1 F^{-1}

To remove most interferences, it is necessary to distill the water sample. As these interferences are neither linear or additive, mathematical compensation will be incorrect. The temperature of the samples and standards must be at the same temperature or results will be incorrect.

APPARATUS

Hach colorimeter

Midget impinger

Assorted laboratory glassware

Distillation apparatus consisting of a 1-liter round-bottom, long-neck boiling flask, a connecting tube, condenser, a thermometer adapter, and a thermometer.

REAGENTS

Hach SPADNS fluoride reagent, Cat. No, 444

Hach standard fluoride solution 1 PPM F^{-1}, Cat. No. 291

Sodium arsenite solution - Add 5 g $NaAsO_2$ to 1 liter distilled water.

Sodium hydroxide solution (0.1N)

ANALYTICAL PROCEDURE

1A. Pass a known volume of air through a midget impinger containing 0.1N NaOH. Collect in series. After sampling, transfer each air sample solution to a 25-ml graduated cylinder and dilute with distilled water to the 25-ml mark.

1B. Fill a 25-ml graduated cylinder with water sample to be analyzed.

2. Fill a 25-ml graduated cylinder with standard 1.0-PPM fluoride solution.

3. Allow standard and unknown samples to equilibrate at room temperature.

4. If the sample contains chlorine, remove it by adding 2 drops of sodium arsenite solution.

5. Pipet into each graduated cylinder 5 ml SPADNS fluoride reagent; stopper and mix well. Transfer each to colorimeter cells.

6. Insert the fluoride meter scale into the Hach colorimeter and use the 9788 color filter.

7. Place the colorimeter cell that contains the prepared standard fluoride solution in the light cell. Press the light switch and adjust the light control for a meter reading of 1.0 PPM fluoride.

8. Place the colorimeter cell that contains the unknown sample in the light cell. Press the light switch and read the PPM (µg/ml) fluoride.

CALCULATIONS

Total $\mu g\ F^-$ in sample = $\mu g/ml\ F^-$ x sample volume (ml)

$mg\ F^-/m^3$ = $\mu g\ F^-$ / liters of air sampled

$mg\ HF/m^3$ = $\mu g\ F^-$ / liters of air sampled x 1.05

References

1. Hach Chemical Co. Engineers Laboratory Methods Manual, 1st Ed. 1969.

2. Standard Methods of Water and Wastewater, 13th Ed. 1971.

FLUORIDE IN URINE

Abstract

Fluoride is separated directly from urine by ion exchange. Fluoride is eluted and determined colorimetrically.

APPARATUS

Chromatographic columns, Kontes No. K-42225 Chromaflex Column No. 2, with 125-ml reservoir.

Assorted laboratory glassware

REAGENTS

Dowex 50 W-X8, 20 to 50 mesh in the free acid form as urine preservative

Dowex 50 W-X8, 100 to 200 mesh in the free acid form

Dowex 1-X8, 100 to 200 mesh in the chloride form

Charcoal, coconut, acid washed, activated, 50 to 100 mesh

Sand, white quartz, 60 to 120 mesh

Sodium hydroxide solution (3M) - Dissolve 120 g NaOH in 1 liter of distilled water.

Eriochrome cyanine R reagent - Dissolve 1.80 g eriochrome cyanine R in a liter of distilled water.

Zirconium reagent - A solution of 0.265 g $ZrOCl_2 \cdot 8H_2O$ in 50 ml of water is made up to 1 liter with conc. HCl.

Sodium hydroxide (0.3M) - Dissolve 12 g NaOH in 1 liter of distilled water.

Mixed color reagent - Equal volumes of zirconium reagent and eriochrome cyanine R reagent are mixed (add zirconium to dye). (Five ml of this mixed reagent is required for each fraction collected.)

Reference solution - To obtain the zero absorbance reading, 10 ml of the dye solution is added to 100 ml of water; then 10 ml of a solution prepared by diluting 7 ml of conc. HCl to 10 ml with water is added.

Fluoride standard - Dissolve 0.221 g NaF in 1 liter of 0.3N NaOH (1 ml = 10 µg fluoride).

PREPARATION OF RESINS

Dowex 50 W-X8, 20 to 50 mesh, for urine preservative - Wash resin in a large column *with 3 volumes of distilled water, then wash with 5 volumes of 3M HCl. (Volume is* that equivalent to the amount of resin.) Finally, wash with distilled water until effluent is neutral to pH test paper. Drain column and transfer resin to a Pyrex tray and dry at 40°C.

Dowex 50 W-X8, 100 to 200 mesh - In large column, wash with 3 volumes of ethyl alcohol, 3 volumes of distilled water, 5 volumes of 3M HCl, then with water until neutral to pH test paper. Store in a 1:1 slurry in distilled water.

Sand - Digest at 100°C for 2 hours with 20% NaOH, wash with distilled water, then digest for 2 hours at 100°C in 1:3 HCl. Finally, wash with distilled water until neutral to pH test paper; transfer to Pyrex tray and dry at 100°C.

COLUMN PREPARATION

Pretreatment Column: Add 2 ml water to column, with stopcock closed, then add 20 ml of 1:1 slurry of charcoal; let all drain except 2 ml water, then add 2 ml 1:1 slurry of 100 to 200 mesh Dowex 50 W-X8. When resin has settled, but water is not completely drained, add a 2-cm-thick layer of sand.

Separation Column: Add 2 ml water to column with stopcock closed. Add 20 ml 1:1 surry of Dowex 1-X8 (100-200 mesh). Twirl tube before water drains to level the resin surface. Add 2 cm of sand before all water drains from column. Convert the resin to the hydroxide form by adding 150 ml of 3 M NaOH. Wash with water until effluent is neutral to pH test paper.

ANALYTICAL PROCEDURE

1. Collect urines in containers containing 5-ml volume of 20-50 mesh Dowex 50 W-X8 per 100 ml of urine.
2. Dilute 25 *ml of preserved urine* to 250 *ml.*
3. Pass 50 ml of diluted urine through the pretreatment column and discard the effluent
4. Pass remaining 200 ml diluted urine through column and collect effulent in a polyethylene bottle.
5. Pass 100 ml of the clarified urine through each of two Dowex 1-X8 columns.
6. Rinse columns with 50 ml distilled water and allow to stand over-night. Do not drain; let approximately 2 ml of water remain on top of resin.

7. Flush the water from the columns with 10 ml 0.3M NaOH. Discard.

8. Elute the fluoride with 5 to 25-ml portions of 0.3M NaOH; collect each 25-ml fraction in a colorimeter tube.

9. Prepare standards of 0 to [illegible] µg F in [illegible] ml 0.3 M NaOH.

10. To each standard and fraction collected, add 5 ml mixed color reagent. Mix by inversion and let stand for 1 hour.

11. Read absorbance at 536 nm.

CALCULATIONS

1. Plot absorbance versus µg F from standards and determine content of each fraction.

2. Add concentration of fluoride in all 10 fractions for each sample.

3. The total fluoride in the fractions is the amount per 25 ml of urine.

4. The µg/liter = fraction total x 40.

Reference

1. Taleitie, N.A., and Brewer, L. W., "*Separation of Fluoride by Ion Exchange: Application to Urine Analysis,*" AIHA Journal, 2, August 1960, p. 287.

FORMALDEHYDE IN AIR

Abstract

Formaldehyde reacts with a modified Schiff's reagent to form a stable, purple-colored complex which can be measured colorimetrically at 560 nm.

APPARATUS

Midget bubblers, all glass

Spectrophotometer

REAGENTS

p-rosaniline, crystalline

Hydrochloric acid, conc. (36% HCl)

Aldehyde-free water - Boiled, double-distilled water

Sodium sulfite, crystalline

Sodium chloride, crystalline

Mercuric chloride, crystalline

Formaldehyde, standard solution, 1 $\mu g/ml$, using 37% formaldehyde solution (40 g HCHO/100 ml of solution)

Sodium tetrachloromercurate II (0.05M) - Dissolve 13.6 g mercury chloride + 5.8 g sodium chloride per liter of aldehyde-free water (stock solution).

Color reagent (1) - To 50 ml of 0.05M sodium tetrachloromercurate II stock solution, add 0.25 g sodium sulfite. Prepare fresh daily.

Color reagent (2) - Dissolve 0.16 g p-rosaniline in 25 ml HCl and dilute to 100 ml with aldehyde-free water.

ANALYTICAL PROCEDURE

1. Collect sample in midget bubbler, using aldehyde-free water as a collecting medium. Collect at least 1 ft^3 of air.
2. To the samples, add 1 ml color reagent No. 1 and mix thoroughly.
3. Add 1 ml color reagent No. 2, mix thoroughly, and allow to stand for 15 minutes.
4. Read absorbance at 560 nm.

5. Prepare a series of standards from 1 to 10 µg formaldehyde in 10 ml of aldehyde-free water. Proceed as in step 2.

6. Plot absorbance versus concentration on graph paper.

7. Determine amount of formaldehyde present in the samples from the standard curve.

CALCULATIONS

$$\text{mg formaldehyde/m}^3 = \frac{\text{µg formaldehyde from calibration curve}}{\text{Vol of air sampled in liters at STP}}$$

Reference

1. Lyles, G.R., Dowling, F. B., and Blanchard, V. J., "Qualitative Determination of Formaldehyde in the Parts per Hundred Million Concentration Level," J. APCA, 15, No. 3, March 1965.

TOTAL IODINE IN OIL

Abstract

Sample is ashed with a chromate-sulfuric acid mixture. Iodine is released and determined colorametrically with starch solution.

5

APPARATUS

Flask, 150 ml, round bottom

Glas-col, 150-ml volume

Variac, 115 volts AC

Distilling apparatus, with dropping funnel

REAGENTS

Chromate solution - saturated $K_2Cr_2O_7$ in distilled water

Sulfuric acid, conc. (96% H_2SO_4)

Phosphorus acid, 30%

Sodium hydroxide, (1N) - Dissolve 40 g NaOH in 1 liter of distilled water.

Postassium permanganate, saturated aqueous solution.

Sulfuric acid (4N) - Add 112 ml H_2SO_4 to 888 ml water.

Sodium nitrite (1.5%) - Dissolve 10.3 g $NaNO_2$ in 100 ml distilled water.

Potassium iodide solution - Dissolve 16.7 g KI in 100 ml distilled water. Prepare fresh daily

Starch solution, 2 g soluble - Starch into 800 ml boiling water. Boil for 15 minutes. Add 1 salicylic acid as preservative.

PROCEDURE

1. Place a 50-g sample in a 150-ml boiling flask equipped with dropping funnel and condenser.
2. Add, dropwise 10 ml saturated chromate solution.
3. Add 50 ml sulfuric acid slowly.
4. Heat to boiling. Add, dropwise, 10 ml 30% phosphorous acid

5. Distill ml into a 50-ml beaker containing 1 ml, 1N NaOH.

6. Evaporate to 15 ml. While boiling, add 2 drops saturated potassium permanganate solution.

7. Continue to boil for 5 minutes.

8. Add 1 ml 4N sulfuric acid (if pink fades, add another drop of permanganate).

9 Let set 2 minutes. Decolorize with sodium nitrite solution.

10. Boil for 5 minutes, cool to room temperature.

11. Transfer to 50-ml volumetric flask with water.

12. Add 3 ml potassium iodine solution and 4 ml starch solution.

13. Dilute to 50 ml. Let stand 30 minutes.

14. Read at 575 nm against reference of 4 ml 0.1N sulfuric acid, plus 1 ml potassium iodine, plus 4 ml of starch, diluted to 50.

15. Prepare iodine standards starting at step No. 11.

Reference

1. *Colorimetric Determination of Nonmetals*, Boltz, D. F., Editor, Interscience Publishers, Inc., New York, 1958.

LEAD IN AIR, URINE, AND ON SWIPES

Abstract

Samples are oxidized with concentrated nitric acid, hydrogen peroxide, and heat. Interfering elements are complexed with ammonium citrate and potassium cyanide. Lead dithizone complex is extracted from alkaline solution into chloroform, and the absorbance is measured colorimetrically at 510-nm wavelength.

APPLICATIONS AND LIMITATIONS

This method has been thoroughly tested and evaluated. For a 100-ml urine sample, the analytical range is 5 µg to 200 µg per liter. The main interferences are due to stannous tin, bismuth, cadmium and thallium.

APPARATUS

Spectrophotometer, for measurement at 510 nm.

Separatory funnel, 125-ml glass with standard taper fittings

Erlenmeyer flask, 500 ml with standard taper fittings

Assorted laboratory glassware

REAGENTS

Nitric acid, conc. (70% HNO_3), redistilled.

Hydrogen peroxide (30% H_2O_2)

2N nitric acid - Dilute 125 ml nitric acid to 1 liter with distilled water.

Nitric acid, 1% solution - Dilute 10 ml nitric acid to 1 liter with distilled water.

Ammonium hydroxide, NH_4OH (10% NH_3)

Hydrochloric acid, conc. (36% HCl)

1N hydrochloric acid - Dilute 83 ml HCl to 1 liter with distilled water.

Chloroform, $CHCl_3$

Dithizone - Dissolve 0.010 g diphenylthiocarbazone in 1 liter of $CHCl_3$.

Phenol red indicator solution, 1% in water with NaOH added.

Ammonium citrate (40%) - Dissolve 400 g ammonium citrate in 500 ml distilled water and add ammonium hydroxide to pH of 8. Dilute to 1 liter with distilled water. Extract with 100 ml dithizone, repeat, if necessary, until there is no color change. Wash the citrate with chloroform to remove the residual dithizone.

Hydroxylamine hydrochloride (20% solution) - Dissolve 20 g $NH_2OH \cdot HCl$ in 50 ml distilled water and add ammonium hydroxide to pH of 8. Extract with dithizone (10-ml portions), wash with chloroform, and acidify with HCl to pH of 2. Dilute to 100 ml with distilled water.

Potassium cyanide (10% solution) - Dissolve 50 g KCN in 100 ml water; extract with dithizone(10-ml portions) until extract remains green. Wash with chloroform. Dilute to 500 ml with distilled water.

Lead standard - Dissolve 1.599 g recrystallized lead nitrate in 1 liter of 1% nitric acid (1 ml = 1 mg lead).

Lead working standard - Dilute 1 ml lead standard to 100 ml with 2N nitric acid (1 ml = 10 µg Pb).

Note: All glassware should be washed in hot 1:1 nitric acid, tap water, then distilled water, before use.

SAMPLE PREPARATION

Air Samples

1. Scrub (use ESP scrubber) electrostatic precipitator tube with distilled water into a suitable beaker. Add 20 ml 2N nitric acid and evaporate to dryness.
2. Using a filter-paper sample, place filter into 150-ml beaker; add 20 ml nitric acid and evaporate to dryness.
3. *Repeat nitric acid additions until a white ash is obtained.*
4. Dissolve the residue in 10 ml 2N nitric acid and transfer to 100-ml volumetric flask. Dilute to volume with 2N nitric acid and remove a suitable aliquot for analysis.

Swipe Samples

Treat as filter paper above.

Urine Sample (or whole blood)

1. To 100-ml aliquot of urine (or 10 g blood) in a 500-ml Erlenmeyer flask with ground joint, add 20 ml nitric acid and 5 ml hydrogen peroxide.
2. Evaporate to dryness; repeat acid addition until a white ash is obtained.
3. Add 5 ml 2N nitric acid and warm to dissolve residue.

ANALYTICAL PROCEDURES

1. To sample or aliquot, add 2 drops phenol red and 15 ml 40% ammonium citrate (blood, add 6 ml) solution and add ammonium hydroxide to a pH of 8.2. Indicator will be red.
2. Add 1 ml 20% hydroxylamine HCl, 5 ml 10% KCN, and 10 ml dithizone. Mix after each addition.
3. Insert extraction funnel and shake contents for 1 minute.
4. Invert and let the organic layer settle. Remove the flask.
5. Draw a portion of the organic layer through a cotton pledget into a cuvette.
6. Measure the absorbance at 510 nm.
7. Prepare standards of 0, 5, 10, 20, and 30 µg Pb in 2N HNO_3 and carry through procedure, starting with step 1.
8. Plot a standard curve of µg Pb versus absorbance and obtain the unknown lead concentrations from this curve.

CALCULATION

$$\mu g\ Pb/\ell\ urine = \frac{\mu g\ Pb\ from\ std\ curve}{Sample\ vol\ in\ m\ell} \times 1{,}000$$

$$mg\ Pb/m^3 = \frac{\mu g\ Pb\ from\ curve}{Vol\ of\ air\ in\ liters\ at\ STP}$$

References

1. Mecherly, P. A., Tilly, A., and Whitman, N.E., "The Determination of Lead in Air and in Biological Material," Am. Ind. Hyg. Assoc. Quart., 18, 1957, p. 161.
2. Methods for Determining Lead in Air and in Biological Materials, a report published by the American Public Health Association, 1790 Broadway New York 19, N. Y., 1944.

METHANOL IN AIR

Abstract

Methanol is oxidized to formaldehyde, and the formaldehyde reacts with modified Schiff's reagent to yield a violet color which is read on a colorimeter at 580 nm.

APPLICATIONS AND LIMITATIONS

This method is simple and fast. In a 1-ft^3 air sample, an air concentration of 10 PPM of methanol can be determined. Limitations are few, although formaldehyde will obviously interfere.

APPARATUS

Midget impingers, all glass

Assorted laboratory glassware

REAGENTS

Ethyl alcohol, absolute

Potassium permanganate reagent - Dissolve 3 g $KMnO_4$ in 25 ml H_2O with 15 ml 85% H_3PO_4 and then dilute to 100 ml with distilled water.

Oxalic-sulfuric acid mixture - Dissolve 5 g oxalic acid in 100 ml 1:1 H_2SO_4.

Schiff's reagent, modified - Dissolve 0.2 g basic fuchsin in 120 ml hot distilled water, add a solution of 2 g sodium sulfite in 20 ml water and mix. Add 2 ml concentrated HCl, dilute to 200 ml with distilled water, and store in a brown glass-stoppered bottle in the refrigerator. (Residual color may be removed by treating with Norit A decolorizing charcoal and filtering through a Whatman No. 42 filter paper.)

Methanol, standard solution - Accurately weight 1.5 ml methanol (in weighing bottle) and make dilutions with distilled water so that 1 ml equals 0.1 mg methanol. Prepare standards of 0- to 2.5-mg methanol.

ANALYTICAL PROCEDURE

1. Collect sample in two midget impingers in series. Use distilled water as collecting medium.
2. Transfer a 5-ml aliquot to a 50-ml beaker.
3. Add 0.25 ml ethanol, mix, and then add 2 · ' $KMnO_4$ reagent.

4. Allow to stand for 10 minutes.

5. Destroy the excess permanganate with 2 ml oxalic-sulfuric reagent.

6. When solution is decolorized, add 5 ml modified Schiff's reagent, mix and allow color to develop for 60 minutes.

7. Read absorbance of standards and samples at 560 nm.

8. Standards are started at step 2 and a calibration curve prepared.

9. Determine amount of methanol in samples using standard curve.

CALCULATIONS

$$\text{mg methanol/m}^3 = \frac{\text{µg methanol found}}{\text{Vol. of air sampled in liters at STP}}$$

References

1. Goldman, F. H., Laboratory Procedures in Industrial Hygiene, U.S. Public Health Service, 1947.

2. Rogers, G. W., "Sampling and Determination of Methanol in Air," J. Ind. Hyg. and Tox. 27, 224, 1945.

NITROGEN DIOXIDE IN AIR

Abstract

Nitrogen dioxide is collected in sulfanilic acid. The diazotized NO_2 is coupled with N-(1-naphthyl)-ethylenediamine, forming an azo dye. The dye color is read at 550 nm.

APPLICATIONS AND LIMITATIONS

The analytical range of this method is 0.005 to 5 PPM by volume or 0.01 to 10 µg/1 when sampling with fritted bubblers.

The main limitations are due to interference from strong oxidizing and reducing agents such as sulfur dioxide and peroxyacylnitrate.

APPARATUS

Spectrophotometer

Grab-sample bottles, 30- to 500-ml sizes

Bubbler, all glass

Assorted laboratory glassware

REAGENTS

N-(1-naphthyl)-ethylenediamine dihydrochloride (0.1%) - Dissolve 0.1 g of the salt in 100 ml of distilled water. When stored in the refrigerator, in a well-stoppered amber bottle, this reagent is stable for several months.

Absorbing reagent - Dissolve 5 g sulfanilic acid in almost a liter of distilled water containing 140 ml glacial acetic acid. Add 20 ml of a 0.1% solution of N-(1-naphthyl)-ethylenediamine dihydrochloride, and make up to a volume of 1 liter. Keep in a brown bottle in the refrigerator.

Potassium permanganate solution - Dissolve 2.5 g potassium permanganate in distilled water, add 2.5 grams (1.36 ml) of conc. sulfuric acid, and dilute to 100 ml.

Sodium nitrite stock solution - Add 2.030 g sodium nitrite to 1 liter distilled water.

Sodium nitrite working solution - Prepare fresh by diluting 1 ml of stock sodium nitrite solution to 100 ml. This solution of 0.0203 g $NaNO_2$ per liter is such that 1 ml of this working standard, added to the absorbing reagent, produces a color equivalent to that of 10 µl of NO_2 or 10 PPM of NO_2 in 1 liter of air at STP.

ANALYTICAL PROCEDURE

For less than 1 PPM NO_2:

1. Place 10 ml absorbing reagent in a fritted glass bubbler.
2. Collect the sample at a 0.4-l/min rate for about 10 minutes or until *sufficient red-violet color has developed.*
3. Allow sample to set for 15 minutes for full color development, transfer to cuvette, and read at 550 nm in the spectrophotometer. Use unexposed absorbing reagent to set instrument at 0 absorbance.

For more than 1 PPM NO_2:

1. Collect sample in an evacuated 250-ml or larger bottle containing 10 ml of absorbing reagent. Shake sample after collecting. Let set for 15 minutes.
2. Read at 550 nm after transferring the liquid containing the NO_2 to a cuvette.

CALIBRATION

1. To eight 25-ml volumetric flasks, add 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, and 0.70 ml of the working nitrite solution.
2. Dilute to 25 ml with absorbing reagent and mix.
3. Allow to set for 15 minutes and then read at 550 nm against a zero of absorbing reagent.
4. Plot the absorbances of the standards against µl of nitrogen dioxide per ml of absorbing reagent. The later values are equal to the corresponding ml of working nitrite solution times 0.4. The plot follows Beer's Law. Draw a straight line through the origin giving the best fit, and determine the slope K, which is µl of NO_2 intercepted at absorbance of exactly 1. For 1-cm cells, the value of K = 0.73.

CALCULATIONS

The molar volume at standard conditions of 760 mm Hg and 25°C is 24.47 liters. 0.72 mole of sodium nitrite produces the same color as 1 mole of nitrogen dioxide. Since 1 ml of the working solution contains 2.03×10^{-5} grams $NaNO_2$ and molecular weight = 69, then

$$\frac{2.03 \times 10^{-5}}{69} \times \frac{24.47}{0.72} = 10^{-5} \text{ liters of } NO_2 \text{ or } 10\ \mu l.$$

1 ml of nitrite solution (10µl NO_2) per 25-ml volume is equivalent to 10/25 or 0.4 µl of NO_2 per ml.

Compute the concentration of nitrogen dioxide in the sample by the following

$$\text{PPM } NO_2 = AK/V$$

where

A = absorbance
K = slope of calibration curve
V = volume of air sampled in liters per ml of absorbing reagent

Reference

1. Saltzman, B. E., "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," Anal. Chem., 26, 1954, p. 1949.

OZONE IN AIR

(Titration Method)

Abstract

Ozone is collected in KI solution and the iodine liberated is titrated with sodium thiosulfate using starch as an indicator.

APPLICATIONS AND LIMITATIONS

This method is rapid, simple, and uses no expensive equipment. The sensitivity is dependent on the volume of air sampled. The main limitation is that the liberated iodine is very sensitive to reducing vapors or dusts such as SO_2 or H_2S. Also strong oxidants such as halogens, peroxides, etc., will liberate iodine.

APPARATUS

Midget bubbler, all glass

Buret, 5-ml capacity

Magnetic stirrer, with teflon-covered bar magnet

REAGENTS

Potassium iodide solution (5%) - Prepare fresh daily

Starch indicator solution - Dissolve 1 g soluble starch in 100 ml of boiling distilled water.

Hydrochloric acid, 1:1 in distilled water.

Potassium dichromate (0.1N) 4.904 g (dried for 2 hours at 110°C) $K_2Cr_2O_7$ dissolve in 1 liter of water.

Sodium thiosulphate (0.01N) - Dissolve 2.5 g $Na_2S_2O_3 \cdot 5 H_2O$ in 1 liter of distilled water. Standardize against $K_2Cr_2O_7$ by the following method. Dissolve 5 g KI and 4 g $NaHCO_3$ in 300 ml H_2O; add slowly 1:1 HCl until no more CO_2 is released, then add 10 ml excess 1:1 HCl. Add 25 ml 0.1 N $K_2Cr_2O_7$ and mix thoroughly. Add stirring bar and place on magnetic stirrer. With stirring, titrate with thiosulfate to a light straw yellow. Add 1 ml starch indicator and titrate until the blue is replaced with the pale green color of $CrCl_3$. From the volume of thiosulfate used, calculate the normality.

ANALYTICAL PROCEDURE

1. Collect samples in 10 ml freshly prepared KI.
2. Transfer collecting solution to an Erlenmeyer flask, add teflon stirring bar, and place on magnetic stirrer.
3. Add 1 ml 1:1 HCl and 1 ml starch indicator.
4. Titrate with standard thosulfate to the colorless end point.

CALCULATION

1 ml 0.01N $Na_2S_2O_3$ = 0.24 mg ozone

Reference

1. Byers, D. H., and Saltzman, B. E., "Determination of Ozone in Air by Neutral and Alkaline Potassium Iodide Procedures," Amer. Ind. Hyg. Assoc. J., 19, 1958 p. 251.

OZONE IN AIR
(Colorimetric Method)

Abstract

Air is drawn through a midget impinger containing 10 ml of neutral potassium iodide solution. The ozone liberated iodine which is determined colorimetrically at 352 nm.

APPLICATIONS AND LIMITATIONS

The analytical range extends from 0.01 PPM to 10 PPM. The method is simple and rapid. Main interferences are reducing compounds such as sulfur dioxide and hydrogen sulfide. Some oxidants such as halogens and hydrogen peroxide will also interfere. The sensitivity of the method is dependent on the volume of air sampled, and the analysis must be completed within 1 hour after sampling.

APPARATUS

Midget impinger, 1 glass

Spectrophotometer

Assorted laboratory glassware

REAGENTS

Absorbing reagent - Dissolve 13.61 g of potassium dihydrogen phosphate, 14.2 g of anhydrous disodium hydrogen phosphate and 10 g of potassium iodide in that order in 1 liter of distilled water. Store in brown bottle in a refrigerator. Make monthly.

Iodine stock solution (0.025M I_2) - Dissolve successively 10 g of KI and 3.1730 g of iodine in exactly 40 ml distilled water. *Standardize with 0.10N sodium thiosulfate.*

Iodine working solution (0.00125M I_2) - Pipet 5 ml of stock solution into a 100-ml volumetric flask and dilute to the mark with the absorbing reagent.

ANALYTICAL PROCEDURE

1. Pipet 10 ml absorbing reagent into the midget impinger.
2. After receiving samples, measure volume and transfer to 1-cm cuvette. Do not dilute with rinse water!
3. Determine the absorbance at 352 nm using distilled water as the reference. Also determine the absorbance of a reagent blank.

4. Run a series of standards through steps 2 and 3 by pipetting 0.2-, 0.4-, 0.6-, and 0.8-ml portions of the working solution (0.1, 0.2, 0.3 and 0.4 μmoles I_2/ 10 ml of absorbing reagent) in separate 25-ml volumetric flasks and dilute to the mark with absorbing reagent. Mix well and read the absorbance of each at 352 nm.

5. Plot absorbances (after subtracting absorbance of reagent blank) versus molar concentration in μmoles/10 ml.

CALCULATIONS

Since 1 mole of ozone liberates 1 mole of iodine, one can read directly from the calibration curve μmoles of ozone if the total sample volume is 10 ml. If the sample was diluted prior to analysis, the proper dilution factor must be included in the calculation.

$$\text{PPM ozone} = \frac{\mu\text{moles ozone} \times 24.45}{\text{volume of air sampled in liters at STP}}$$

Reference

1. "Tentative Methods for the Analysis of Oxidizing Substances in the Atmosphere," American Public Health Association, Washington, D.C., 44101-02-70T, 1972.

SILICA IN AIR

Abstract

Samples are digested in phosphoric acid to remove silicates, dissolved in hydrofluoric acid, and silica content is determined colorimetrically as silicomolybdate (420 nm) or as molybdenum blue (820 nm).

APPLICATIONS AND LIMITATIONS

Concentrations from 5 µg to 140 µg can be detected in the molybdenum-blue range and from 0.1 mg to 2.5 mg in the silicomolybdate range. Sulfides, phosphate, and large amounts of iron interfere and cause low results.

APPARATUS

Phillips beakers, 250 ml

Funnel, 50-mm, with stem bent at 45 degrees

Precision heater, 550-watt, mounted on rotating table

Crucible tongs, padded with rubber

Constant-temperature water bath

Plastic buret, 25 ml

Polyethylene beakers, 125 ml

Polyethylene pipette, calibrated, 1 ml

Plastic stirring rods

Polyethylene, thin sheet

Spectrophotometer

REAGENTS

Hydrofluoric acid (48%)

Phosphoric acid (85%)

Hydrochloric acid, 1:10

Boric acid solution (5%) - Dissolve 200 g of boric acid crystals in 4 liters of distilled water. Filter through a 0.45-micron membrane filter. Store in a polyethylene container.

Molybdate reagent - Dissolve 50 grams of ammonium molybdate tetrahydrate in about 400 ml of water, acidify with 40 ml of concentrated sulfuric acid, cool, and dilute to 500 ml. Store in the dark.

Sulfuric acid (10N) - 555 ml of concentrated sulfuric acid is added cautiously to 1.5 liters of water and diluted to 2 liters when cool.

Reducing solution

a. 9 g of sodium bisulfite dissolved in 80 ml of water.

b. 0.7 g of anhydrous sodium sulfite, plus 0.15 g of 1-amino, 2-naphthol, 4-sulfonic acid dissolved, in that order, in 10 ml of water. Solutions a and b are combined and diluted to 100 ml. Store in refrigerator. Remake every month.

Stock silica solution - 250 mg of finely ground, acid-washed quartz is dissolved in 10 ml of 48% hydrofluoric acid and diluted with water to 500 mL (1 ml = 0.5 mg SiO_2). Store in polyethylene container.

Working silica solution (20 µg SiO_2/ml) - Dilute 4-ml stock solution to 100 ml with distilled water.

ANALYTICAL PROCEDURE

1. Preheat heater, voltage set at 75 volts, for 45 minutes.
2. A 200-mesh weighed sample containing no more than 2.5 mg SiO_2 or a filter on which airborne particulates have been collected is placed into a Phillips beaker.
3. 5 ml of nitric acid and 2 ml $HClO_4$ are added and the sample heated to absence of brown fumes and near dryness. The process is repeated until a white residue remains. A blank should be carried through all steps of the analysis. If a bulk sample is used, only the nitric acid is used as a blank.
4. Add 25 ml 85% phosphoric acid, place bent funnel in beaker, place on heater, and start rotator.
5. From the time the sample boils, time for 12 minutes. After each minute of heating, swirl beaker by grasping it with padded crucible tongs to prevent superheating.
6. At the end of 12 minutes, remove beaker and swirl for 1 minute to dissolve any gelatinous silica from sides of beaker. Let cool to room temperature on cool surface.

7. When cool, remove funnel cautiously and wash down beaker with 125 ml hot (60-70°C) distilled water. Swirl vigorously to dissolve all the syrupy phosphoric acid.

8. Filter the sample with suction through a 47-mm membrane filter (0.45 μ). Wash thoroughly with 1:10 HCl.

9. Place the filter discs flat in the bottom of a 150-ml polyethylene beaker and add 0.5 ml of 48% hydrofluoric acid with a calibrated polyethylene pipette. Prevent evaporation of the hydrofluoric acid by floating a thin polyethylene disc, slightly larger than the filter, upon the acid and allow it to stand for 30 minutes to dissolve the siliceous components.

10. Without removing filter or polyethylene disc, add 25 ml of water and 50 ml of 5% boric acid solution.

11. Stir with a plastic rod and place the beaker in a constant temperature water bath controlled at 40°C to 50°C. Let stand for 10 minutes, by which time the excess hydrofluoric acid will have been inactivated by the boric acid and the solution temperature will have risen to 35°C or 40°C.

12. Add 4 ml of ammonium molybdate reagent while stirring, and let stand 20 minutes at 35°C to 40°C for development of the yellow silicomolybdate color.

13. Remove the beaker from the water bath and destroy phosphomolybdate by adding 20 ml to 10N sulfuric acid rapidly while stirring. If a pronounced yellow coloring remains, pour into a photometer cell and read immediately at 420 nm.

14. If the yellow color is barely perceptible, add 1 ml of reducing solution, 2 to 5 minutes after addition of the sulfuric acid, and stir. After 20 minutes, read the blue color at 820 nm.

15. A calibration curve in the silicomolybdate color range is made by diluting 1-, 3-, 5-, and 7-ml aliquots of the 0.5-mg/ml stock standard to 25 ml in polyethylene beakers and proceeding as in step 10. Absorbance versus mg SiO_2 is plotted.

16. A calibration curve in the molybdenum-blue range is made by diluting 1-, 3-, 5-, and 6-ml aliquots of the 20-μg/ml working standard to 25 ml in polyethylene beakers and proceeding as in step 10. Absorbance versus μg SiO_2 is plotted.

CALCULATIONS

Milligrams or micrograms of SiO_2 per sample is read from the appropriate calibration curve.

$$\text{mg } SiO_2/\text{gram of sample} = \frac{\text{mg } SiO_2 \text{ in sample}}{\text{sample wt in grams}}$$

$$\%\ SiO_2 = \frac{\text{mg } SiO_2 \times 0.1}{\text{g of sample}}$$

or

$$\mu\text{g } SiO_2/\text{gram of sample} = \frac{\mu\text{g } SiO_2 \text{ in sample}}{\text{sample wt in grams}}$$

$$\%\ SiO_2 = \frac{\mu\text{g } SiO_2 \times 0.0001}{\text{gram of sample}}$$

$$\text{mg } SiO_2/m^3 = \frac{\mu\text{g } SiO_2 \text{ from calibration curve}}{\text{vol. of air sampled in liters at STP}}$$

Reference

1. Talvitie, N. A., and Hyslop, Frances, "Colorimetric Determination of Siliceous Atmospheric Contaminant," AIHA Journal, 19, 1958.

SILICA IN BULK SAMPLES

Abstract

Silicates are dissolved in phosphoric acid. Quartz is separated by filtration and determined by volatilization with HF.

APPARATUS

Furnace, capable of reaching 1000°C

Phillips beaker, 250 ml

Funnel, 50 mm with stem bent at 45 degrees

Precision heater, 550-watt, mounted on rotating table

Crucible tongs, with rubber tubing sleeves

Funnel, 70 mm long stem

Funnel rack

Graduated cylinder, 25 ml and 100 ml

Graduated cylinder, 10 ml plastic

Platinum crucible, 25 ml

Crucible tongs, platinum-tipped

Sand bath

Filter paper, 11 cm Whatman No. 42

Filter paper pulp

REAGENTS

Phosphoric acid, conc. (85% H_3PO_4)

Fluorboric acid

Sulfuric acid, 1:1 dilution

Hydrofluoric acid (48% HF)

Hydrofluoric acid, 1:9

Silica standard - Purified and finely ground sea sand, 99.9%, may be used.

ANALYTICAL PROCEDURE

1. Preheat heater, voltage set at 75 volts, for 45 minutes.
2. Weigh two 0.5-g, 200-mesh samples into Phillips beakers.
3. Add 25 ml 85% phosphoric acid, place bent funnel in beaker, and place on heater. Start rotator.
4. From the time the samples boil, time for 12 minutes. After each minute of heating, swirl beaker by hand to prevent superheating.
5. At the end of 12 minutes, remove beaker and swirl for 1 minutes *to dissolve any gelatinous silica from sides of beaker. Let cool* to room temperature on cool surface. Removed funnel cautiously.
6. When cool, wash down beaker with 125 ml hot (60-70°C) distilled water. Swirl vigorously to dissolve all the syrupy phosphoric acid.
7. Wash down upper beaker with 10 ml fluoboric acid (use plastic graduate). Swirl to mix.
8. Wash down beaker with 25 ml hot water.
9. Filter through Whatman No. 42 paper which contains a small amount of filter pulp.
10. Transfer sample quantitatively to the filter with distilled water.
11. Wash 10 times with hot 1:9 HCl followed by two washes with water.
12. Transfer paper + residue to a tared platinum crucible. Dry, then ignite at low heat to char paper, then heat for 20 minutes to 950°C.
13. Cool crucible, dessicate, and weigh. This weight is the <u>phosphoric acid residue</u>.
14. Moisten residue with 1:1 H_2SO_4, then add 5 ml 48% HF. Heat gently on a sand bath to dissolve the quartz.
15. Increase heat to volatilize the acids.
16. Repeat the addition of H_2SO_4 and HF to ensure complete volatilization of the silica.
17. Ignite at 950°C for a few minutes, cool, dessicate, and weight. This residue is the <u>HF acid residue</u>.

CALCULATION

Wt sample	=	_____ g
Wt crucible + H_3PO_4 residue	=	_____ g
Wt crucible	=	_____ g
Wt. H_3PO_4 residue	=	_____ g (A)
Wt crucible + HF residue	=	_____ g
Wt cruible	=	_____ g
Wt HF residue	=	_____ g (B)
$\frac{A \times 100}{\text{Wt sample}}$	=	_____% H_3PO_4 residue (C)
$\frac{B \times 100}{\text{Wt sample}}$	=	_____% HF residue (D)
C - D	=	_____% free silica

Reference

1. Talvitie, N. A., "Determination of Quartz in Presence of Silicates Using H_3PO_4," Anal. Chem., 23, 1951, p. 623.

SULFUR DIOXIDE IN AIR

Abstract

Sulfur dioxide is absorbed from the air in a solution of potassium tetrachloromercurate (TCM). The complex which is formed is reacted with pararosaniline and formaldehyde and determined colorimetrically at 548 nm.

APPLICATIONS AND LIMITATIONS

This method is sensitive, reproducible, and selective. The lower limit of detection is 0.01 PPM (26$\mu g/m^3$) of SO_2 in a 30-liter air sample. The analytical range is 0.2 to 35 μg in 25 ml of final solution. The interferences can be eliminated easily. Oxides of nitrogen are destroyed by adding sulfamic acid. Ozone is destroyed by allowing a time lapse of 20 to 30 minutes from sampling to start of analysis. Heavy metals are complexed by the addition of EDTA. CAUTION: The TCM reagent is very poisonous, so use care at all times.

APPARATUS

High-efficiency bubbler, all glass wrapped with aluminum foil

Spectrophotometer

Assorted laboratory glassware

REAGENTS

Absorbing reagent, 0.04M potassium tetrachloromercurate (TCM) - Dissolve 10.86 g of mercuric chloride, 5.96 g potassium chloride, and 0.1 g ethylenediaminetetraacetic acid disodium salt (EDTA) in 1000 ml of distilled water. Keep in dark cool place; discard if precipitate is formed.

Sulfamic acid (0.6%) - Dissolve 0.6 g sulfamic acid in 100 ml distilled water. Prepare every 3 days.

Hydrochloric acid (1M) - Dilute 86 ml of conc. HCl to 1 liter with distilled water.

Phosphoric acid (3M) - Dilute 205 ml of conc. H_3PO_4 to 1 liter with distilled water.

Stock pararosaniline (0.2%) - Dissolve 0.2 g of the dye in 100 ml of 1M HCl.

Pararosaniline reagent - To a 250-ml vol. flask, add 20 ml of stock pararosaniline and 25 ml of 3M H_3PO_4, and dilute to volume with distilled water.

Formaldehyde (0.2%) - Dilute 5 ml of 37% formaldehyde to 1 liter with distilled water. Prepare daily.

Stock iodine solution (0.1N) - Dissolve 12.7 g iodine and 40 g KI in 25 ml water. When dissolved, dilute to 1 liter with distilled water.

Working iodine solution (0.01N) - Dilute 50 ml of stock iodine solution to 500 ml with distilled water.

Standard 0.01N Sodium Thiosulfate - See ozone procedure for preparing this standard

Standard sulfite solution (= 350 µg/ml SO_2) - Dissolve 0.4 g of sodium sulfite (Na_2SO_3) or 0.3 g of sodium metabisulfite ($Na_2S_2O_5$) in 500 ml of distilled water. The actual concentration is found by back titration by the following:

1. Pipet 25 ml of distilled water into 500-ml conical flask labeled B.
2. Pipet 25 ml of standard sulfite solution into a 500-ml conical flask labeled A.
3. Pipet 50 ml of 0.01N iodine solution to flasks A and B. Stopper the flasks and allow to react for 5 minutes.
4. Titrate each with standard 0.01N thiosulfate solution to a pale yellow color. Add 2 ml starch solution and continue titrating until the disappearance of the blue color.
5. Calculate the concentration of SO_2 by the following

$$SO_2(\mu g/ml) = \frac{(A-B)\,NK}{V}$$

A = ml of thiosulfate solution required for titration of the sample,

B = ml of thiosulfate solution required for titration of the blank,

N = normality of the thiosulfate solution

K = milliequivalent weight for SO_2 = 32030

V = ml of sample taken

Working sulfite solution - Pipet 2 ml of the standard sulfite solution into a 100-ml volumetric flask and dilute to the mark with 0.04M TCM. This solution is stable for 1 month in the refrigerator.

ANALYTICAL PROCEDURE

1. Add 50 ml absorbing reagent to high-efficiency bubbler. Collect between 4 and 5 liters of air.
2. Transfer a 10-ml aliquot of the sample to a 25-ml graduated cylinder and wait 20 minutes after sampling to allow the ozone to decompose.

3. *Prepare a reagent blank at this point by adding 10 ml of unexposed* absorbing reagent to a 25-ml graduated cylinder.

4. To each flask, add 1 ml of 0.6% sulfamic acid and allow to react for 10 minutes to destroy the nitrite from oxides of nitrogen.

5. Add 2 ml of the 0.2% formaldehyde, then 5 ml of pararosaniline reagent. Dilute to volume with distilled water.

6. After 30 minutes, determine the absorbances of the samples, and blank at 548 nm. Use water as the reference. Rinse cuvette after reading to prevent a film from forming.

7. Prepare a calibration curve by pipetting 0, 1, 2, 4, and 6 ml of the working sulfite solution into 25-ml graduated cylinders and adding sufficient 0.04M TCM to each to bring the volume to 10 ml. Proceed as in step 4.

8. Plot μg SO_2 against the absorbance of the standards. Draw a straight line through the origin giving the best fit, and determine the slope K which is μg/absorbance unit.

CALCULATIONS

$$SO_2 \text{ PPM} = \frac{(A-A_o)\ 0.382\ K}{V}$$

A = sample absorbance

A_o = reagent blank absorbance

0.382 = volume (μl) of 1 μg of SO_2 at STP

K = slope, μg absorbance unit

V = sample volume in liters corrected to STP

$$SO_2 \quad mg/m^3 = \mu g\ SO_2 / \text{ liters of air sampled at STP}$$

$$= \frac{(A - A_o)\ K}{V}$$

References

1. *Sulfur Dioxide Content of the Atmosphere, ASTM Standard D2914, 1971*

2. Scaringelli, F. G., Saltzman, B. E. and Frey, S. A. "Spectrophotometric Determination of Atmospheric Sulfur Dioxide," Anal Chem., Vol. 39, No. 14, 1967, p. 1709.

TRICHLOROACETIC ACID IN URINE

Abstract

Certain chlorinated hydrocarbons, aldehydes, and acids undergo the *Fujiwara pyridine-alkali* reaction which produces a characteristic pink color. Estimation of exposures to trichloroethylene by urine analysis is carried out by development of a pyridine-potassium hydroxide plus trichloroacetic acid complex in an aliquot of raw urine. The complex concentration is measured at 530-nm wavelength. Quantities greater than 35 mg/liter of trichloroacetic acid in the urine indicate an exposure to trichloroethylene.

APPARATUS

Assorted laboratory glassware

Spectrophotometer

REAGENTS

3.3M potassium hydroxide - Dissolve 185 g KOH in 1 liter of distilled water.

Pyridine

Toluene

Trichloroacetic acid stock solution - Dissolve 1.0 g TCA in 1 liter of distilled water. Standardize by titration with standard alkali.

Trichloroacetic acid standard - Dilute 5 ml TCA stock solution to 100 ml with distilled water (1 ml = 50 µg TCA).

ANALYTICAL PROCEDURE

1. Mix 1 ml toluene, 5 ml 3.3M KOH, and 10 ml pyridine in a 40-ml centrifuge tube.
2. Add 1 ml urine and place in a boiling-water bath for 3 minutes.
3. Cool immediately in an ice-water bath.
4. Treat a blank and standards of 10, 25, and 50 µg TCA in the same manner i.e., 1 ml standard + 5 ml 3.3M KOH + 10 ml pyridine.
5. Remove the tubes from the ice bath when cool, and pipet 5 ml organic phase into a 50 ml beaker containing 2 ml distilled water. Mix well.
6. Measure the absorbance of the blank, standards, and samples at 530 nm within 10 minutes of final mixing.

CALCULATION

Plot μg TCA versus absorbance of standards. Read sample concentration from this standard curve.

mg TCA/liter urine = μg TCA in 1-ml urine aliquot

References

1. Elkins, H. B., The Chemistry of Industrial Toxicology, J. Wiley & Sons, Inc., New York, 1959.

2. Seto, T. A. and Schultz, M.O., "Determination of Trichloroethylene, Trichloroacetic Acid, and Trichloroethanol in Urine," Anal. Chem., 28, 1956, p. 1625.

SECTION B

GENERAL RADIOCHEMICAL PROCEDURES

A number of chemical procedures are used by Sandia Laboratories Environmental Health Laboratory for the analysis of radioactive materials. Sandia Laboratories has maintained an environmental monitoring program (soil, water, and vegetation) since 1959. This program determines whether there is increased radiation exposure to the general public and to what magnitude. A number of routine measurements are made for gross beta activity and plutonium.

Personnel working with radioactive materials such as plutonium, uranium, tritium, etc., are routinely sampled in the bioassay program. Bioassay is the analysis of body fluids or wastes to detect possible exposure to radioactive materials. This is valuable when exposure has been due to radioisotopes that do not emit penetrating gamma radiation. (Whole body counters are used when high gamma radiation is emitted.)

Other routine programs consist of tritium swipes and gross alpha, beta, and gamma counting of swipes and air filters for surface contamination.

ACTINIDES IN URINE AND WATER

Abstract

Some of the actinides that may be determined by this method are ^{241}Am, ^{230}Th, ^{231}Po, ^{233}U, ^{237}Np, ^{239}Pu, and ^{244}Cm. Urine is ashed using nitric acid and hydrogen peroxide. The ash is dissolved in hydrochloric acid and the actinides electroplated from an ammonium chloride plus hydrochloric acid electrolyte. The isotope is identified and quantitated by alpha spectrometry.

APPARATUS

Electroplating device (see Figure 2)

Silver foil discs, 0.005 inch thick

Platinum wire, electrode, 0.04 inch diameter, 10% rhodium

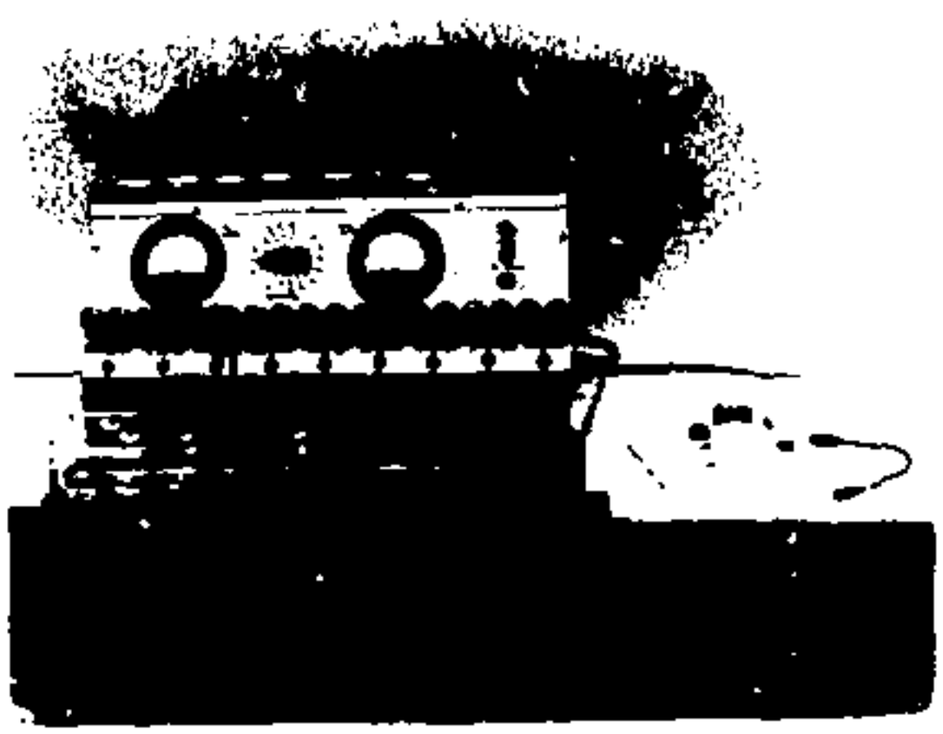

Figure 2. Electroplating Device

REAGENTS

Hydrochloric acid, conc. (36% HCl)

Hydrochloric acid, 2N - Add 167 ml conc. HCl to water and dilute to 1 liter.

Methyl red indicator solution

Ammonium hydroxide, conc. (30%)

ANALYTICAL PROCEDURE FOR URINE

1. Ash 100 ml urine with 20 ml nitric acid and 6 ml 30% H_2O_2. Add additional nitric acid until a white ash is obtained.
2. Cool and dissolve ash in 5 ml 2N HC1; heat to dissolve if necessary. Also prepare a blank for electrodeposition at this step by adding 5 ml of 2N HC1 to a 100-ml beaker.
3. Add 2 drops of methyl red indicator and neutralize with ammonium hydroxide.
4. Just acidify with 2N HC1 and transfer to electrolysis cell with distilled water.
5. Electroplate at 5 volts and 100 ma for 60 minutes.
6. Run alpha spectra on standards and samples.

ANALYTICAL PROCEDURE FOR WATER

1. Measure 300 ml of water into a 400-ml beaker and add 5 ml of conc. HNO_3. Evaporate just to dryness DO NOT BAKE.
2. Dissolve residue in 5 ml 2N HC1 and proceed as in step 3 under URINE.

Reference

1. Mitchell, R. F., "Electrodeposition of Actinide Elements at Tracer Concentrations," Anal. Chem., 32, No. 3, March 1960, p. 326.

CESIUM-137 IN SOIL AND VEGETATION

Abstract

After preparation of the sample, cesium is quantitatively concentrated from acidic medium by use of potassium hexacyanocobalt (II) ferrate (II) (KCF). Cesium-137 is then determined by γ - counting.

APPARATUS

Assorted laboratory equipment

KCF Chromat Column - The column consists of a 6-inch-long, 3/4-inch polyethylene drying tube that has a serrated tip on one end. The column is filled to a height of 1 inch with a water slurry of 50-100 mesh KCF supported by a glass wool plug.

REAGENTS

Conc. nitric acid (15.4N)

Anhydrous sodium carbonate (Na_2CO_3)

Potassium hexacyanocobalt (II) ferrate (II) (50-100 mesh KCF)

SAMPLE PREPARATION

Soil

1. If the sample is not dry, heat in an oven at 90°C for 2 hours. Place ~50 g in a roller mill and mix for 30 minutes. Screen 10-20 g of the sample through No. 10 mesh screen.

Vegetation

1. Place several grams of vegetation in a Waring blender and blend until the sample is thoroughly cut and mixed.
2. Place about 10 g in a porcelain crucible and heat in a muffle furnace at 450°C until a white ash remains.

ANALYTICAL PROCEDURE

1. Weigh out 5 g of the soil or vegetation ash and place in a nickel crucible. Add 10 g of Na_2CO_3, mix, and heat in a muffle furnace at 900°C until fusion has taken place.

2. Cool and dissolve the fusion product in distilled water.

3. Acidify the sample with conc. HNO_3 and pour through a prepared KCF column.

4. Transfer resin material to appropriate counting vessel with distilled water. Let stand and remove excess water.

5. Gamma-count for 100 minutes.

Reference

1. Boni, A. L., Anal. Chem., 38, 89, 1966.

CESIUM-137 IN SOIL, URINE, VEGETATION, AND WATER - METHOD II

Abstract

After preparation of the sample, cesium is separated from the bulk of the sample by carbonate scavenging and silicotungstate precipitation. Cesium is purified and counted as the insoluble chloroplatinate.

APPARATUS

Assorted laboratory equipment

REAGENTS

Conc. hydrochloric acid (36% HCl)

6N hydrochloric acid - Dilute 500 ml conc. HCl to 1 liter with distilled water.

Conc. nitric acid (70% HNO_3)

2N nitric acid - Dilute 125 ml conc. HNO_3 to 1 liter with distilled water

Chloroplatinic acid, (5% solution) - Dissolve 5 g $H_2PtCl_6 \cdot 6H_2O$ in 100 ml distilled water.

Silicotungstic acid - Dissolve 116 g $SiO_2 \cdot 12WO_3 \cdot 26H_2O$ in 250 ml distilled water.

Ethanol (95% ethyl alcohol)

8N sodium hydroxide - Dissolve 160 g NaOH in 500 ml distilled water.

Sodium carbonate, saturated solution - Add Na_2CO_3 to 200 ml distilled water until no more dissolves. Add 20 g excess.

Cesium carrier solution - Dissolve 18.95 g CsCl in 500 ml distilled water (1 ml = 30 mg Cs).

Strontium carrier solution - Dissolve 30.5 g $SrCl_2 \cdot 6H_2O$ in 500 ml distilled water (1 ml = 20 mg Sr).

SAMPLE PREPARATION

Soil

1. Mix 200 g soil in roller mill. Screen 10 g soil through 20-mesh screen into 400-ml beaker.
2. Add 1 ml Cs, and 1 ml Sr carrier solutions. Add 50 ml conc. HNO_3. Heat to near boiling and stir 10 minutes.
3. Transfer to centrifuge tube; centrifuge, and discard the residue.
4. Pour supernate into original beaker and evaporate to dryness.
5. Add 20 ml 2N HNO_3 and heat to dissolve residue. Transfer to clean centrifuge tube. Keep volume less than 50 ml.

Urine

1. To 1 liter urine sample in 2-liter beaker, add 20 ml conc. HNO_3, 1 ml Cs, and 1 ml Sr carrier solutions. Evaporate to dryness.
2. Add 20 ml 2N HNO_3, warm to dissolve residue, and transfer to centrifuge tube.

Vegetation

1. Pulverize 100 g dried vegetation and place in large crucible. Fire at 450°C for 1 hour until only gray ash remains. Weigh 2 g ash into 150-ml beaker.
2. Add 1 ml Cs and 1 ml Sr carrier solutions, and 20 ml conc. HNO_3. Heat to near boiling and stir 10 minutes.
3. Let cool and filter through Whatman No. 50 paper into centrifuge tube. Wash with 2N HNO_3 and keep volume less than 50 ml.

Water

Treat as for Urine above.

ANALYTICAL PROCEDURE

1. To sample in centrifuge tube, add 8N NaOH until pH of 8. Let cool to room temperature and add 5 ml saturated Na_2CO_3 solution.
2. Centrifuge and pour supernate into clean 400-ml beaker. Wash precipitate with 50 ml hot distilled water. Centrifuge, and add wash to beaker. Repeat wash. Discard precipitate or save for Sr determination.

3. *Slowly add 10 ml conc. HCl to beaker. Heat to boiling for several* minutes and add 2 ml silicotungstic acid solution. Heat and stir until Cs silicontungstate precipitates. Transfer to centrifuge tube and chill in ice bath.

4. Let stand 15 minutes. Centrifuge, and discard the supernate.

5. Wash precipitate with 10 ml 6N HCl, centrifuge, and discard wash. Repeat wash if salts are excessive.

6. Dissolve precipitate in 5 ml 8N NaOH. Add 20 ml 6N HCl; centrifuge, and discard the yellow precipitate.

7. *Add 2 ml* H_2PtCl_6 solution and heat on boiling water bath. Let cool and filter precipitate onto a weighed filter disc. Wash with 5 ml 6N HCl, 5 ml distilled water, and 5 ml ethanol.

8. Dry filter 20 minutes at 110°C. Let cool, and weigh and mount for counting.

CALCULATION

$$\text{dpm } {}^{137}\text{Cs/g, or per liter} = \frac{\text{net cpm}}{\text{(recovery)(detector efficiency) (g or liter sample)}}$$

ENRICHED URANIUM IN URINE

Abstract

Uranium is separated from urine by coprecipitation with ammoniacal alkaline earth phosphate precipitate. The precipitate is ashed, and the uranium is purified by solvent extraction. The extract is evaporated onto a steel planchet for counting.

APPARATUS

Glass-stoppered graduates, 25-ml.

Vycor crucibles, 50-ml

REAGENTS

Conc. hydrochloric acid (36% HCl)

Conc. ammonium hydroxide, NH_4OH (30% NH_3)

Conc. nitric acid (70% HNO_3)

Conc phosphoric acid (85% H_3PO_4)

3N ammonium hydroxide - Dilute 200 ml conc. NH_4OH to 1 liter with distilled water.

2N HNO_3-2N $NaNO_3$ solution - Dissolve 170 g $NaNO_3$ in 200 ml distilled water, add 125 ml conc. HNO_3, and dilute to 1 liter with distilled water.

0.1M tri-n-octylphosphine oxide (TOPO) - Dissolve 19.2 g TOPO in 500 ml cyclohexane. Store in amber glass bottle.

ANALYTICAL PROCEDURE

1. To 1 liter urine in a 2-liter beaker, add 20 ml conc. HNO_3, 5 ml conc. H_3PO_4, and heat to 85°C.
2. While stirring, add conc. NH_4OH until precipitation occurs, then 10 ml excess.
3. Continue heating and stirring for 60 minutes. Cover the beaker and let stand overnight.
4. Check completeness of precipitation by adding a few drops of ammonium hydroxide.

5. Decant, or siphon off the supernate, being careful not to disturb the precipitate.

6. Filter the precipitate onto a Whatman No. 50 filter paper. Wash the residue with 3N NH_4OH. Transfer the filter and residue to a 50-ml Vycor crucible.

7. Dry the sample at 110 °C and ignite to 900°C for 1 hour until only white ash remains. Let cool to room temperature.

8. Dissolve the residue in 5 ml conc. HCl and evaporate gently to dryness.

9. Add a few drops conc. HCl and warm to dissolve the salts.

10. Add 10 ml 2N HNO_3-2N $NaNO_3$ solution and transfer to a 25-ml glass-stoppered graduate. Wash crucible with 10 ml nitrate solution and add to graduate. Wash with 5 ml more to complete transfer.

11. Add 5 ml 0.1M TOPO in cyclohexane and extract for 2 minutes

12. Remove two 2-ml aliquots of the extract and evaporate onto concentric ring planchets. Flame planchets to remove all organic matter.

13. Count planchets in low-background alpha counter, and calculate disintegrations per minute per liter of urine.

CALCULATION

From count rate, aliquot, and detector efficiency, calculate disintegrations per minute per liter of urine by:

$$\text{dpm per liter} = \frac{(5)(\text{cpm on planchet})}{(2)(\text{detector efficiency})}$$

References

1. Toni, A. L., "Urinalysis Method for Enriched Uranium," Health Physics, 2, 1960, p. 288.

2. White, J. C., The Use of Trialkyl Phosphine Oxides as Extractants in the Fluorometric Determination of Uranium, Oak Ridge National Laboratory, ORNL-2161, November 1956.

GROSS BETA ACTIVITY IN SOIL, URINE, VEGETATION, AND WATER

Abstract

Urine samples are concentrated and K^{40} activity separated by alkaline phosphate preceiptation. A portion is taken for low-level beta count. Foreign activities in soil and vegetation are leached from these materials with nitric acid and mounted on planchets for a low-level beta count. Water scale is converted to the nitrate form.

APPARATUS

Assorted laboratory glassware

REAGENTS

Conc. nitric acid (70% HNO_3)

Conc. phosphoric acid (85% H_3PO_4)

Sodium hydroxide (40% solution) - Dissolve 40 g NaOH in distilled water and dilute to 100 ml with distilled water.

Sodium hydroxide (5% solution) - Dissolve 5 g NaOH in distilled water and dilute to 100 ml with distilled water.

8N nitric acid - Dilute 500 ml conc. HNO_3 to 1 liter with distilled water.

2N nitric acid - Dilute 125 ml conc. HNO_3 to 1 liter with distilled water.

0.01M (0.02N) ethylene diamine tetraacetic acid (EDTA) disodium salt - Dissolve 3.72 g reagent-grade Na_2EDTA in 1 liter of distilled water and dilute to volume (1 ml equivalent to 1 mg $CaCO_3$).

Indicator solution - Eriochrome Black T., commercially available through Van Waters and Rogers, Inc., Catalog No. 66140.

Buffer solution, pH 10 - Commerically available through Van Waters and Rogers, Inc., Catalog No. 66140.

ANALYTICAL PROCEDURE

Soil

1. If the sample is not dry, heat in an oven at 90°C for several hours. Place 50-100 g in a roller mill and mix for 30 minutes. Screen about 10 g of the sample through No. 10 mesh screen.

2. Weigh out exactly 1 g of the screened soil and place in a 250-ml beaker. Add 20 ml of 8N HNO_3. Place on a hot plate and heat to gentle boiling with occasional swirling.

3. Filter the sample through Watman No. 41 filter paper. Rinse the sample with 2N HNO_3. Collect the filtrate in a 50-ml beaker.

4. Reduce the volume to a few ml and transfer the contents onto a tared-2-inch stainless-steel planchet with repeated washes of 2N HNO_3.

5. Calculation:

$$dpm/g = \frac{\text{net cpm}}{(\text{detector efficiency})(\text{counter correction})^*}$$

Urine

1. To 1000 ml of urine in a 2-liter beaker, add 50 ml of conc. HNO_3. Heat to 80°C and stir for 30 minutes. Add 4 ml of 85% H_3PO_4 and stir for 10 minutes.

2. Add 40% NaOH until the insoluble phosphates precipitate (pH 8 to 9). Stir for 30 minutes. Allow to cool and settle for 30 minutes. (Check for completeness of precipitation by adding a few additional drops of 40% NaOH.)

3. Without disturbing the precipitate, siphon off most of the liquid, using a water aspirator.

4. Filter the precipitate through Whatman No. 41 paper, washing the beaker and filter paper with 5% NaOH. Discard the filtrate.

5. Wash the beaker and filter paper with 8N HNO_3, catching the dissolved precipitate in a 150-ml Erlenmeyer flask. Wash four more times with 10 to 15-ml portions of acid.

6. Evaporate the combined washings to dryness under moderate heat. Add small portions of conc. HNO_3, and increase the heat until the residue is a white ash.

7. Dissolve the residue in 10 ml of 2N HNO_3 by heating gently, then transfer the liquid to a 10-ml volumetric flask. Allow the flask to cool, then dilute to volume with distilled water.

8. Pipette exactly 1 ml into a tared 2-inch stainless-steel planchet and evaporate the liquid to dryness, using a small hot plate. Beta-count.

*See Figures 3 and 4.

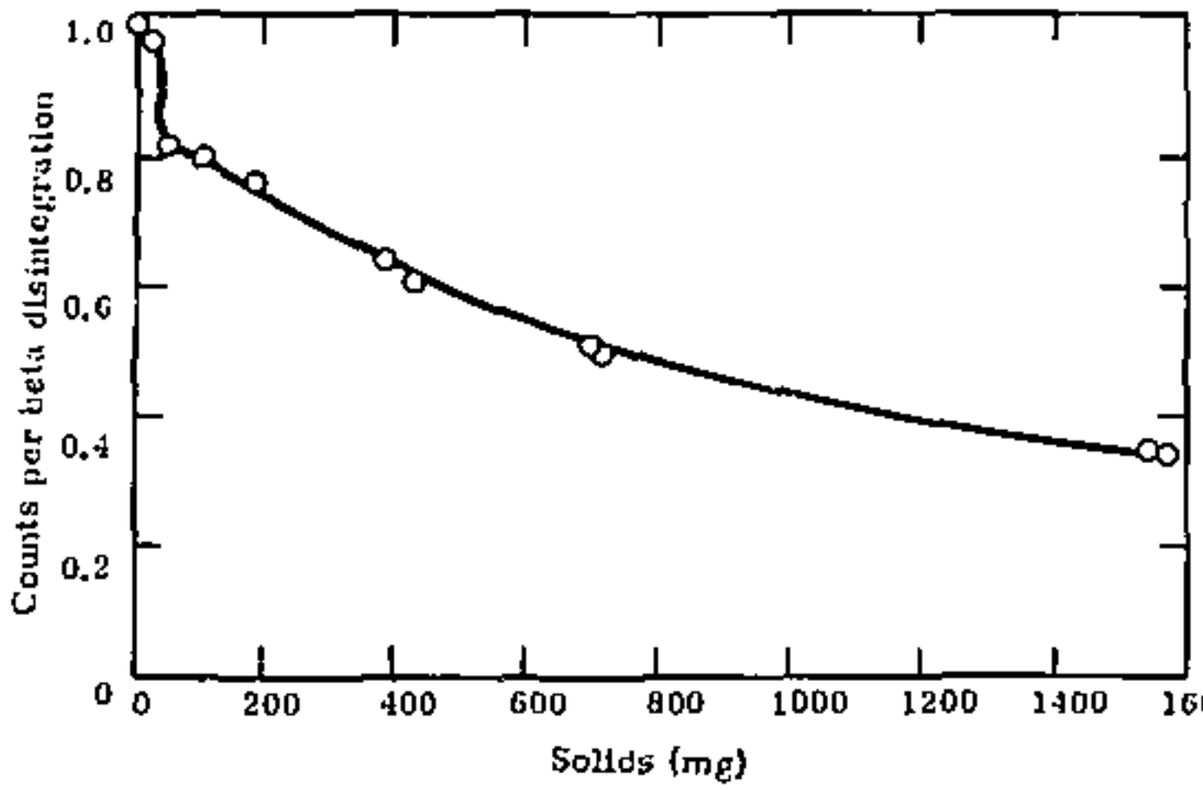

Figure 3. Counter Correction Curve For 1-Inch Planchetts

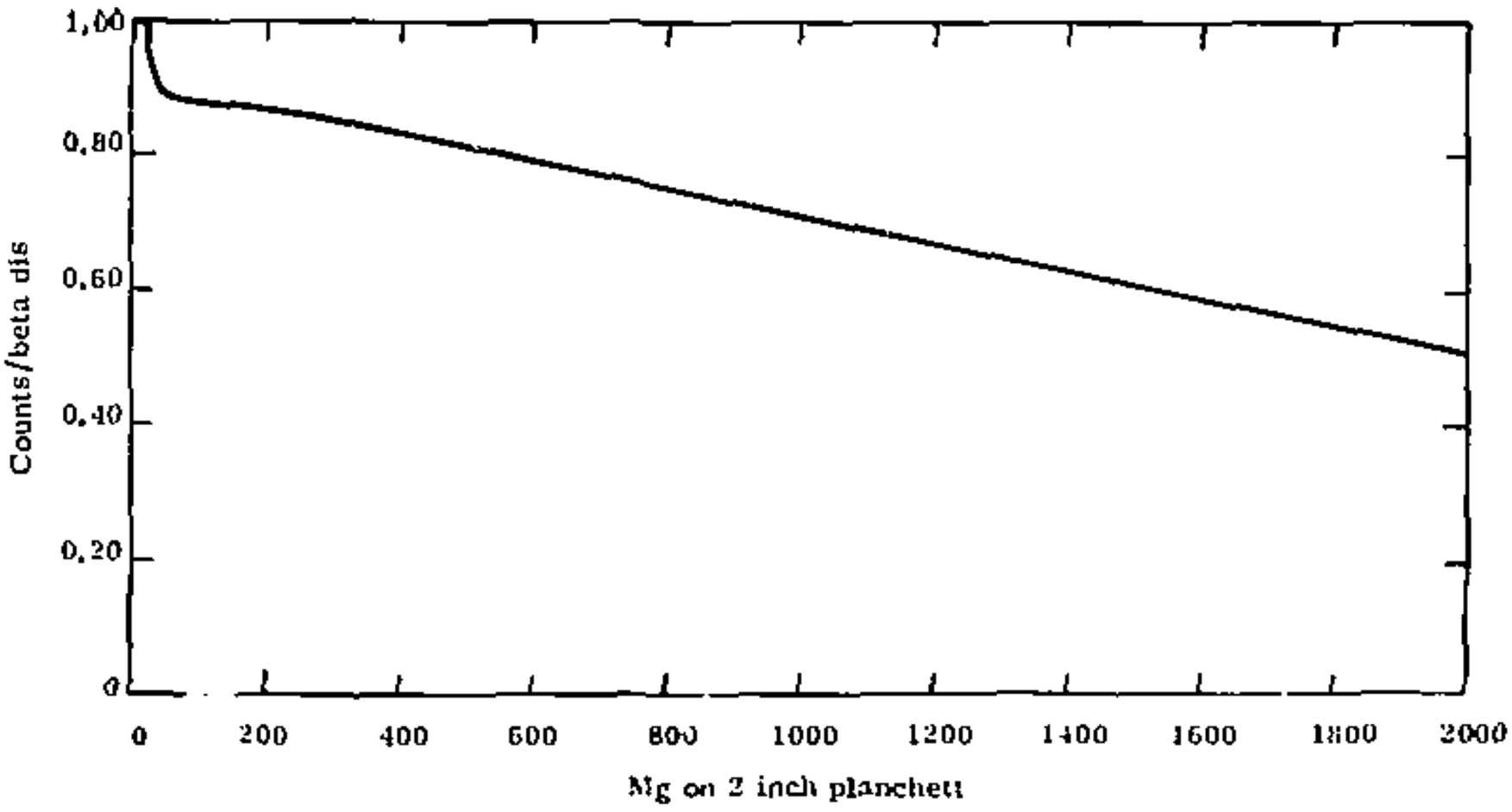

Figure 4. Counter Correction Curve For 2-Inch Planchetts

9. Calculation:

$$dpm/liter = \frac{(1000)(counter\ dpm)}{(chem.\ efficiency)(sample\ volume,\ ml)}$$

Vegetation

1. Place several grams of vegetation in a Waring blender and blend until the sample is thoroughly cut and mixed.

2. Place about 10 g in a porcelain crucible and heat in a muffle furnace at 450°C until a white ash remains.

3. Cool and measure 1 g into a 250-ml beaker; continue as in step 2 under "Soil."

4. Calculation:

$$dpm/g\ ash = \frac{net\ cpm}{(detector\ efficiency)(counter\ correction)(weight\ of\ ash)}$$

Water (Dissolved Solids)

1. Determine hardness of the water sample by titrating a 50-ml aliquot with EDTA as follows:

   a. To a 50-ml aliquot in a 250-ml beaker, add 4 drops indicator, 10 drops buffer, and swirl to mix. The solution should be wine-red.

   b. Titrate to a deep blue end-point, without the slightest trace of purple. In a 50-ml aliquot, 1 ml titrant = 20 mg/liter or 20 PPM hardness as $CaCO_3$.

2. Calculate aliquot to be used in gross beta determination. The final deposit on the planchet should be 4-7 mg/cm^2, or 80-140 mg for a 2-inch-diameter planchet.
   ml aliquot for 2 inch-diameter planchet = $\frac{(110 \pm 30) \times 1000}{PPM \times 2^*}$

3. Prepare all planchets beforehand.

   a. Wipe the outer rim with a light film of silicone stopcock grease to prevent creep of the scale during evaporation.

   b. Weigh to the nearest 0.1 mg.

*Since the deposit is in nitrate form and all dissolved solids will appear on the planchet, the empirical factor 2 will convert conventional hardness figures to nitrate deposit.

4. Filter all sample aliquots through a membrane hydrosol-type filter of 0.45-micron pore size.

NOTE: All samples should be shaken thoroughly, a proper aliquot filtered, and the filter paper saved for gross beta counting of total suspended solids.

5. Transfer the calculated filtered aliquot to a proper beaker, add 2 ml conc. HNO_3, and boil.

   a. If the original aliquot is 200 ml or less, boil down to a few ml, transfer quantitatively into the planchet, and evaporate to dryness.

   b. If the original aliquot is greater than 200 ml, boil down to a tenth the original volume and transfer to a smaller beaker. When volume is below 20 ml, transfer by portions to the prepared 2-inch planchet.

6. Evaporate to complete dryness.

7. Reweigh the planchets and beta-count.

8. Calculation:

$$\text{dpm/l} = \frac{(1000)(\text{counter dpm})}{(\text{absorption correction})(\text{sample volume, ml})}$$

Water (Suspended Solids)

1. Transfer the membrane filter containing the suspended solids directly to a weighed planchet.

2. Lay filter solids side down into the planchet previously wetted with a few drops of acetone, folding the filter into quarters, if necessary, to make it fit. Then add about 1 ml acetone to the planchet, thoroughly wetting the filter, and let stand until the filter is substantially dissolved.

3. Burn off the acetone and flame the residue briefly.

4. Let cool, weigh, and beta-count.

5. Calculation:

$$\text{dpm suspended solids/l water} = \frac{(1000)(\text{counter dpm})}{(\text{absorption correction})(\text{sample volume, ml})}$$

Reference

1. Analysis of Radionuclides in Water, Training Course Manual, U. S. Department of Health, Education and Welfare, Public Health Service, March 1965.

PLUTONIUM IN URINE AND SOIL

Abstract

Plutonium is coprecipitated with the alkaline earth phosphates. The precipitate is dissolved in nitric acid and the plutonium is separated by ion exchange. The separated plutonium is electrodeposited on stainless steel and the alpha activity determined by spectrometry.

APPARATUS

Dowex 1 x 2 ion exchange resin - 50-100 mesh in the nitrate form (see Note 1)

Sea sand, acid-washed (see Note 2)

Ion exchange columns, 250-mm column, 125-ml reservoir, Kontes #K-4225

Electrodeposition apparatus (see Note 3)

Magnetic stirrer-hot plate

Beakers, 3 liter, pyrex

REAGENTS

Nitric acid, HNO_3, concentrated (15.4N)

Nitric acid (7.2N HNO_3) - Add equal volume conc. HNO_3 to distilled water

Phosphoric acid, (H_3PO_4), concentrated, 85%

Hydrochloric acid (HCl), concentrated, 11.6N

Hydrochloric acid (8N) - Add 667 ml conc. HCl to 333 ml distilled H_2O.

Hydrochloric acid (2N) - Add 172 ml conc. HCl to 828 ml distilled H_2O.

Acid wash solution (8N HCl + 0.3N HNO_3 - Add 690 ml conc. HCl + 20 ml conc. HNO_3 to 290 ml distilled H_2O.

Eluting Acid (0.36N HCl +0.01N HF) - Add 31 ml conc. HCl + 0.3 ml conc. HF to 968 ml distilled H_2O.

Potassium hydroxide (8N) - Dissolve 448 gm KOH in 1000 ml distilled H_2O.

Potassium hydroxide (2N) - Dissolve 112 gm KOH in 1000 ml distilled H_2O.

Sodium oxychloride (5% NaOCl)

Indicator solution (0.01% phenolphthalein in 50% ethanol in water)

Ammonium hydroxide, concentrated (28% NH_3)

Plutonium spike solution, ^{236}Pu in 0.002 N HNO_3, ~6.5 dpm/ml

ANALYTICAL PROCEDURE FOR URINE

1. *Combine entire 24-hour urine specimen (record volume) in 3-liter beaker, measure specific gravity + 100 γ spike of* ^{236}Pu.
2. Add 50 ml HNO_3 + 5 ml H_3PO_4 per liter of urine.
3. Heat with stirring to 80°C.
4. Precipitate phosphates with concentrated ammonium hydroxide; be sure of complete precipitation.
5. Continue stirring for an additional 30 minutes at 80°C.
6. *Cool and let sit overnight covered.*
7. Siphon to a very small volume.
8. Dissolve precipitate in 50 ml 7.2N HNO_3, heat to 80°C, cool and proceed with ion exchange procedure.

ANALYTICAL PROCEDURE FOR SOIL BY ACID LEACHING

1. Add 100 g of soil and a spike of Pu-236 tracer (5 to 10 DPM) to a 1-liter beaker.
2. Add cautiously 300 ml of conc. HNO_3. The soil will foam. When reaction stops, add 100 ml conc. HCl and heat on a magnetic stirrer-hot plate at 80°C for 1 hour. Cool and allow mixture to settle.
3. *Filter through a glass fiber filter to a 1-liter beaker. Wash residue in filter* with 1:1 HNO_3. SAVE FILTRATE.
4. Return residue and filter to the original 1-liter beaker, add 300 ml conc. HNO_3 and 100 ml conc. HCl, and heat at 80°C for 1 hour. Cool and allow mixture to settle.
5. Filter and wash as in step 3. Combine filtrate and discard the residue and filter.
6. Concentrate solution to about 200 ml by heating. Add conc. HNO_3 from time to time to destroy all organic matter.
7. *If siliceous matter is present,* dilute with 200 ml water and filter through Whatman No. 40 filter paper. Wash the residue with 1:1 HNO_3. KEEP THE FILTRATE.
8. Transfer the filter paper and residue to a platinum crucible and ignite in a muffle furnace at 500°C for 15 to 30 minutes.
9. Cool and add 2 ml of HF and 2 ml of HNO_3. Place on a sand bath and evaporate to dryness. Repeat the addition of HF and HNO_3 until the solution is clear.

10. Add 4 ml of HNO_3 and evaporate to dryness. Repeat three times.

11. Dissolve the salts in HNO_3 and filter. Add the filtrate to the solution from step 7. Discard the filter.

12. Heat the combined filtrate and concentrate to 150 ml. Add 10 mg of solid sodium nitrite and heat until the nitrite decomposes. Cool and proceed with ion exchange procedure.

ION EXCHANGE PROCEDURE

1. *Transfer the material from step 8 for urine or step 12 for soil to a* prepared Dowex column (see Note 1-A).

2. Wash beaker with two 50-ml portions of 7.2N HNO_3; add to column. Discard effluent.

3. In the hood, wash column with 100 ml HCl-HNO_3 wash solution. Discard effluent.

4. Eluate plutonium with 100 ml HCl-HF. Collect in 50-ml beaker.

5. Add 10 ml conc. HNO_3 to eluate.

6. Evaporate just to dryness.

7. Dissolve residue in conc. HCl, evaporate to dryness. Repeat.

8. Dissolve in 1 ml 8N HCl with heat.

9. Cool + 2 drops PP + 8N KOH dropwise to [illegible].

10. Add 5 ml 2N KOH + 2 ml 5% NaOCl. Transfer to electrolysis cell. Insert platinum anode.

11. Electroplate at 4.5 volts (100 ma) for 5 hours.

12. Remove cell (do not disconnect volta[illegible]) Wash disc in distilled water, flame, and alpha-count.

CALCULATIONS

$$pCi^{239}Pu/24\ hour\ sample = \left(\frac{cpm\ 239)(DPM^{236}Pu)}{(cpm\ 236)(volume)(2.22)}\right.$$

NOTE 1: Preparation of ion exchange resin

a. Wash resin thoroughly with distilled, demineralized water. Decant liquid.

b. Add equal volume 2.0N HNO_3 to resin; stir on magnetic stirrer for 30 minutes. Decant acid.

c. Wash resin with distilled, demineralized water until essentially neutral to pH paper.

d. Store in a 1:1 slurry with distilled water in a plastic squeeze bottle.

NOTE 1-A: Preparation of Dowex column

a. Transfer 250 mm of 1:1 resin slurry to column; be sure stopcock is closed. Let settle 5 minutes.

b. Drain water to resin level (should be 125 mm). Top with 1 cm sea sand.

c. Immediately before use, pass 125 ml 7.2N HNO_3 through resin.

d. Do not let column go dry.

NOTE 2: Preparation of sea sand

a. Clean white sea sand by digestion at 100°C in 20% sodium hydroxide and 1:3 HCl.

b. Wash acid from sand with distilled water. Dry and store covered.

NOTE 3: Preparation of electrolysis cell

a. Wash glass cells in hot conc. HNO_3, followed by water and distilled water. Drain dry.

b. Assemble cell as follows:

(1) Into cap place a stainless steel disc with mirror finish up.

(2) Place "O" ring on disc.

(3) Thread cell onto "O" ring and tighten.

(4) Fill cell with distilled water to check for leaks.

(5) If no leaks are found, pour out water and add sample.

Reference

1. Silker, W. B., "A Rapid Method for Determination of Plutonium in Urine," Health Physics 11, 965 (1965).

POLONIUM-210 IN URINE AND WATER

Abstract

Polonium-210 is selectively deposited from acidified urine or water onto a nickel disc. The activity is determined by alpha proportional counting.

APPARATUS

Mechanical stirrer with glass stirring hooks

Nickel disc, pure Ni, 0.025- x 0.875-inch diameter, with 0.125-inch hole, 0.063 inch from edge.

REAGENTS

Conc. nitric acid (70% HNO_3)

Conc. hydrochloric acid (36% HCl)

6N hydrochloric acid - Dilute 500 ml conc. HCl to 1 liter with distilled water.

Trichloroethylene

ANALYTICAL PROCEDURE

1. To 100 ml urine or water in 250-ml beaker, add 20 ml 6N HCl. Heat to 50°C in constant-temperature bath.
2. Clean Ni disc by rinsing consecutively with trichloroethylene, conc. HNO_3, distilled water, conc. HCl, and distilled water.
3. Let disc air-dry, and make sure surfaces are bright.
4. Attach the Ni disc to a glass stirring hook and suspend in the sample for 1 hour while stirring.
5. Remove the disc and stirrer, and rinse with distilled water. Let disc air-dry.
6. Count the activity on both sides of the disc, using a low-background counter.

CALCULATION

$$\text{dpm/liter} = \frac{(1000)(\text{count, side 1} + \text{count, side 2})}{(\text{ml urine aliquot})(\text{detector efficiency})}$$

References

1. Milligan, M. F., et al., Analytical Procedures of the Industrial Hygiene Group, Los Alamos, LA-1858 (2nd ed.), 1958.

SODIUM-24 IN AIR, BLOOD, URINE, AND WATER

Abstract

Sodium-24 activity is determined directly by gamma-ray spectrometry. The 2.76-mev gamma-ray emission is counted with a 3- x 3-inch thallium-activated sodium iodide crystal detector and 4096 channel analyzer system. Interfering activities may be separated by zinc uranylacetate precipitation if necessary.

APPARATUS

Counting vials, 20-ml capacity, glass or plastic, with screw caps

Filter paper, 47-mm-diameter, Whatman No. 41

REAGENTS

Sequester-Sol, CAMCO clinical reagent No. 205

ANALYTICAL PROCEDURE

Air Samples

1. Collect air sample with 47-mm Whatman No. 41 filter. Place filter in small plastic envelope and seal to prevent contamination of instruments.
2. Count filter directly with 3- x 3-inch crystal detector.
3. Determine the ^{24}Na activity by comparison with a known standard.

Blood Samples

1. Pipette 5 ml whole blood into counting vial containing 2 drops Sequester-Sol. Cap tightly and mix.
2. Count the sample in a 5/8- x 3-inch well-crystal, and determine the activity by comparison with a standard prepared in a solution of equal volume.

Urine Samples and Water Samples

Treat as blood samples, but omit addition of Sequester-Sol.

CALCULATION

The neutron dose in rads is determined from the equation

$$D = (1.63 \times 10^{5})(A),$$

where

D = mean whole body neutron dose in rads,

and

A = ^{24}Na activity in microcuries per ml whole blood.

Reference

1 Cofield, R. E., Neutron Exposure Dosimetry of Humans by In Vivo Gamma Measure of Na^{24}, Oak Ridge National Laboratory, ORNL-Y-1283, September 1959.

STRONTIUM-90 IN SOIL, VEGETATION, AND WATER

Abstract

The only important alkaline earth fission products are barium and strontium. Initial separation from other fission products is made by nitrate salt precipitation from cold, fuming nitric acid. Calcium is removed by washing with anhydrous acetone. Strontium is separated from barium by precipitation of barium chromate. Strontium is precipitated as the oxalate for counting.

APPARATUS

Assorted laboratory glassware and equipment

REAGENTS

Fuming nitric acid (90% HNO_3)

Conc. nitric acid (70% HNO_3)

2N nitric acid - Dilute 125 ml conc. HNO_3 to 1 liter with distilled water.

0.5N nitric acid - Dilute 31 ml conc. HNO_3 to 1 liter with distilled water.

Glacial acetic acid (99.8% $HC_2H_3O_2$)

6M acetic acid - Dilute 345 ml glacial acetic acid to 1 liter with distilled water.

Conc. ammonium hydroxide, NH_4OH (30% NH_3)

1N ammonium hydroxide - Dilute 67 ml conc. NH_4OH to 1 liter with distilled water.

6M ammonium acetate - Dissolve 462 g $NH_4C_2H_3O_3$ in 1 liter distilled water.

Hydrogen peroxide (30% H_2O_2)

Ammonium oxalate $(HN_4)_2C_2O_4$

Ammonium oxalate, saturated solution - Add $(HN_4)_2C_2O_4$ to 1 liter of distilled water until no more dissolves. Add 50 g excess, and store in polyethylene bottle.

1.5M potassium chromate - Dissolve 306 g K_2CrO_4 in 1 liter distilled water.

10N sodium hydroxide - Dissolve 400 g NaOH in 1 liter distilled water.

2M sodium carbonate - Dissolve 212 g Na_2CO_3 in 1 liter distilled water.

Barium carrier - Dissolve 19.0 g $Ba(NO_3)_2$ in 100 ml distilled water and dilute to 1 liter with 0.5 N HNO_3 (1 ml = 10 mg Ba).

Iron carrier - Dissolve 48.4 g $FeCl_3 \cdot 6H_2O$ in 100 ml distilled water and dilute to 1 liter with 1.5N HNO_3 (1 ml = 10 mg Fe).

Strontium carrier - Dissolve 32.4 g $Sr(NO_3)_2 \cdot 4H_2O$ in 100 ml distilled water and dilute to 1 liter with 0.5N HNO_3 (1 ml = 10 mg Sr).

Acetone, anhydrous

Methyl red indicator solution

SAMPLE PREPARATION

Soil

1. Dry soil sample thoroughly at 110°C. Mix 30 minutes in roller mill, and screen to 10-mesh size.
2. Weigh 10 g dry, 10-mesh soil into 150-ml beaker. Add 2 ml Sr carrier, 2 ml Ba carrier, and 20 ml conc. HNO_3. Swirl to mix, and let stand overnight.
3. Heat to 85°C and stir for 20 minutes. Let sample cool.
4. Filter through Whatman No. 42 filter paper and wash with 2N HNO_3. Collect filtrate in 150-ml beaker and evaporate to dryness.

Vegetation

1. Dry vegetation thoroughly at 110°C. Pulverize in blender until thoroughly cut and mixed.
2. Ignite in suitable Vycor crucible at 450°C until only gray ash remains.
3. Weigh 2 g ash into 150-ml beaker. Add 2 ml Ba carrier, 2 ml Sr carrier, and 20 ml conc. HNO_3. Swirl to mix, and let stand overnight.
4. Heat sample and evaporate to dryness. Add 20 ml conc. HNO_3 and 5 ml 30% H_2O_2. When foaming stops, evaporate to dryness.
5. Add 20 ml 2N HNO_3 to dissolve residue and filter through Whatman No. 41 filter paper. Wash with 2N HNO_3.
6. Collect filtrate in 150-ml beaker and evaporate to dryness.

Water

1. To 1 liter water in 2-liter beaker, add 2 ml Ba carrier and 2 ml Sr carrier. Heat to 85°C and stir 20 minutes.
2. While stirring, add 10 ml conc. HN_4OH and 2 g $(HN_4)_2C_2O_4$ and stir for 20 minutes. Let sample stand overnight to cool and settle.
3. Decant the clear supernate, and pour the residue into centrifuge tubes. Centrifuge, and discard the supernate.

4. Wash with 20 ml 1N NH_4OH and discard wash.

5. Add 20 ml conc. HNO_3 and heat to dissolve the precipitate. Transfer to 150-ml beaker and evaporate to dryness.

ANALYTICAL PROCEDURE

1. Add 10 ml 2N HNO_3 to dissolve sample, and transfer to centrifuge tube. Add 10N NaOH until alkaline, and add 2M Na_2CO_3 until precipitation is complete. Centrifuge, and discard supernate.

2. Wash the precipitate with 50 ml hot distilled water, centrifuge, and discard the wash. Repeat wash.

3. Dissolve the precipitate in 5 ml conc. HNO_3. Chill in an ice bath, and add 25 ml cold, fuming HNO_3. Let stand cold for 15 minutes, centrifuge, and carefully discard the supernate.

4. Wash the precipitate with 20 ml cold, anhydrous acetone. Centrifuge, and discard wash. Repeat the wash twice.

5. *Dissolve the precipitate in 2 to 5 ml distilled water. Repeat the* precipitation and wash as in steps 3 and 4 above.

6. Dissolve the precipitate in 10 ml distilled water and add 1 ml Fe carrier. Add conc. NH_4OH by drops until the Fe has precipitated. *Centrifuge, and pour supernate into clean centrifuge tube.*

7. Add 2 drops methyl red indicator and acidify with 2N HNO_3 until indicator remains red (pH = 5). Add 1 ml 6M $HC_2H_3O_2$ and 2 ml 6M $(NH_4)C_2H_3O_2$.

8. Dilute to 20 ml and heat on water bath. Add 2 ml 1.5M K_2CrO_4 and continue heating for 10 minutes.

9. Centrifuge and decant supernate into clean tube. Add 2ml Ba carrier, 1 ml 1.5M K_2CrO_4, and digest on hot-water bath 10 minutes. Centrifuge, and pour supernate into clean tube.

10. Add 5 ml conc. NH_4OH, 5 ml saturated $(NH_4)_2C_2O_4$, and digest on hot-water bath 10 minutes. Centrifuge, and discard supernate.

11. Slurry precipitate with 5 ml distilled water and filter onto weighed Whatman No. 42 filter. Wash filter with H_2O and ethanol.

12. Dry filter at 110°C for 20 minutes. Let cool, and weigh and mount for counting. Let stand 15 days before counting.

Calculation

$$DPM\ ^{90}Sr/liter = \frac{(1000)(cpm)}{(chem.\ recovery)(detector\ efficiency)(ml\ sample)}$$

$$DPM\ ^{90}Sr/gram = \frac{cpm}{(chem.\ recovery)(detector\ efficiency)(g\ sample)}$$

Reference

1. Sunderman, D. N., and Townley, C. W., The Radiochemistry of Barium, Calcium, and Strontium, National Academy of Science, NAS-NS-3010, January 1960.

TRITIUM IN URINE, WATER, AND ON SWIPES

Abstract

Liquid scintillation counting is the method of detecting radioactivity by means of a solution of fluors and a photomultiplier tube. The scintillation solution converts the radioactivity to light and the phototube responds by producing a charged pulse which can be counted.

The widest application of liquid scintillation counting in the Environmental Health Laboratory is the determination of tritium in biological fluids, swipes, and water. Untreated urine and water are added directly to a scintillation mixture, cooled to 6 °C, and the count rates measured with a scintillation spectrometer. Swipes are placed directly in counting vials, wetted with water, and the scintillator fluid added before cooling and counting.

APPARATUS

Liquid scintillation spectrometer, three-channel

Counting vials - 25 ml glass with plastic screw cap

Assorted laboratory glassware

REAGENTS

p-dioxane, spectral grade or commercially available.

2,5-diphenyloxazole (PPO), primary scintaillator

1,4-bis-2-(5-phenyloxazolyl)-benzene(POPOP), secondary scintillator

Napthalene, recrystallized from alcohol, or commercially available.

Scintillation mixture - Dissolve 4 g PPO, 0.05 g POPOP, and 100 g naphthalene in 1 liter p-dioxane. Store in amber glass bottle, away from direct light.

ANALYTICAL PROCEDURE

Adjust spectrometer for channels-ratio counting mode (Nuclear-Chicago operating manual, pp. 4-24 through 4-32). See Figure 5. Check operation by counting reference and standard unquenched tritium. Check settings as posted on unit.

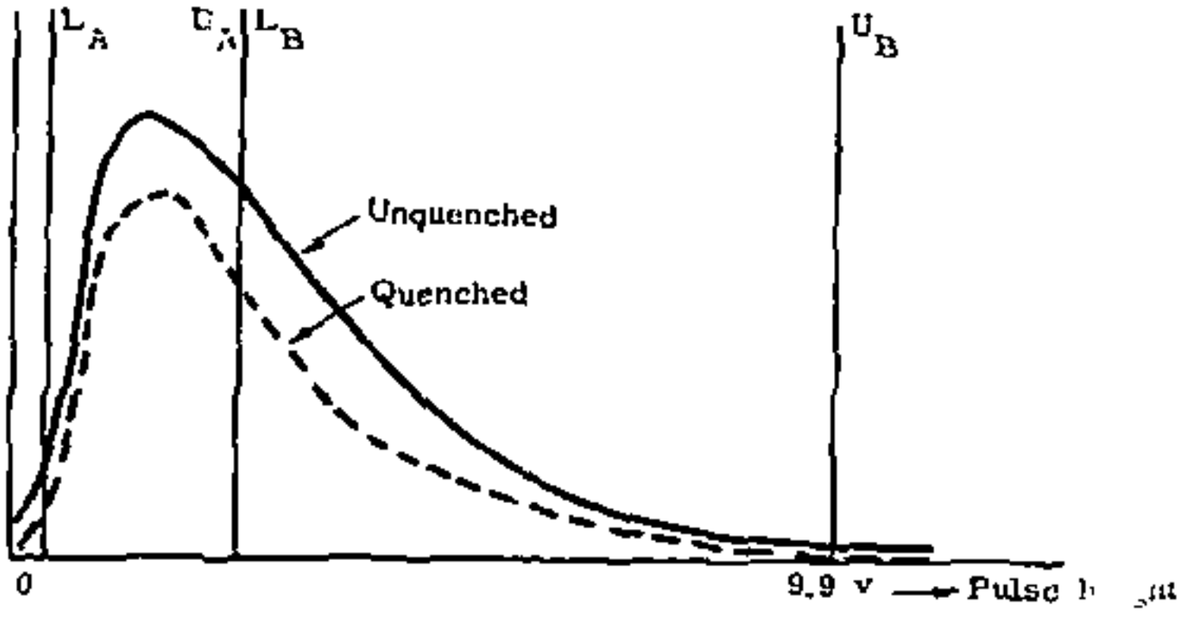

Figure 5. Channels Ratio Analyzer Relationship

Urine

1. Into counting vial, pipette 1 ml urine; add 15 ml scintillator fluid; cap and mix thoroughly.
2. Wipe outside of vial to remove fingerprints.
3. Place in freezer and cool to 6°C before counting.

Water

Into counting vial, pipette 1 ml water, add 15 ml scintillator fluid, and treat as urine.

Swipes

1. Into counting vial, place opened swipe (47 mm).
2. Wet swipe with 1 ml distilled water.
3. Add 15 ml scintaillator fluid.
4. Treat as urine.

CALCULATIONS

Sample cpm = _____

Subtract blank cpm = _____

Corrected cpm = _____

$\frac{\text{cpm}}{\text{\% eff*}}$ = dpm

*See Figure 6

$$\frac{\text{dpm}}{2.22 \times 10^{6} \text{ dpm}} = \mu c \text{ tritium/ml}$$

$$\mu c \text{ tritium} \times 10^{3} = \mu c \ ^{3}H/\text{liter}$$

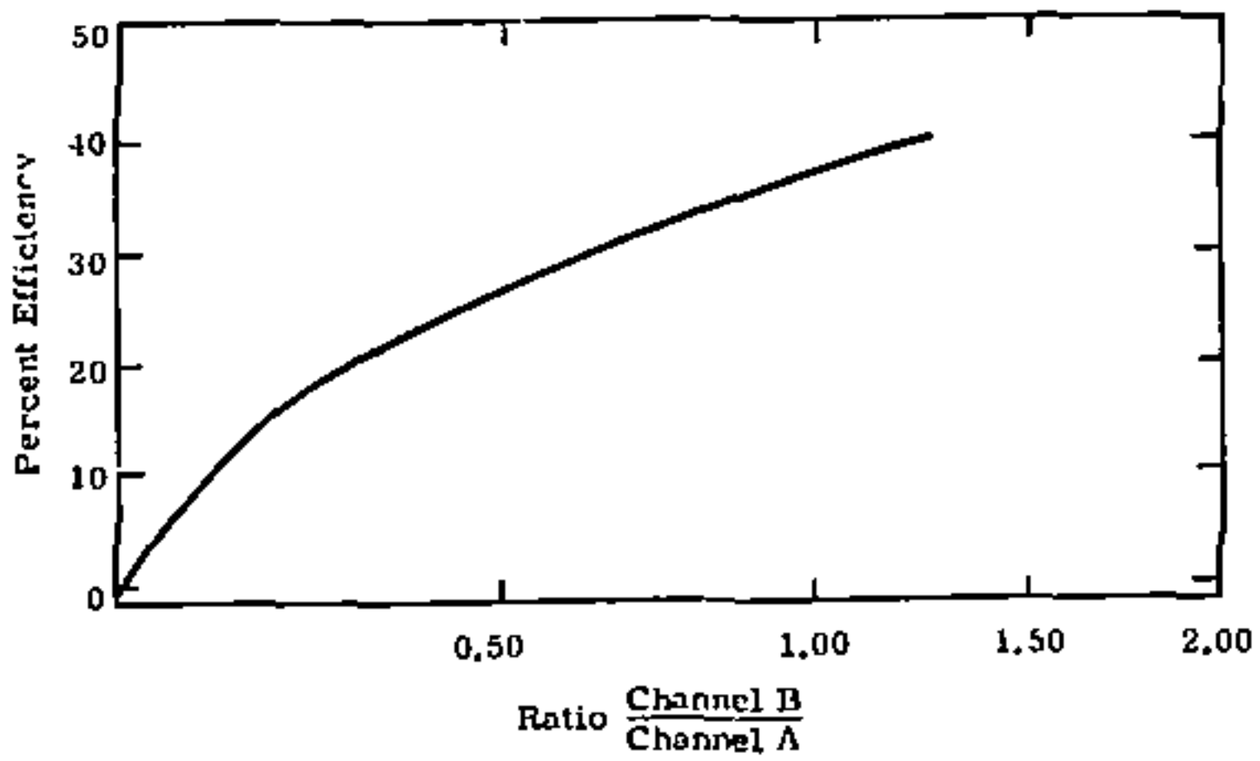

Figure 6. Percent Efficiency Correction Curve

References

1. Butler, F. E., "Determination of Tritium in Water and Urine," Anal. Chem., 33, 1961, p. 409.

2. Langham, W. H., et al., "Assay of Tritium Activity in Body Fluids with Use of a Liquid Scintillation System," J. Lab. Clin. Med., 47, 1956, p. 819.

3. Instruction Manual, Nuclear-Chicago Liquid Scintillation Spectrometer, Model 6860.

TOTAL URANIUM ON FALLOUT TRAYS AND IN SOIL, URINE, AND WATER

Abstract

Fused mixtures of uranium in sodium fluoride (2% lithium fluoride) exhibit strong fluorescence (at 560 nm) in ultraviolet radiation. The intensity of fluorescence is proportional to uranium concentrations from less than 0.001 PPM to more than 10 PPM. The method is nearly specific for uranium, and sensitivities in the range of 0.0004 microgram (±10%) per fusion button can be obtained. Large amounts of quenching interferences are removed, and uranium purified, by solvent extraction.

APPARATUS

Fluorophotometer with reflectance attachment (see Figure 7)

Forceps with Pt tips

Fusion dishes, Pt (see drawing, Anal. Chem., 28, 1956, p. 1651 and Figure 8)

Heat lamp, infrared

Fusion rack (see Figure 8)

Didymium glasses

Blast burner, for propane and compressed air

Pellet maker (see Figure 8)

Glass-stoppered graduates, 25-ml, tall form

REAGENTS

Conc. nitric acid (70% HNO_3)

Conc. hydrochloric acid (36% HCl)

Conc. sulfuric acid (96% H_2SO_4)

2N nitric acid - Dilute 125 ml conc. HNO_3 to 1 liter with distilled water

Uranium standard - Dissolve 2.110 g $UO_2(NO_3)_2 \cdot 6H_2O$ in liter of 2N HNO_3 (1 ml = 1 mg U).

Fusion mixture (NaF-2% LiF) - To 1 pound of NaF, add 9 g LiF, and mix in a roller mill for 8 hours.

0.1M tri-n-octylphosphine oxide (TOPO) - Dissolve 19.2 g TOPO in 500 ml cyclohexane. Store in amber glass bottle.

2N HNO_3 - 2N $NaNO_3$ solution - Dissolve 170 g $NaNO_3$ in 200 ml distilled water, add 125 ml conc. HNO_3, and dilute to 1 liter with distilled water.

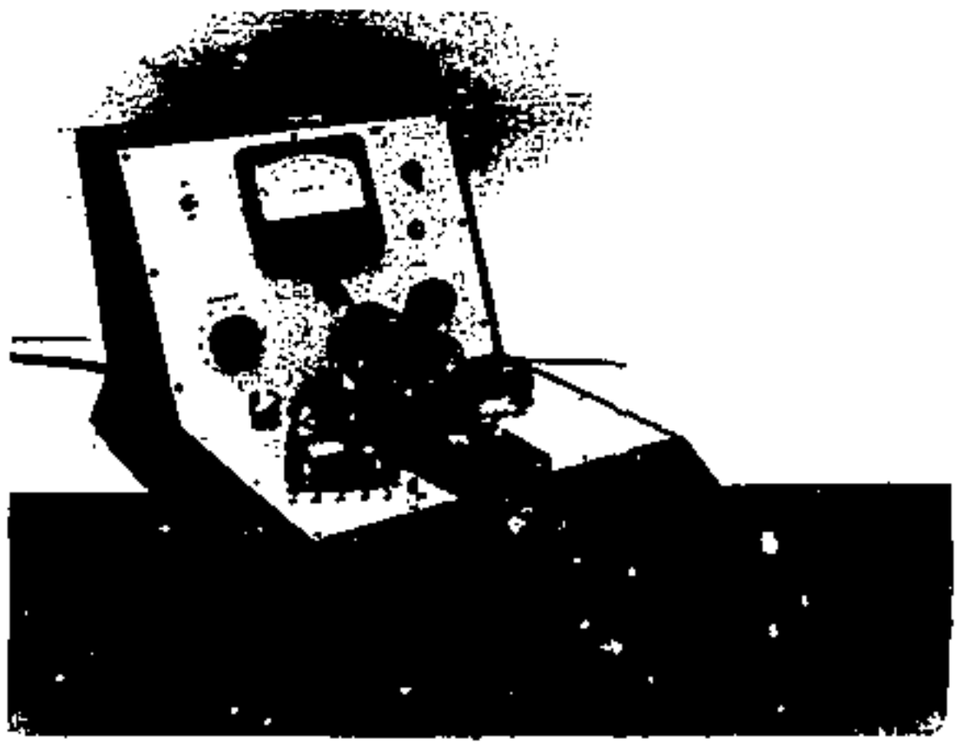

Figure 7. Fluorophotometer

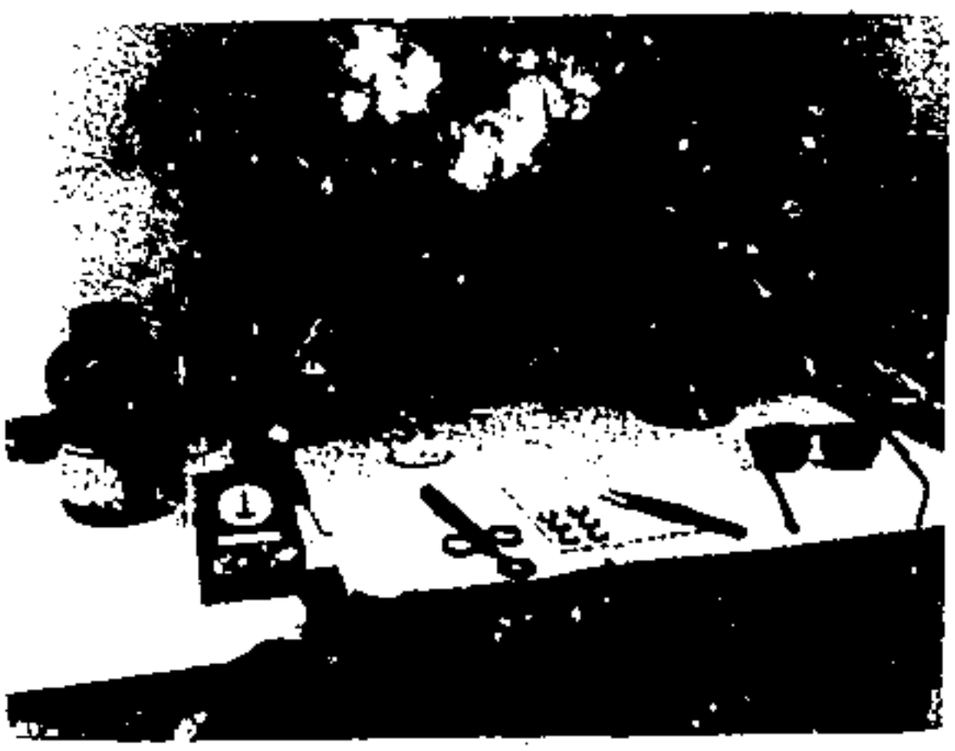

Figure 8. Fusion Rack, Dishes, and Pellet Maker

SAMPLE PREPARATION

Fallout Trays

1. Remove cellophane collector sheet from fallout plate. Wad sheet up so that sticky side is inside. Place wad in 400-ml beaker.
2. Ignite the cellophane with a match and let burn to a small ash in beaker.
3. Wet the ash with conc. HNO_3 and evaporate to dryness. Dissolve the residue in minimum of 2N HNO_3, warming, if necessary, to complete dissolution.
4. Transfer sample to 50-ml volumetric flask with 2N HNO_3, and dilute to volume with 2N HNO_3.

Soil Samples

1. Dry the sample at 110°C and screen to 10-mesh size. Mix the sample in a roller mill for 30 minutes.
2. Weigh 10 g soil into a 150-ml beaker and add 30 ml conc. HNO_3. Heat to near boiling and stir for 30 minutes.
3. Let cool and filter through Whatman No. 50 filter paper into a 50-ml volumetric flask. Wash with 2N HNO_3 and dilute to 50 ml with 2N HNO_3.
4. Pipette 1-ml aliquot into 25-ml glass-stoppered graduate. Add 20 ml 2N HNO_3-2N $NaNO_3$ solution and 5 ml 0.1M TOPO.
5. Extract for 2 minutes. Let phases separate and take aliquot of TOPO extract for analysis.

Urine and Water Samples

Treat 100-ml urine aliquots with 1 ml conc. HCl. Water samples may be concentrated by evaporation with 2N HNO_3 to a smaller volume and aliquoted for analysis.

ANALYTICAL PROCEDURE

1. Pipette 0.1 ml prepared sample into fusion dish. Samples, standards, and blank should be analyzed in triplicate.
2. Evaporate the aliquots to dryness under heat lamp. To TOPO extracts, add 1 drop conc. H_2SO_4 and dry on hot plate. Place fusion dishes on fusion rack.

3. Ignite blast burner and adjust flame so that a trace of green appears in the flame. Fire the dishes to a red heat for 10 seconds to destroy all organic matter.

4. Fill a 250-ml beaker about half full of fusion mixture. Pack the pellet maker firmly with the mixture by tamping in the beaker. Wipe the excess from barrel with Kimwipes and release the pellet into the dish. Use a 0.3- to 0.4-g pellet in each dish.

5. Heat each dish until all the flux melts. Use didymium glasses to watch the melt through the bright flame. Move burner slowly away from center of dish until molten flux creeps evenly up the sides of the dish.

6. Fuse each sample for exactly 1 minute. Let cool 15 minutes before measuring fluorescence. Make readings within 1 hour of fusion time.

7. Let photometer warm up for 15 minutes. Place fused standard (0.1 μg U) into the slide recess and move into reading position.

8. Set sensitivity to 5, while depressing 0.1 scale key, and adjust until microammeter deflects to about midscale. Use the scale that is equal to amount of U in standard: 0.01 scale key for 0.01 μg U.

9. Adjust meter to full-scale deflection with the fine voltage control. Depress zero key and adjust meter to zero with zero knob. Slide empty recess into reading position. Depress 0.1 scale key and adjust background control to zero the meter. Repeat these adjustments until a suitable balance is obtained.

10. Place fused samples in slide recess. Push slide in and operate scale keys to obtain meter reading.

11. Plot μg U versus net fluorescence (microammeter reading) for a standard curve.

CLEANING Pt FUSION DISHES

Any flux remaining in the Pt dishes can be removed with hot conc. H_2SO_4. Rinse dishes repeatedly in hot 2N HNO_3. An ultrasonic cleaner is useful for these washings. Rinse the dishes with distilled water and store in a covered beaker of distilled water or 2N HNO_3.

Always handle the dishes with Pt-tipped forceps. The dishes may require occasional buffing to reduce background contamination.

References

1. Centanni, F. A., Ross, A. M., and DeSesa, M. A., "Fluorometric Determination of Uranium," Anal. Chem., 28, 1956, p. 1651.

2. Sandell, E. B., Colorimetric Determination of Traces of Metals, Vol. 3, Interscience Publishers, Inc., New York, 1959.

3. White, J. C., The Use of Trialkyl Phosphine Oxides as Extractants in the Fluorometric Determination of Uranium, Oak Ridge National Laboratory, ORNL-2161, November 1956.

SECTION C

INSTRUMENTAL ANALYSIS

Highly sophisticated instrumentation has become available over the years for the qualitative and quantitative analysis of both inorganic and organic compounds and has provided the analyst with faster and more accurate results than ever before.

Some of the instrumental techniques that are used in this section are atomic absorption spectrophotometry; emission spectroscopy; fluorescence, infared and ultraviolet spectrophotometry; gas or vapor phase chromatography; and a variety of electrochemical methods.

GENERAL PROCEDURES FOR ATOMIC ABSORPTION SPECTROSCOPY

Abstract

The atomic absorption spectrophotometer is the instrument of choice for quantitating PPM to PPB amounts of metals in air samples, biological samples, commercial products, swipes, and water. Its advantages are (1) ease of sample preparation--normally, all that is required is sample dissolution; (2) sensitivity--most metallic elements are easily quantitated in the PPM to PPB range; (3) selectivity--with very rare exceptions, the sensitive lines of one element do not overlap the sensitive lines of another; and (4) minimum matrix interferences--if present, procedures for elimination of these interferences are listed in Table I.

This atomic absorption section contains divisions which describe the equipment, sample preparation, reagents, data collection, and calculations. Installation, operation and standardization closely follow the manufacturer's instructions.* Safety precautions, regarding use of compressed gases, wearing safety glasses when the burner is in operation, etc., are given in the AA Methods Manual.

APPLICATIONS AND LIMITATIONS

1. The analytical working range for each metal is given in Table I. Higher concentrations can be determined by dilution of the sample.
2. The sensitivity and interferences for each metal is given in Table I.
3. The coefficient of variation for the analysis is approximately 2% depending upon the instrument and the absorbance of the sample.
4. As, In, Se, Te, Tl, and Hg are very volatile elements and must not be heated any more than necessary in sample preparation.

APPARATUS

Atomic absorption spectrophotometer - Perkin-Elmer Model 303 or 305 including the necessary burner heads for air-acetylene and nitrous oxide-acetylene flames and the appropriate hollow cathode lamps.

Control box-burner regulator - supplied with (1) air which has been filtered to remove oil, water, and other impurities; (2) acetylene-commercially available; and (3) nitrous oxide--commerically available. Note: Heating tape is wound around the second stage of the regulator to prevent freeze-up.

*See Reference 1, herein referred to as the AA Methods Manual.

TABLE I

Atomic Absorption Parameters

Element	Sensitivity (μg/mℓ)	Range of Method (μg/mℓ)	Type of Flame	Analytical Wavelengths (Å)	Interferences	Remedy
Be	0.03	0.03 - 8	Reducing N_2O C_2H_2 (rich)	2349	> 500 μg/mℓ at high conc. Si + Mg	(1)
Ca	0.07	0.07 - 10	Reducing Air - C_2H_2	4227	Si, Al, PO_4	(2)
Cd	0.01	0.04 - 5	Oxidizing Air - C_2H_2 (lean)	2288	None	
Co	0.15	0.15 - 8	Oxidizing Air - C_2H_2	2407	None	
Cr	0.2	0.2 - 10	Reducing Air - C_2H_2	3579	Fe + Ni	(3)
Cu	0.1	0.1 - 10	Oxidizing Air - C_2H_2	3247	None	
Fe	0.1	0.1 - 10	Oxidizing Air - C_2H_2	3483	Ni	(4)
K	0.1	0.1 - 10	Oxidizing Air - C_2H_2	7665	K is partially ionized in the Air - C_2H_2 flame	(5)
Mg	0.007	0.007 - 0.7	Oxidizing Air - C_2H_2	2852	Si, Al, Cu at high concentrations	(6)
Mn	0.05	0.05 - 4	Oxidizing Air - C_2H_2	2795	None	
Mo	1.0	1.0 - 60	Reducing N_2O C_2H_2	3133	Ca and other ions	(7)
Na	0.02	0.02 - 5	Oxidizing Air - C_2H_2	5890	Na is partially ionized in the Air - C_2H_2 flame	(8)
Ni	0.2	0.2 - 20	Oxidizing Air - C_2H_2	2320	None	
Pb	0.5	0.5 - 30	Oxidizing Air - C_2H_2	2170, 2833	None	
Sn	5.0	5.0 - 300	Reducing Air - C_2H_2	3246, 2354	None	
Zn	0.025	0.025 - 2	Oxidizing Air - C_2H_2	2139	None	

1. If these interferences are known to be present, add 500 μg/mℓ Al, Si, or Mg to all standards
2. Add 1% La to both standards and samples.
3. Add 200 μg/mℓ Fe to both standards and sample solutions. Add Ni in amount equal to the amount of Cr in each standard.
4. Add 200 μg/mℓ Ni to both standards and samples.
5. Add Na at a ratio of 2 parts Na to each part K in both standards and samples.
6. Due to the high sensitivity of Mg and the effect of sample dilution, no interferences exist.
7. Add 1000 μg/mℓ Al to both standards and samples.
8. Add K at a ratio of 2 parts K to each part Na in standards and samples.

TABLE I (cont)

Element	Sensitivity ($\mu g/m\ell$)	Range of Method ($\mu g/m\ell$)	Type of Flame	Analytical Wavelengths (A)	Interferences	Remedy
Al	1.2	1.2 - 50	Reducing N_2O C_2H_2 (rich)	3093	Fe, HCl H_2SO_4 V, Ti, $HC_2H_3O_2$ Al is partially ionized	(9)
Li	*0.04*	*0.04* - 2	Oxidizing Air - C_2H_2 (lean)	6708	None	
Pd	*0.4*	*0.4* - 15	Oxidizing Air - C_2H_2 (very lean)	2476	Al, Co, Ni, Pt, Rh, Ru	(10)
Si	5.0	5.0 - 150	Reducing N_2O C_2H_2	2516	Fe only when using a multi-element lamp containing Fe	(11)
Ag	0.1	0.1 - 10	Oxidizing Air - C_2H_2	3281	Iodate, permanganate, *and tungstate* H_2SO_4 and H_3PO_4 $HC_2H_3O_2$	(12)
Te	0.5	0.5 - 25	Oxidizing Air - C_2H_2	2143	None	
Tl	0.5	0.5 - 20	Oxidizing Air - C_2H_2	2768	None	
Ba	0.1	0.1 - 50	Reducing N_2O C_2H_4	5536	Alkali salts	(13)
As	0.5	0.5 - 50	Oxidizing Air - C_2H_2	1937 (EDL)		

9. Add alkali metal salts (1000--2000 $\mu g/m\ell$) to sample and standard solutions.
10. Add 0.5% La or 0.01M EDTA.
11. Use a secondary silicon resonance line of 2507, 2528, or 2524.
12. Remove interfering substances or add these to standard solutions.
13. Add 1000 $\mu g/m\ell$ KCl to samples and standard solutions.

Recorder, "Servo-Riter," 0-10 mv, Texas Instruments.

Atomic absorption accessories - See AA Methods Manual for Delves sampling Cup, Boat Method, graphite furnace, flameless mercury analyzer, etc.

150-ml beakers with watchglass covers

10-ml and 100-ml graduated cylinders

125-ml and 150-ml polyethylene bottles

Hot plate capable of temperature to 400°C

Platinum crucibles

Teflon beakers

REAGENTS

Hydrogen peroxide (30% H_2O_2)

Hydrogen fluoride (hydrofluoric acid, 48% HF)

Double distilled or deionized water

Redistilled conc. nitric acid (70% HNO_3)

Conc. hydrochloric acid (36% HCl)

Conc. sulfuric acid (95% H_2SO_4)

Conc. perchloric acid (70% $HClO_4$)

6N hydrochloric acid - Add 500 ml conc. hydrochloric acid to 500 ml distilled water.

Acid digestion mixture I; 8:1:1 conc. HNO_3: conc. H_2SO_4: conc. $HClO_4$

Stock standards ; Make up 1000 µg/ml solutions as their chlorides of each of the elements listed in Table I, being sure to acidify them properly to keep the metals in solution. As, Be, Bi, and Sb are easily hydrated to their insoluble oxychlorides or hydroxides; therefore the stock solutions of these elements must be in at least 6N acid. Others are stable in 1N acid. Keep all stock solutions in polyethylene bottles. Hg and Tl form insoluble chlorides in their lower oxidation states; therefore, add 5 ml conc. nitric acid, prior to dilution to volume, to provide an oxidizing medium and ensure their higher valence states. Commercially prepared aqueous stock standards of 1000 µg/ml may also be used.

Working solutions - From each of the 1000 µg/ml stock standards, prepare working standards to cover the range for each metal as given in Table I. *All working standards should be acidified as strongly as stock standards* and stored in polyethylene bottles. Remake every day for best results. When analyzing for any of the metals where interferences are known to occur, as is indicated in *Table I, standards should be prepared according* to the "Remedy" listed in the table.

SAMPLE PREPARATION

Air samples and swipes

1. *Transfer samples to 150-ml beakers and add 5 ml of conc.* HNO_3. Cover each beaker with a watchglass and heat on a hot plate (140°C) in a fume hood until sample chars or a light yellow solution remains. *Repeat addition of* HNO_3 *until a white residue remains. Proceed with* step 4.

2. For samples containing BeO, 5 to 10 ml of acid digestion mixture I is used. The samples are heated at 200-400°C until digestion is complete and white SO_3 fumes are evolved. Cool, and quantitatively transfer to a 10-ml graduated cylinder.

3. For samples containing As, In, Se, Te, Tl, and Hg, the residue from step 1 is dissolved in 2 ml of 6N HCl and quantitatively transferred to a 10-ml graduated cylinder with distilled water.

4. The residue from step 1 is heated several minutes on a high temperature hot plate (400°C) and convereted to a salt by three successive evaporations with conc. HNO_3 or 6N HCl. The ash is then dissolved with 6N HCl or conc. HNO_3 and quantitatively transferred to a 10-ml *graduated cyellnder. Aliquots of this can be diluted if necessary or* the volume can be reduced by evaporation to get the concentration within the working range of the metal.

Ores, Soils, and Dusts

1. Ignite a 1.0000±0.005-g dried 200-mesh sample in a platinum crucible at 900°C. Cool and transfer the ignited sample to a 100-ml teflon beaker.

2. Dissolve the sample by adding 10 ml of HF and 10 ml of HCl and evaporating to dryness on a low-temperature hot plate. Repeat the addition of HF and HCl and evaporate to dryness.

3. Add 5 ml of HCl and evaporate to dryness. Repeat.

4. Dissolve the residue in 6N HCl or conc. HNO_3 and quantitatively transfer to a 100-ml graduated cylinder with distilled water. Aliquots of this can be diluted if necessary to get the metal concentration within the working range of the method.

Vegetation

1. Place several grams of dried vegetation in a Waring blender and blend until the sample is thoroughly cut and mixed.

2. Place about 10 g in a platinum or porcelain crucible and heat in a muffle furnace at 450°C until a white ash remains.

3. Continue with step 1 under "soils."

Urine or Whole Blood

1. To 100 ml aliquot of urine or 10 g blood in a 500-ml Erlenmeyer flask, add 20 ml conc. HNO_3 and 5 ml H_2O_2.

2. Evaporate to dryness; repeat conc. HNO_3 addition until a white ash is obtained.

3. Add 5 ml conc. HNO_3 or 6N HCl; warm to dissolve residue, and quantitatively transfer to a 10-ml graduated cylinder.

Analytical Procedure

1. Turn on power to atomic absorption unit; install lamp to be used, and adjust lamp current to the recommended setting.

2. *Turn on ventilation system over the* [illegible] *unit.*

3. Turn on acetylene, nitrous oxide, and air to the control box and adjust fuel and air flow as indicated in the AA Methods Manual.

4. Install the proper burner head according to the "type of flame" as listed in Table 1.

5. Set wavelength control to the proper analytical wavelength for the metal of interest and adjust the ENERGY meter to maximum energy, constantly keeping the needle within the black or green portion of the dial by adjusting the GAIN knob.

6. Turn on the fuel flow to the burner and ignite. Aspirate the series of standards and the samples and record the absorbance. Prepare a calibration curve *by plotting on linear graph paper the absorbance versus*

the concentration of each standard in µg/ml. From the calibration curve, read the concentration (µg/ml) of the samples. Blank values, if any, are subtracted from each sample.

CALCULATIONS

1. On an air sample; $mg/m^3 = \frac{\text{ml solution}}{1000} \times \frac{\mu g/ml}{\text{vol. air sample in } m^3}$

2. On a swipe: $mg = \frac{\text{ml solution} \times \mu g/ml}{1000}$

3. In a liquid: $\% = \frac{\mu g/ml}{10{,}000}$

4. In a solid: $\% = \frac{\text{ml solution} \times \mu g/ml}{\text{wt original sample (grams)} \times 10{,}000}$

Reference

1. Analytical Methods for Atomic Absorption Spectrophotometry, The Perkin-Elmer Corporation, Norwalk, Conn., 1974.

MERCURY IN URINE

Abstract

Urine samples are decomposed with nitric acid and then the mercury is reduced to the elemental state with stannous chloride. The mercury vapor is passed through an absorption cell with quartz end windows using the 253.7-nanometer mercury resonance line. Commerical atomic absorption equipment is used to measure the quantity of mercury present.

APPLICATIONS AND LIMITATIONS

The sensitivity for a 1.0-ml urine sample is 1 µg/l. The range extends up to 0.1 mg/l. Metals such as copper, gold, or platinum form alloys with mercury and thus will cause a negative response. Water vapor or organic solvents that absorb at 253.7 nanometers cause a positive response. Another limitation of this method is that some organic-mercury compounds are not decomposed by the cold acid digestion technique.

APPARATUS

Mercury evolution train - This consists of a rotometer covering the 0 to 5-l/min range, a high-efficiency bubbler, a midget impinger as a safety trap, a drying tube filled with magnesium perchlorate, and the absorption cell. All components are connected to an air supply line with minimum lengths of tygon tubing.

High-efficiency bubbler; 100-ml size

Pipets; 1-, 2-, and 5-ml sizes.

Volumetric flask; 1000 ml

REAGENTS

Conc. HNO_3 (70% HNO_3)

6N HCl - Add 500 ml conc. hydrochloric acid to 500 ml distilled water.

Stannous Chloride Solution; 20% (W/V) in 6N HCl - Dissolve 10 g of stannous chloride in 50 ml of 6N HCl.

Stock standard; 1000 µg/ml - Available commercially or prepare by dissolving 1.353 g of mercuric chloride in 100 ml of 6N HCl.

Working standard; 1 µg/ml - Pipet 1 ml of the 1000-µg/ml stock standard into a 1-liter volumetric flask. Add 20 ml of conc HNO_3 and dilute to volume with distilled water. Prepare fresh daily.

ANALYTICAL PROCEDURE

1. Transfer 2 ml of urine sample to a high-efficiency bubbler.
2. Add 5 ml of HNO_3 and allow to react at room temperature for at least 3 minutes.
3. Dilute to 50 ml with distilled water; add 1 ml of stannous chloride, and connect the flask to the bubbler tube in the generating train.
4. Open air valve and pass air through the train at 2 l/min.
5. Record the detector response on the recorder.
6. Run standards of 0.001 to 1 µg mercury in the same manner.

CALCULATIONS

1. Make a calibration curve by plotting peak height or area under the curve versus µg mercury on semilog graph paper.
2. From the calibration curve, read µg mercury for each of the samples.
3. Mercury concentration (µg/ml) = $\frac{\text{µg mercury found}}{\text{ml of sample taken}}$

Reference

1. Hatch, W.R., and Ott, W. L., "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry," Anal. Chem., 40, 2085 (1968).

GENERAL PROCEDURES FOR SPECTROGRAPHIC ANALYSIS

Abstract

The emission spectrograph is a useful tool in the Environmental Health Laboratory, since it can accept a wide range of sample types with a minimum amount of sample preparation. It is especially useful because of its trace-element sensitivity for many metals. These factors have influenced laboratories to investigate the use of the emission spectrograph as an analytical tool for such routine programs as (1) beryllium swipes and air-sample monitoring, and (2) qualitative and semiquantitative analysis of swipes, settled dusts, and commercial products. The general methods outlined are used in the Sandia Laboratories Environmental Health Chemistry Laboratory.

APPARATUS

Spectrograph, 3.4-meter Ebert Plane Grating, Jarrell Ash Company, Newtonville, Mass. Bilateral slit, adjustable from 0 to 400 micron width; 30,000-grooves-per-inch replica grating; 4- x 20-inch plate holder; electrical racking and step-jogging mechanism; and remote grating rotation.

Power source, AC/DC power supply, Jarrell Ash Company, AC spark (0-10 amp), DC arc (0-15 amp) 0- to 60-second preburn, 0- to 3-minute exposure time.

Arc-spark stand, Jarrell Ash Company. Water cooled, adjustable jaws, air chimney with adjustable damper for draft from 0 to 0.20 inch of water, motor for rotating disc electrodes and rotating platform electrodes, and inlet from regulated 80% argon-20% oxygen tank for use in argon atmosphere excitation.

7-step filter, Jarrell Ash Model No. 16-830

Photoprocessor, Calumet Photographics, Inc., Elk Grove Village, Illinois, with thermostatically controlled tanks for developer, fixer, stop bath, and wash tanks. Adjustable nitrogen burst system on developer, fixer, and wash cycles.

Seidel calculator, Jarrell Ash Model No. 40-100, with working curve strips and background correcting device.

Photographic plates, Kodak SA No. 1

Electrodes, Ultra Carbon Corp. No. 1989 and 100 u

Comparator microphotometer, Jarrell Ash Console Model No. 21-000, nonrecording, with 0 to 40-micron continuously adjustable slit width, and 0.1-, 0.5-, 0.7-, 1.2-, 1.6-, and 2.0-mm step-adjustable slit height; has electrical scanning drive up to 3/4 mm at 6 microns/sec.

Qualitative master plate - Plate marked with the positions of persistent lines of 48 elements using an Fe reference spectrum.

Vials, Spex Industries Nos. 3111 and 3119, 1/2-inch diameter × 1 inch long, polystyrene with polyethylene cap, 2-ml capacity, with 1/8-inch-diameter Plexiglass balls.

Wig-L-Bug, Spex Industries No. 3140, with 1-hour timer and fan-cooled motor

Assorted laboratory glassware

EXCITATION AND EXPOSURE CONDITIONS

Arc	10 amp DC
Preburn	2 sec
Exposure	30 sec
Filter	7-step filter in step 2
Slit height	2 mm minimum
Slit width	10 microns
Step height	2 mm minimum
Analytical gap	2 mm
Grating position	9.50 degrees
Atmosphere	Air

PROCESSING CONDITIONS

1. Develop for 3 minutes in D-19 developer which is still clear enough for one to see the bottom of the tank at a temperature of 70°F. Use 2-sec nitrogen burst every 10 sec on developer, fixer, and final wash.
2. Stop development by dipping 10 to 15 seconds in 2% acetic acid stop bath which is not more than 1 month old.
3. Fix for 3 minutes in Kodak Rapid Fixer (Kodak 2-part solution) fixing bath which is not more than 3 months old.
4. Rinse for 3 minutes in cold running tap water.
5. Rinse again in distilled water to eliminate water spots
6. Plates may be dabbed gently with lint-free paper toweling before drying.
7. Dry for 3 minutes with emulsion side up in the oven, with heater on high and blower on.
8. Plate may be marked to identify specific lines for qualitative identification.

DENSITOMETRY

Use the following settings:

a. Slit width, 10 microns

b. Slit height, 0.5 mm

c. Set 0% T with ZERO ADJ. knob after 15 minutes minimum warmup time.

d. Set 100% T using SPAN knob after setting 0% T, using a clear area of the plate either just over or just under the lines of interest.

GENERAL METHODS, QUALITATIVE

Swipes

1. Load the swipes into Ultra Carbon No. 1989 hollow-cup electrodes.

2. Excite and process, using conditions as outlined above.

3. Using the qualitative master, identify the unknown elements. For positive identification of an elements presence in the sample, a minimum of three persistent lines must be matched or measured perfectly.

Solids

1. Grind sample, if necessary, to allow introduction of a uniformly mixed portion of the sample into a No. 1989 hollow-cup electrode.

2. Excite and process using conditions as outlined above.

3. Identify the unknown elements using the qualitative master plate.

4. To identify the elements found as major (M), minor (m), or trace (tr) quantities in the sample, compare visually, using the comparator microphotometer with standards or other samples of known concentration.

Liquids

1. Transfer the liquid into a No. 1989 hollow-cup electrode.

2. Evaporate the liquid by air draft, heating lamp, or oven, as necessary.

3. Excite, process, and identify using steps 3 and 4 under "Solids."

GENERAL METHODS, QUANTITATIVE

No deviation from the commonly accepted quantitative spectrographic methods, *abundant in literature, are used.*

The internal standard is chosen with the following criteria.

1. Equivalent burning rates; e.g., Mo for Be unknown.
2. Minimal chance of presence of the internal standard in the sample; e.g., Pd or In in trace-metal analysis of water.

References

1. ASTM Committee E-2 on Emission Spectroscopy, Methods for Emission Spectrochemical Analysis, American Society for Testing and Materials, Philadelphia, Pennsylvania, 1964.
2. Harrison, George R., MIT Wavelength Tables, The Technology Press, *John Wiley & Sons, Inc., New York, 1939.*
3. Harvey, Charles E., Semiquantitative Spectrochemistry, Applied Research Laboratories, Glendale, California, 1964.
4. Kroonen, J., and Vader, D., Line Interference in Emission Spectrographic Analysis, Elsevier Publishing Company, New York, 1963.

BERYLLIUM IN AIR SAMPLES AND SWIPES

(Spectrographic Method)

Abstract

Air samples or swipes are wet-ashed in a digestion mixture of sulfuric, perchloric and nitric acid; a known amount of molybdenum is added as an internal standard and the sample diluted to known volume. Aliquots of the samples and standard solutions containing molybdenum are transferred to hollow-cup electrodes. The electrodes are arced in a 10-amp DC arc, the Be lines are measured on a densitometer, and the beryllium concentrations are calculated.

Sample Type:	4-inch Whatman Hi-Vol Air Samples
	42.5-mm or greater Whatman Swipes
	Millipore Filter Air Samples
Sensitivity:	0.1 μg Be/total sample
Accuracy:	±20%, 0.1-1.0-μg range
	±10%, 1.0-3000-μg range

APPARATUS AND REAGENTS

Emission spectrograph

Power supply

Comparator-microphotometer

Developing equipment

Kodak SA No. 1 plates

Electrodes, Ultra Carbon Corp. No. 1989 and Ultra Carbon Corp No. 1000 waterproofed with Krylon spray.

Pipettes, 2 ml, 100 lambda

Digestion mixture, 8:1:1 70% HNO_3:70% $HClO_4$:95% H_2SO_4

Beryllium stock solution - Dissolve 19.638 g $BeSO_4 \cdot 4H_2O$ in a liter of 0.1N H_2SO_4 (1 ml = 1 mg Be).

Beryllium working solution - Into a 100-ml glass-stoppered volumetric flask, pipette 1 ml beryllium stock solution, add 1 ml conc. HNO_3, and dilute to volume with distilled H_2O (1 ml = 10 μg Be).

Molybdenum stock solution - Dissolve 0.91 g $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in some distilled H_2O in a 100-ml volumetric flask, add 10 ml conc. HNO_3, and dilute to volume (1 ml = 5 mg Mo).

Molybdenum internal standard solution - To a 250-ml volumetric flask, add 10 ml conc. HNO_3 and pipette 50 ml molybdenum stock solution (1 ml = 1 mg Mo).

Beryllium standards - To each of seven 100-ml volumetric flasks, add 1 ml conc. HNO_3. Then add serially 0.1, 0.3, 1, 3, 10, and 30 ml of beryllium working solution; to the seventh, add 1 ml of beryllium stock solution. Bring to 100-ml volume with distilled H_2O. Thus, the standards will have 0.001, 0.003, 0.01, 0.03, 0.1, 0.3, and 1 μg Be in 0.1 ml.

ANALYTICAL PROCEDURES

1. Fold sample into a 100-ml beaker, add 2.0 ml molybdenum internal standard solution and 10 ml digestion mixture.
2. Place on hot plate and cover with a coverglass.
3. Evaporate to ≈3 ml, or until just fuming.
4. Let cool, add 2-3 ml conc. HNO_3, and replate to evaporate to SO_3 fumes.
5. Cool, transfer quantitatively to a 10-ml glass-stoppered graduate, and dilute to 10 ml.
6. Transfer three 100λ portions into three No. 1989 waterproofed hollow-cup electrodes; triplication is necessary to meet required accuracy.
7. Evaporate solution in electrodes slowly. When the electrodes appear dry, increase heat to drive off the last traces of $HClO_4$ and H_2SO_4.

EXPOSURE PLAN

1. Allow 2 mm of plate height for each of the samples.
2. Load the plate holder with SA No. 1 plates. Position the grating at 9.50 such that the wavelengths between 3000 Å and 3300 Å all fall on the plate.
3. Adjust the slit width to 10 microns.
4. Adjust the slit height to 2 mm to conform with the planned plate in procedure 1 above, and set the step height accordingly.
5. Set the 7-step filter to the second notch in all samples.

EXPOSURE

Start (1) samples for 30 seconds with 10-amp DC arc and 2-second preburn.

DEVELOPMENT

Proceed as specified in "General Spectrographic Methods."

PROCEDURE - DENSITOMETRY (AIR SAMPLES)

1. Turn on MASTER and SCALE switches, and allow to warm up for at least 15 minutes.

2. *Set slit height to 0.5 mm and slit width to 10 microns and record* percent transmittance.

3. Align selection for optimum range.

Internal Standard	Range, μg *on Electrode*	*Be Line, %T*
Mo 3133, 5%T	0.001-0.1	3130, 100%
Mo 3133, 5%T	0.1-5	3131, 5%
Mo 3133, 5%T	2-30	2650, 5%

Use standard curves for quantitation.

4. Calculate the μg Be on each electrode and average the figures for each sample.

5 $\mu g\ Be/m^3$ air sample = $\frac{\mu g/\text{electrode} \times \text{dilution factor}}{\text{air sample volume in } m^3}$

$$= \frac{\mu g \times 10}{m^3}$$

Reference

1. Brucato, P., and Bieliski, R.J., Rapid Analysis of Beryllium in Air-Borne Dust by Emission Spectrographic Techniques, Technical Report No. 1060, February 6, 1964. (From Technical Information Department, Engineering Research Center, P.O. Box 900, Princeton, New Jersey.)

ANALYSIS OF COMPRESSED BREATHING AIR

Abstract

This method describes the analytical techniques used in analyzing compressed breathing air and the specification requirements are listed by the Compressed Gas Association Inc., 500 Fifth Avenue, New York, N.Y. Table II lists the CGA Specification G-7.1 1966. Grade D gaseous is the breathing air used at Sandia Laboratories.

TABLE II

Compressed Gas Association Specification

Limiting Characteristics	TYPE I (GASEOUS) GRADE									TYPE II (LIQUID)	
	A	B	C	D	E	F	G	H	J	A	B
% O_2 (v/v) Balance Predominantly N_2 (Note 1)	atm.	atm.	atm/ 19-23	atm/ 19-23	atm/ 19-23	atm/ 19-23	atm/ 19-23	atm/ 19-23	atm/ 19-23	19-25	19-23
Water		none condensed	note 2	note 2	note 2	note 2	note 2	note 2	1 -10.4°F		note 2
Hydrocarbons (condensed) in Mg/m^3 of gas at NTP (Note 3)		none	5	5	3						
Carbon Monoxide			50	20	10	5	5	5	1		5
Odor											none
Carbon Dioxide				1000	500	500	500	500	0.5		5
Gaseous Hydrocarbons (as methane)						25	15	10	0.5		10
Nitrogen Dioxide							2.5	0.5	0.1		0.5
Nitrous Oxide									0.1		0.5
Sulfur Dioxide							2.5	0.5	0.1		0.5
Halogenated Solvents							10	1	0.1		1
Acetylene									0.05		0.5
Permanent Particulates											15

Note 1: The term "atm" (atmospheric) denotes the oxygen content normally present in atmospheric air, the numerical values denote the oxygen limits for synthesized air.

Note 2: The water content of compressed air required for any particular grade may vary with the intended use from saturated to very dry. If a specific water limit is required, it is to be stated as a [illegible] dewpoint or concentration in ppm (v/v). The dewpoint is at pressure [illegible] atmospheric pressure (760 mm Hg).

Note 3: [illegible] the gaseous hydrocarbon limits [illegible]

ANALYTICAL PROCEDURES

1. The percent oxygen should be determined by (A) an apparatus employing a comparison tube filled with a color reactive chemical or by (B) a gas chromatograph. The technique used must be specific for oxygen.

2. The water content should be determined by (A) supporting the cylinder in an inverted position (valve at the bottom) for 5 minutes. The cylinder and contents should be at room temperature (22°C). The cylinder valve is then opened slightly (USE CAUTION) while the cylinder remains inverted, and the air is vented with a barely audible flow into an open dry container for one minute. (CAUTION: A rapid gas flow may cause any liquid to disperse and not collect in the container.) Any water in the breathing air will condense on the dry container, or by (B) Karl Fischer titration apparatus.

3. The condensed hydrocarbon content should be determined by (A) supporting the cylinder in an inverted position (valve at the bottom) for 5 minutes. The cylinder and contents should be at room temperature. The cylinder valve is then opened slightly (USE CAUTION) while the cylinder remains inverted and the air is vented with a barely audible flow into an open dry container for one minute. (CAUTION: A rapid gas flow may cause any liquid to disperse and not condense in the container.) Any oil in the breathing air will condense on the dry container. (B) scrubbing the air sample with spectral-grade carbon tetrachloride which is then examined by an I.R.

4. The carbon monoxide content should be determined by (A) a gas-cell-equipped infrared analyzer. The I.R. is to be calibrated at appropriate intervals with calibration gas standards at 4.6 microns or by (B) a gas chromatograph specific for carbon monoxide.

5. Odor should be checked directly by smelling of a moderate flow of air from the container being tested. The presence of a pronounced odor should render the air unsatisfactory for breathing purposes.

6. The carbon dioxide content should be determined by (A) a gas-cell-equipped infrared analyzer. The analyzer is to be calibrated with calibration gas standards at 4.3 microns or by (B) a gas chromatograph specific for carbon dioxide.

7. The gaseous hydrocarbon content should be determined by (A) a gas chromatograph with a flame ionization detector. The G.C. is to be calibrated by use of methane gas standards. (B) By a gas cell equipped I.R. The I.R. is to be calibrated with methane standards at 3.5 microns.

8. The nitrogen dioxide content should be determined by (A) a gas cell equipped infrared analyzer. The I.R. is to be calibrated with gas standards at 6.2 microns. (B) by a suitable colorimetric method.

9. The sulfur dioxide content should be determined by (A) a gas cell equipped infrared analyzer. The I.R. is to be calibrated with gas standards at 7.3 microns. (B) by a suitable colorimetric method.

10. The halogenated solvent content should be determined by (A) an electronic halide detector or (B) by a gas-cell equipped I.R.

11. The acetylene content should be determined by (A) a gas cell equipped I.R. The I.R. is to be calibrated with gas standards at 13.7 microns or by (B) a gas chromatograph.

Reference

1. Commodity Specification for Air, CGA Specification G-7.1 Compressed Gas Association Inc., 500 Fifth Avenue, New York, N.Y. 10036.

CARBON MONOXIDE IN AIR AND COMPRESSED AIR TANKS

Abstract

[illegible] spectrophotometry in the 2- to 14-micron range using a long-path gas cell. Compressed air tanks are also analyzed by this method.

APPLICATIONS AND LIMITATIONS

The analytical range extends from 10 to 500 PPM or higher by using an aliquot of the sample. Any gas that absorbs infrared radiation at the analytical wavelength will interfere. But by scanning the complete I.R. spectrum they can usually be detected as having additional absorption lines. Water vapor is removed by use of drying agents on the inlet of the I.R. cell.

APPARATUS

Infrared spectrophotometer, 2- to 15-micron range

10-meter-path-length gas cell

Vacuum pump and manometer

Tedlar or Mylar bags (5 liter or larger)

Gas syringes (100 µl to 1000 µl)

Gas tank regulators

REAGENTS

Drying agent - Drierite or anhydrous calcium chloride

Carbon monoxide tank with known concentration

CO free air

ANALYTICAL PROCEDURE

1. The 10-meter-path-length gas cell is connected to a manometer via a T connection.
2. The gas cell is evacuated to about 1.0 mm Hg.
3. The plastic bag sample is introduced into the cell through a drying tube. Wait 15 minutes for equilibrium to become established.

6b. If a rigid sample container is used, record the equilibrium pressure ($P_{equil.}$) and fill the cell to atmospheric pressure with CO-free air or nitrogen.

6c. If the sample is a compressed air tank, fill the evacuated gas cell to atmospheric pressure with air from the tank.

6. Scan the spectrum from 4-6 microns (2500-1667 cm^{-1}); the absorbance at 4.67 microns (2141 cm^{-1}) is measured by the baseline technique.

5. A calibration curve relating absorbance at 4.67 microns and concentration is prepared for a series of known volumes of CO introduced into the I.R. cell. The procedure is as follows:

Evacuate the gas cell to 1.0 mm Hg, then bring to atmospheric pressure by permitting air to enter via a calibrated wet-test meter.

Evacuate the gas cell again to 1.0 mm Hg; CO is added with the aid of a gas syringe through a rubber septum attached to the gas cell. The pressure is then brought to atmospheric pressure with CO-free air or nitrogen and the absorbance at 4.67 micron is measured for use CO "span gas" of known concentration.

The concentration is calculated from the quantity of CO added and the volume of the cell, i.e., 1 ml of CO, is added and the volume of the cell is 3.85 liters; then

$$\text{PPM CO} \quad \frac{\text{vol. of CO added } (\mu l)}{\text{vol. of I.R. cell (liters)}} = \frac{1000\ \mu l}{3.85} = 260$$

CALCULATIONS

The concentration of the unknown is read from the calibration curve. The observed concentration from the calibration curve is corrected for the volume of sample actually introduced into the gas cell as the following:

$$\text{PPM} = C_{obs.} \times \frac{V_c}{V_s}$$

Where

$C_{obs.}$ = observed concentration from the calibration curve (PPM)

V_c = volume of I.R. cell (liters)

V_s = volume of sample (liters)

For samples introduced from bags or rigid containers with volumes greater than the volume of the I.R. gas cell, $V_s = V_c$, and the sample concentration is C_{obs}. For samples introduced by pressure measurement

$$PPM = C_{obs} \times \frac{P_a}{P_a - P_{equil}}$$

P_a = atmospheric pressure

P_{equil} = equilibrium pressure after connection of the sample container to the I.R. cell.

Reference

1. "Intersociety Tentative Method," Health Laboratory Science, 7, 78 (Jan. Supplement 1970).

FLASH-POINT TESTING WITH PENSKY-MARTENS CLOSED FLASH TESTER

Abstract

This method describes the Pensky-Martens closed flash tester as used in ASTM method D 93-62, test for Flash Point by Pensky-Marten Closed Tester.

APPLICATIONS AND LIMITATIONS

This test is used on fuel oils as well as viscous materials and suspensions of solids. This procedure is not applicable to drying oils, solvent-type liquid waxes or cut-back asphalts. (See ASTM D-1310.)

APPARATUS

Pensky-Martens Tester - AST Specification E-134 (see Figure 9)

Thermometers, Range 20°F to 230°F and 200°F to 700°F.

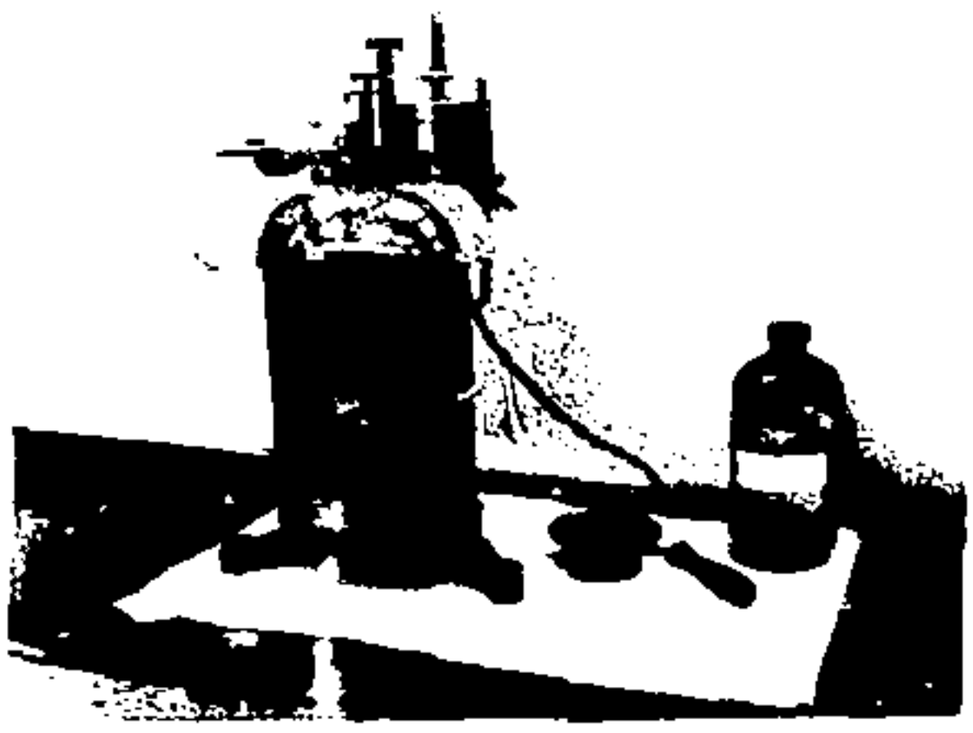

Figure Pensky-Martens Tester

ANALYTICAL PROCEDURE

1. Fill the cup with materi o be tested to the level indicated by the filling mark. Place the on the cup and set cup on the stove and lock into position.
2. Insert the rmometers an eld the test flame.

c. [illegible] apparatus at a rate of [illegible] per minute [illegible] the thermometer is [illegible]

d. Apply a test flame by operating the [illegible] control knob, so that flame is [illegible] the vapor space of the cup. Return [illegible] lowest position for [illegible] application.

e. Repeat the flash test [illegible] at which a distinct flash [illegible] the inside of the cup. Sometimes the test flame [illegible] surrounded with a bluish haze as the flash point temperature is approached. Do not confuse the true flash with this [illegible].

CALCULATIONS

Observe and record the barometric pressure. For each 2 mm below the 760 mm barometric reading, add 1.0 F to the flash point. For each 25 mm above 760 mm, subtract 1.0 F from the flash point.

References

1. ASTM 1965 Book of Standards, D93 Standard Method of Test for Flash Point by Pensky-Martens Closed Tester.

MOCA [illegible]

[illegible] procedures on the analysis of [illegible] 1971, pp. 201-[illegible], and "Meth[illegible] [illegible] Control," [illegible], et al.

*4,4' Methylene bis (2-chloroaniline)

Abstract

Air samples are collected on Whatman No. 41 filter paper, 37-to 0.8-micron cellulose membrane filters, ESI® collectors, or in suitable organic solvents. The oil mist is extracted or washed into an organic solvent and quantitated using either fluorescence, infrared, or ultraviolet spectrophotometry.

APPARATUS

Infrared spectrophotometer with NaCl cells

Fluorescence spectrophotometer

Ultraviolet spectrophotometer with silica cells

ESI® collection kit

Whatman No. 41 filter paper 47-mm size

Cellulose membrane filters 37 mm (0.8 micron)

Assorted laboratory glassware

REAGENTS

Solvents, such as ether, CCl_4, isooctane, chloroform, etc.

Standard oil, from which oil mist is generated (100 mg/ml) - Weigh 10 g of oil into 100 ml of a suitable solvent.

ANALYTICAL PROCEDURE

1. 1- to 100-μg/ml standards of the oil in question are prepared in a suitable solvent.
2. Samples are collected and the oil is extracted, using the solvent used to prepare standards.
3. Spectra are run at the particular wavelength at which the oil has maximum absorbance.
4. The amount of oil is quantitated using the standards for the particular oil by measuring the peak height and plotting this value versus concentration in μg/ml.

CALCULATIONS

$$\mu g/m^3 = \frac{\mu g \text{ of fibers}}{\text{liters of air sampled}} \times \text{dilution factor if any}$$

References

1. Rice, L.M., American Industrial Hygiene Journal, 41, 422 (1980).

2. Cappuccino, M., et al., Arch. Environ. Health, 12, 509 (1966).

ORGANIC SOLVENTS IN AIR

Abstract:

A measured volume of air is drawn through a charcoal tube to trap the organic vapors present. The chemicals are transferred to a graduated cylinder and desorbed with carbon disulfide. An aliquot is then injected into a gas chromatograph and the areas of the resulting peaks are determined and compared with areas obtained from the injection of standards.

APPLICATIONS AND LIMITATIONS

The sampling device is small, portable, and involves no liquids. Interferences are minimal, and most of those which do occur can be eliminated by altering chromatographic conditions. Precision of the analytical method is [illegible].

A disadvantage of the method is that the amount of sample which can be taken is limited by the number of milligrams that the tube will hold before overloading. When the amount of water in the air is so great that condensation occurs in the tube, organic vapors will not be trapped. When two or more solvents are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample, since, with differences in polarity, one may displace another from the charcoal.

It must be emphasized that any compound which has the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention-time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason it is important that a sample of the bulk solvent(s) be submitted at the same time so that identity(ies) can be established by other means.

APPARATUS

Charcoal tubes - Glass tube with both ends flame sealed, 7 cm long with a 6-mm OD and a 4-mm ID, containing two sections of 20/40 mesh activated charcoal separated by a 2-mm portion of urethane foam. The activated charcoal is prepared from coconut shells and is fired at 600 °C prior to packing. The absorbing section contains 100 mg of charcoal; the backup section, 50 mg. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of glass wool is placed in front of the absorbing section.

Gas chromatograph - Equipped with a flame ionization detector.

Column: (20 ft x 1/8 in.) with 10% FFAP stationary phase on 80/100 mesh, acid washed DMCS Chromosorb W solid support.

Recorder with disc integrator for determining peak areas.

Hamilton syringes—10 µl, and convenient sizes for making standards.

Pipets, glass, 10-ml size.

Graduated cylinders, 10-ml size for making standard solutions.

REAGENTS

Spectrograde carbon disulfide

Bulk sample of the compound under study.

Helium, Grade A

Hydrogen, prepurified

Compressed air, filtered

ANALYTICAL PROCEDURE

1. *Preparation of samples.* Each charcoal tube is scored with a file in front of the first section of charcoal and broken open. The glass wool is removed and discarded. The charcoal in the first (larger) section is transferred to a 10-ml graduated cylinder. The separating section of foam is removed and discarded; the second section is transferred to another graduated cylinder. Ten ml of CS_2 is added to each graduated cylinder.

2. GC conditions. The typical operating conditions for the gas chromatograph are:

   A. 65 cc/min (70 psig) helium gas flow

   B. 65 cc/min (24 psig) hydrogen gas flow to detector

   C. 500 cc/min (30 psig) air flow to detector

   D. 200°C injector temperature

   E. 200°C manifold detector temperature

   F. Isothermal oven or column temperature—refer to Table III for specific compounds.

3. Injection. The first step in the analysis is the injection of the sample into the GC. To eliminate difficulties arising from blowback or distillation within the syringe needle, one should employ the solvent flush injection technique. The 10 µl syringe is first flushed with solvent several times to wet the barrel and plunger. The needle is then

TABLE III

Organic Solvent Parameters

Organic Solvent	Range or Limits (mg/sample) Lower	Upper	Min. Sample Vol.(a)	GC Column Temperature(°C)	Molecular Weight
Benzene	0.01	10	0.5	90	78.1
Carbon tetrachloride	0.20	10 (est)	10	60	154.0
Chloroform	0.10	10 (est)	0.5	80	119
p-Dioxane	0.05	10 (est)	1	100	88.1
Ethylene dichloride	0.05	10 (est)	1	90	99.0
Methyl ethyl ketone	0.01	8	0.5	80	72.1
Styrene	0.10	15	1.5	150	104
Tetrachloroethylene	0.06	21	1	130	166
1,1,2-trichloroethane	0.05	10	10	150	133
1,1,1-trichloroethane (Methyl Chloroform)	0.05	11	0.5	150	133
Trichloroethylene	0.05	13	1	90	131
Toluene	0.01	12	0.5	120	92.1
Xylene	0.02	10	0.5	100	106

(a) Minimum volume, in liters, required to measure 0.1 times the OSHA limit. Maximum volume in all cases is 10*l*. All volumes quoted assumed at 760 mm Hg and 25°C.

immersed in the sample and a 5-µl aliquot is withdrawn, taking into consideration the volume of the needle, since the sample in the needle will be completely injected. After the needle is removed from the sample and prior to injection, the plunger is pulled back a short distance to minimize evaporation of the sample from the tip of the needle. Duplicate injections of each sample and standard should be made. No more than a 3% difference in area is to be expected.

4. Measurement of area. The area of the sample peak is measured by an electronic integrator or some other suitable form of area measurement, and preliminary results are read from a standard curve prepared as discussed below.

5. Calibration of standards. It is convenient to express concentration of standards in terms of mg/10 ml CS_2 because samples are desorbed in this amount of CS_2. The density of the specific compound is used to convert mg into microliters for easy measurement with a microliter syringe. A series of standards, varying in concentration over the range of interest, is prepared and analyzed under the same GC conditions and during the same time period as the unknown samples. Curves are established by plotting concentration in mg/10 ml CS_2 versus peak area.

   Note: Since no internal standard is used in the method, standard solutions must be analyzed at the same time that the sample analysis is done. This will minimize the effect of known day-to-day variations during the same day of the FID response.

CALCULATIONS

1. Read the weight, in mg, corresponding to each peak area from the standard curve for the particular compound. No volume corrections are needed, because the standard curve is based on mg/10 ml CS_2 and the volume of sample injected is identical to the volume of the standards injected.

2. Corrections for the blank must be made for each sample.

$$\text{Correct mg} = \text{mg}_s - \text{mg}_b$$

where

mg_s = mg found in front section of sample tube, and

mg_b = mg found in front section of blank tube.

A similar procedure is followed for the backup sections.

3. Add the corrected amounts present in the front and backup sections of the same sample tube to determine the total measured amount in the sample.

4. $$mg/m^3 = \mu g/liter = \frac{\text{total mg} \times 1000}{\text{vol. of air in liters at STP}}$$

Reference

1. White L. D., et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer. Ind. Hyg. Assoc. J., 31: 225 (1970).

COMPOSITION OF COMMERCIAL AND PROPRIETARY PRODUCTS

Abstract

A certain percentage of the laboratory workload is analysis of commercial or proprietary products for determining potential toxic hazards. The chemist may be asked to determine the composition of a solvent free from solids, or he may be given a resin solution or a paint and asked to determine the solvent in which the solid material is dissolved or suspended.

Through his experience and academic training, an analytical chemist has usually gathered a large mental file of information useful in recognizing a compound's characteristics and in evaluating those characteristics. The actual analysis of an unknown almost invariably proceeds on the basis of these value judgments via well-known schemes toward qualitative and quantitative determination of composition.

The Analysis Process

Gathering Initial Observations

Many times the major component of a product can be assumed or inferred from one or more of the following easily gathered sources of information:

1. Name - Usually a trade name but sometimes gives a helpful hint at the major component.

   Example: Tellurac (R. T. Vanderbilt Co.) is an organic salt of tellurium.

   Liqui-Moly (Lockrey Co.) is a molybdenum sulfide lubricant.

   Thiofact (National Aniline Div., Allied Chemical Corp.) is a sulfur containing indigo pigment.

2. Source - Sometimes useful in characterizing chemical class.

   Example: Shell Chemical Co. is famous for petrochemicals, thus, the product is most likely an organic chemical and amenable to infrared and/or gas chromatographic analysis.

   Pennsylvania Glass Sand Corporation products would almost certainly contain silica as a major ingredient.

   Thiokol Chemical Corporation is famous for its polysulfide-based rubber formulations.

5. Use- Often very helpful in determining chemical class.

Examples: Typewriter roller cleaners are used to dissolve inks, so they are usually low-boiling-point organic solvents or solvent mixtures.

Gunpowder solvents almost always contain nitrobenzene or some other nitro product.

Bactericides and algicides for water treatment often contain *quaternary ammonium salts amenable to infrared analysis*

4. Physical Characteristics - Usually very helpful but possibly misleading.

Practically all industrial products are secret formulations purposely doctored in some way to disguise the major constituents and active ingredients.

a. Physical state is the most easily noted physical characteristics and one of the most difficult to mask. It must be remembered, however, that an emulsifying, wetting, or gelling agent can alter the physical state from an immiscible to a miscible liquid, from a suspension to a colloid, or from a liquid to a solid.

b. *Color is only rarely helpful. Most manufacturers use coloring agents* as disguises only too successfully. The very distinctive fluorescent green of fluorescein is evident in a multitude of products from household liquid detergents to industrial leak detectors. In none of these products is fluorescein of any functional use whatever.

c. Smell can often lead to an immediate value judgement for the major component. A sulfur-containing material often smells like H_2S (rotten eggs or SO_2 (a burnt match). Amines smell fishy, esters and higher ketones fruity, and aldehydes musty.

d. Other physical characteristics such as density, melting and boiling point, and index of refraction should not be determined at this point unless a specific compound is already highly suspect.

5. Chemical Characteristics: *These are the most significant properties* yielding the most useful data. The single most important factor to consider in analyzing a commercial product for its constituents is to approach it step by step, by proceeding from the simple to the more complex tests in a meaningful fashion. Many such schemes appear in literature, both for organic and inorganic qualitative analysis.

a. Ignition in a Bunsen burner flame: If it burns completely, boils away, sublimes, or chars in a flame, it is at least partially organic. If it leaves a residue or ash, it is at least partially inorganic. The color of the flame above the sample often indicates which elements are present.

b. Solubility: Though this is strictly speaking a physical characteristic, it is a most helpful dicator of chemical composition. Try water, alcohol, and petrol- m ether as "indicator" solvents. If it is soluble or partially soluble n water, determine the pH. Then make the solution acid and b basic to observe for precipitation, gas evolution, or change in color.

c. Using the acidified olution from the above test, add to one portion one drop 1% $KMnO_4$ to st for reducing agents.

d. To another portion add 5 drops 10% KI--starch to test for oxidizing agents.

e. Metals content and rity: Use the emission spectrograph to determine metals content of s ds and liquids suspected of containing metals. The spectrograph is a good fast tool for determining major constituents metals. A generally weak spectrum showing sodium, calcium, aluminum, iron, and magnesium in small or trace quantities indicates an organic product. The purit of the compound in question can be inferred from the abundance of el ents in small or trace amounts. Most helpful are the phosphorus l boron lines which are so weak that if they show up at all they indic a phosphate or borate in major amounts.

f. Liquid purity and q ation: Use the gas chromatograph for determining the number of c ponents in an organic liquid. The resulting gas chromatogram not only t the number of low-to-medium boiling fractions quickly a ace...tely, but can be saved for future quantitation. Is is also wise to n e the shape of the peak--a long "tail" can be indicative of a pol or nonpolar compound depending upon the column used.

g. *Water content: Ad pinch of anhydrous copper sulfate, shake, and* observe color. If ter is present, the white anhydride turns blue. Of course, all wat solutions reset in this way, but so will water in minor amounts in ganic mixtures. This test is most helpful in determining amena lity to later infrared analysis using NaCl windows.

6. Solvents: Since a subst tial percentage of most commercial products is the solvent, a detailed disc sion is presented here.

Solvents vary widely i in general, the following rules hold:

1. The lower molecul weight alcohols, ketones, and esters are soluble in varying egrees in water. All of these except methanol, ethylene glycol, and glycerine can be separated by saturating the water solution with NaOH or NaCl.

2. The water insoluble alcohols, esters, ketones, ethers, and unsaturated hydrocarbons are soluble in 80% H_2SO_4 (80 ml conc. H_2SO_4 to 100 ml with H_2O). An 80-20 mixture of H_2SO_4 and H_3PO_4 gives essentially the same solubility. Dilution of the acid layer to 3 or 4 times the original volume and addition of Na_2SO_3, causes all of these except the unsaturated hydrocarbons to come out of solution with either reagent. The H_3PO_4 lessens hydrolysis of esters.

3. Aromatic hydrocarbons are almost insoluble in 80% H_2SO_4, but the solubility goes up as the number of alkyl groups increases. Aliphatic hydrocarbons and halogenated aliphatic hydrocarbons are insoluble in 80% H_2SO_4. Trichloroethylene and perchlorethylene, even though they are double-bonded, are not soluble in 80% H_2SO_4.

4. Aromatic hydrocarbons and halogenated aromatic hydrocarbons are soluble in fuming H_2SO_4 (30-33% free SO_2).

5. The aliphatic hydrocarbons and halogenated aliphatic hydrocarbons are insoluble in fuming H_2SO_4 unless they are highly branched. Trichloroethylene and perchlorethylene are slowly soluble in fuming H_2SO_4.

6. The refractive intercept, calculated by taking one-half the specific gravity from the refractive index gives an indication of the type of hydrocarbon present. The value of the refractive intercept is about 1.0649 for all common aromatic hydrocarbons and 1.0460 for all chain aliphatic hydrocarbons. The cyclic aliphatic hydrocarbons have a refractive intercept close to 1.0400.

7. A low refractive intercept indicates a greater specific gravity compared to the refractive index. This value cannot be used to identify types of solvents other than hydrocarbons, since the value varies for each alcohol, ketone, ester, and halogenated hydrocarbon.

8. The dispersion gives an indication of the presence of aromatic hydrocarbons. The value on the scale (Z value) of the Abbe refractometer, manufactured by Bausch and Lomb, is around 23 or 24 for aromatic hydrocarbons, whereas other solvents usually give 17, 18, or 19. On the Zeiss Abbe-type refractometer, the aromatic hydrocarbons give a reading of about 35 and other solvents a reading of about 41.

9. Aromatic hydrocarbons have a specific gravity close to 0.87 and a refractive index close to 1.50.

ANALYSIS

When steam distillation is necessary, the water layer and solvent layer are separated. The cerate test for alcohols (described later) is run on the water layer. If this test is positive and methanol is thought to be present, the layer should be tested for methanol as described later under "Test for Methanol."

Any other components usually found in solvents can be separated from the water layer by saturating the water with NaOH or NaCl.

Any solvent recovered from the water layer is added to the solvent layer and the combined solvent dried thoroughly by adding anhydrous Na_2SO_4 and allowing the solvent to stand overnight. Drying is necessary, since many solvents form azeotropes with H_2O, or the water which distills over is soluble in some of the components, thereby changing the constants.

Solvents which do not require steam distillation are also dried over anhydrous Na_2SO_4.

One hundred ml or more of the dry solvents is distilled through a good fractionating column. A record is kept of the temperature at which the solvent starts to come over and of the temperature when 1 ml, 2 ml, etc., are collected. These data are used to construct a graph of temperature versus cumulative volume. This curve indicates the boiling point of components since, at these boiling points, the volume increases without a corresponding increase in temperature. If the graph is drawn as the distillation proceeds, the fractions can be chosen so that each component is represented by a fraction. Of course, there will also be fractions which are between the steps and are mixtures of components.

Sufficient fractions should be collected so that the change in constants from fraction to fraction can be evaluated.

In addition to these data, it is helpful to have as much data as possible on the original solvent. The following system will give much information which cannot be obtained from distillation.

Determine specific gravity, Z value, and refractive index on the original solvent.

Add 20 ml of the original to a 25-ml graduate, and add 2.0 ml of H_2O and mix thoroughly; read the amount of solvent which is soluble and calculate % solubility. Take the constants (specific gravity, Z value, and refractive index) of the supernatant (insoluble portion). Calculate the constants on the soluble portion. For instance:

Sp. gr. original - (% insol.)(sp. gr. insol.) / (% sol.) = (sp. gr. sol.)

The solvents which are completely extracted by this procedure include acetone, methanol, ethyl alcohol, and both n- and isopropyl alcohol. Any of these, except methanol, can be recovered from the water layer by saturating the water layer with NaOH. In difficult cases, the recovered solvent can be distilled from NaOH, using semimicro methods. The distillate, in most cases, has constants very close to the constants of the pure component.

Besides the solvents which are infinitely soluble in water, there are some like ethyl acetate, butyl alcohol, and methyl ethyl ketone which can be partially extracted with water. Take the part which was left from the first water extraction and add to a 100-ml graduate. Bring to 100 ml with water and mix thoroughly. Determine the solubility and convert to % solubility in terms of the original.

(% sol.)(%insol.) on 1st extraction = % solubility in terms of the original.

Take the constants on the supernatant and calculate the constants on the soluble portion. If you wish, the water layer can be separated and saturated with NaCl to salt out the soluble solvent. If this is done, the recovered solvent can be dried over anhydrous Na_2SO_4 and constants taken, or the material can be distilled.

It is well to remember that the recovered solvent is only part of that which is present. The remainder will be entirely soluble in 80% H_2SO_4 or an 80-20 mixture of H_2SO_4 and H_3PO_4.

The supernatant from H_2O extraction is removed and placed in another graduate. Add an equal volume of 80% H_2SO_4 or an 80-20 H_2SO_4-H_3PO_4 mixture. (The latter causes less hydrolysis of esters, so that by diluting the acid layer to 3 or 4 volumes and saturating with Na_2SO_4, the esters can be recovered along with the other components, except unsaturated hydrocarbons, unchanged.) Mix the acid and solvent thoroughly, and determine % solubility. Calculate what % this is of the original.

(% sol.)(% water insol.) = % in terms of the original.

Take the constants on the supernatant (insoluble in 80% H_2SO_4 or 80-20 H_2SO_4-H_3PO_4) and calculate the constants on the soluble portion.

If the solvent contains turpentine, the acid layer will be red. Esters give an orange color. Alcohols and ketones usually give only a very light yellow.

If esters are present, this is indicated by a higher calculated specific gravity than the specific gravity of alcohols and ketones.

The portion insoluble in 80% H_2SO_4 is recovered and placed in a graduate, and twice as much fuming H_2SO_4(30-33% free SO_3) is added. This is carefully and thoroughly mixed. The % solubility is determined. Calculate what this represents in terms of % of this original. Take the constants on the portion which is insoluble in fuming H_2SO_4 (must be pipetted by vacuum because of the fuming H_2SO_4).

The soluble portion is an aromatic or halogenated aromatic hydrocarbon, and the remainder consists of aliphatic hydrocarbons or halogenated aliphatic hydrocarbons.

Part of the original solvent or parts of the fractions from distillation can be used to test for esters, ketones, alcohols, and halogenated hydrocarbons. (If steam-distilled, the water layer will have to be checked for methanol.)

I. Test for Miscibility

APPARATUS

Graduated cylinders, 25-ml, glass stoppered

Pipettes, 10-ml, volumetric

REAGENTS

Hydrochloric acid, conc.

Sulfuric acid (80% vol.)

Dimethyl sulfate (Caution: Keep off skin.)

ANALYTICAL PROCEDURE

1. Pipette 10-ml sample into dry, tared, graduated cylinder. Weigh and calculate specific gravity.

2. Add 10 ml water and mix gently.

   a. Complete miscibility excludes:

      (1) Saturated aliphatic hydrocarbons

      (2) Aromatic hydrocarbons

      (3) Halogenated, saturated aliphatic or aromatic hydrocarbons

      (4) Organic acids

      (5) Weakly acidic compounds, such as:

         (a) Phenols

         (b) Enols

(c) Primary and secondary nitro compounds

(d) Oximes

(e) Amino acids

(6) Neutral compounds

i Add 10 ml solvent to 10 ml conc. HCl (or 80% H_2SO_4); mix gently by inverting several times. Let settle; note volumes.

a. Complete miscibility includes:

(1) Alcohols

(2) Esters

(3) Aldehydes

(4) Ketones

(5) Unsaturated compounds

(6) Anhydrides

(7) Ethers

(8) Quinones

b. Completely insoluble

(1) Saturated aliphatic and aromatic hydrocarbons

(2) Halogenated saturated aliphatic and aromatic hydrocarbons

i Add, cautiously, 10-ml sample to 10 ml dimethyl sulphate in graduated cylinder; stopper and invert several times (watch for pressure when relieving stopper). Solubility is an index to the aromatic content. If, however, the solubility exceeds 25%, dilute the sample accurately with heptane, benzene, or petroleum ether and repeat.

CALCULATIONS FOR MISCIBILITY

$$\% \text{ miscibility} = \frac{100 \times (\text{vol. orig.} - \text{vol. final})}{\text{vol. orig.}}$$

II. Test for Halogenated Hydrocarbons Using the Beilstein Test

ANALYTICAL PROCEDURE

1. Prepare a small copper wire, supported in a glass tubing handle, with a small loop at the end.
2. Heat the wire until only a yellow flame exists. Do not melt wire; use edge of flame.
3. Cool wire loop. Dip into sample.
4. Heat at the edge of the flame. A green color indicates a halogen.

III. Determination of Aromatic Content by Refractive Index and Dispersion Measurement

APPARATUS

Refractometer, Abbe type

Graph paper, rectangular

REAGENTS

Pure benzene

Pure isooctane (2,2,4 trimethylpentane)

Standards, 20%, 40%, 60%, 80% mixture (by volume) of benzene in isooctane

ANALYTICAL PROCEDURE

1. Determine index of refraction and dispersion values, using the refractometer, for the standards and unknown sample.
2. Plot index versus % aromatic.
3. Determine specific dispersion using the refractometer nomograph and density of samples.
4. Plot specific dispersion.
5. Compute the aromatic composition of unknown, using the two graphs.

IV. Determination of Methyl Ketones

APPARATUS

Spot plate, white

REAGENTS

Acetone

Sample solvent

Sodium nitroprusside, 5%

Sodium hydroxide, 30%

Acetic acid, glacial

ANALYTICAL PROCEDURE

1. Into spot plate depressions, add 1 drop 5% sodium nitroprussside + 1 drop 10% NaOH to a drop of aqueous or alcoholic sample and to a drop of acetone for comparison.
2. After a short time, add 1 or 2 drops acetic acid.
3. A purple color indicates the presence of a methyl ketone.

V. Determination of Esters

REAGENTS

Hydroxylamine, saturated alcoholic solution

Potassium hydroxide, saturated alcoholic solution

Amyl acetate

Hydrochloric acid (0.5N) — Dilute 4.1 ml HCl to 100 ml

Ferric chloride solution (1%) - Dissolve 1 g ferric chloride/100 ml H_2O.

APPARATUS

Crucible, porcelain, 20-ml volume

Micro burner + porcelain triangle

Ring stand for triangle support

ANALYTICAL PROCEDURE

1. To a drop of the unknown in a crucible, add one drop NH_2OH + HCl solution + 1 drop KOH solution. Heat until bubbling begins.
2. Cool, add 1 drop HCl + 1 drop $FeCl_3$.
3. Intense violet indicates the presence of an ester.
4. To a drop of amylacetate, add 1 drop NH_2OH+HCl + 1 drop KOH; heat. Cool, add 1 drop HCl + 1 drop $FeCl_3$. Note color for comparison with sample.

VI. Determination of Alcohols (Ceric Test)

REAGENTS

Ceric nitrate reagent - Dissolve 90 g ceric ammonium nitrate in 225 ml warm 2N HNO_3.

ANALYTICAL PROCEDURE

1. To 2 ml of aqueous solution of unknown in a test tube, add 0.5 ml ceric nitrate reagent. Shake.

2. In the presence of alcohols, glycols, hydroxy acids, hydroxy esters, and hydroxy aldehydes and ketones that contain no more than 10 carbon atoms, the solution changes from a bright yellow to amber, yellow-orange, or red. (Note that phenols produce a green-brown or brown precipitate.)

VII. Determination of Methanol

REAGENTS

Potassium permanganate reagent - Dissolve 3 g $KMNO_4$ in 15 ml 85% H_3PO_4; combined with 85 ml distilled water.

Oxalic acid reagent - Dissolve 5 g oxalic acid in 100 ml 1:1 H_2SO_4

Schiff's reagent, modified - Add 0.2 g of fuchsin to 120 ml of hot water, cool, add a solution of 2 g anhydrous sodium bisulfite in 20 ml of water. Mix thoroughly. Add to mixture 2 ml conc. hydrochloric acid; dilute to 200 ml with water. Store in a well-stoppered brown bottle in the refrigerator. If any residual color remains in the reagent, remove by passing a stream of SO_2 through the reagent.

Standard methanol solution - Dilute 1 [illegible] to 200 ml with deionized water (1 ml equivalent to 5 mg CH_3OH).

APPARATUS

Graduated cylinders, glass-stoppered, 25 ml or 100 ml

Pipettes

ANALYTICAL PROCEDURE

1. To 5ml of unknown (aqueous) in a 25-ml graduated cylinder, add 0.25 ml [illegible]yl alcohol, mix, and add 2 ml $KMNO_4$ reagent.
2. Allow to [illegible] for 10 minutes.
3. Decolorize solution with 2 ml oxalic acid reagent.
4. Add 2 ml Schiff's reagent; mix and allow to set for one hour. Read at 550 m
5. Compare with standard CH_3OH (1-2.5 mg), treated the same way and at the same time.
6. A violet color indicates methanol.
7. If color is too intense, dilute entire sample to 100 ml with water, and read again.

Instrumental analysis and techniques have become extremely helpful in product identification. The following table indicates a possible approach.

Type	Methods to be Tried
Organic liquid	Gas chromatography, infrared analysis of G.C. fractions, fractional distillation, density, refractive index, infrared analysis of fractions.
Organic solid	KBr pellet infrared, Soxhlet extraction, organic qualitative scheme, inorganic cations and anions
Inorganic liquid (Water solution) and inorganic solid	Spectrograph - anion qualitative scheme, atomic absorption
Glues, emulsions, soaps, etc.	Solvent extraction, gas chromatography, infrared analysis, ASTM standard methods

After the analysis of a product, it is sometimes of great value to synthesize it on the basis of the determined constituents. For example, a commerical paint solvent is found to consist of five components, each contributing 20% to the total mixture; a synthetic sample is made and the infrared spectra of the commercial and synthetic samples are compared. Any previously undetected component or any variation in quantitative ratios will be immediately evident.

References

1. Cheronis, N. D., Entrikin, J. B., and Hodnett, E.M., Semimicro Qualitative Organic Analysis, Interscience Publishers, Inc., New Yo. k 1966.

2. Feigl, Fritz, Spot Tests in Inorganic Analysis, translated by Ralph E. Oesper, Elsevier Publishing Company, New York, (5th English Edition), 1962.

3. Feigl, Fritz, Spot Tests in Organic Analysis, translated by Ralph E. Oesper, Elsevier Publishing Company, New York (6th English Edition), 1960.

4. Lange, N. A., Handbook of Chemistry, McGraw-Hill Book Co., New York (Revised Tenth Edition, 1967).

5. Handbook of Chemistry and Physics, Chemical Rubber Publishing Co., Cleveland (52nd Edition, 1972).

6 Conley, Robert T., Infrared Spectroscopy, Allyn and Bacon, Inc., Boston (1966).

7. Bellamy, L. J., The Infra-red Spectra of Complex Molecules, John Wiley & Sons, Inc., New York (2nd Edition 1966).

WATER DETERMINATION IN GASES, SOLIDS, AND ORGANIC SOLVENTS

Abstract

Water in various samples is determined by Karl Fischer titration using the Precision Scientific Company Auto-Aquatrator.

APPLICATIONS AND LIMITATIONS

The Karl Fischer reagent, consisting of a mixture of pyridine, sulphur dioxide, iodine, and methanol reacts with water to give a resistance charge due to the depolarization effect on the electrode. The Auto-Aquatrator conductometric titration eliminates errors of colorimetric-type end points, records true constant end points, and permits titration of suspension or colored solutions.

APPARATUS

Precision Auto-Aquatrator, follow manufacturers setup procedures.

Glass syringe, Hamilton No. 705, 0-0.05 ml

REAGENTS

Karl Fischer reagent, Harleco No. 3786 or equivalent

Karl Fischer water standard, 1 mg H_2O/ml Harleco No. 1849 or equivalent

Karl Fischer solvent mixture diluent, Harleco No. 3796 or equivalent.

Methanol, spectroanalyzed or equivalent.

ANALYTICAL PROCEDURE - DIRECT TITRATION METHOD

In the direct titration mode, Karl Fischer reagent is added automatically to a moisture-bearing sample until a moisture-free state is reached.

1. Set selector to "direct adjust" and adjust meter to full scale with "Direct Adjust" knob.
2. Set selector to "Direct Titration" and set meter low set point (left red needle) to 8 μamps. Set meter high set point (right red needle) to 15 μamps.
3. Set "End Point Hold" to 30 seconds.
4. Fill Karl Fischer burette.

5. *Pour 25 ml methanol solution in the reaction vessel so as to cover the* electrode tip.

6. Turn on stirrer and stir slowly.

7. Add enough Karl Fischer reagent until a dark brown color is reached.

8. Inject 50 µl of water so either a yellow color appears or the current drops. Stopper the opening and vacuum-purge the vessel with the pump switch provided.

9. Press "start" button and allow unit to titrate to the end point.

10. The system is now ready for calibration (step 11) or running of actual samples. (step 12).

11. For calibration, the following method is followed.

    a. A microliter syringe (1 µl = 1 mg) is weighed before and after water introduction into sample vessel for the actual weight of water dispensed.

    b. The solution is titrated with Karl Fischer reagent and the volume recorded.

    c. Karl Fischer titer = $\frac{\text{mg water introduced}}{\text{volume of KF reagent}}$

12. A weighed amount of sample is introduced to the reaction vessel and the solution is then titrated with Karl Fischer reagent and the volume recorded.

CALCULATIONS

Sample weight = $\underline{A}$ mg.

Total volume of KF reagent required to reach end point = $\underline{B}$ ml

KF titer = $\underline{C}$ $\frac{\text{mg } H_2O}{ml\ KF}$ (from calibration step)

So mg water in sample = $\underline{B} \times \underline{C} = \underline{D}$

% water in sample = $\frac{\underline{D} \times 100}{\underline{A}}$

Reference

1. Operating instruction Manual for Precision Auto-Aquatrator, Precision Scientific Co., Chicago, Illinois, 1972.

SECTION D

CALIBRATION OF FIELD INSTRUMENTS

Abstract

In recent years a large variety of electronic monitoring instruments have been developed for measuring concentrations of chemical air contamination. These are secondary measuring devices that possess many potential sources of error and as such must be calibrated often. This section gives the overall procedures for calibration of the field instruments currently in use at *Sandia Laboratories*.

Calibration of field instruments may be defined as the determination of the actual values of the scale readings of that particular instrument. Instrument calibration includes three variables: (a) instrument reading or indication; (b) quantity of contaminant in the air; and (c) quantity of air sampled. To correlate these factors, a microchemical laboratory and analytical chemists are essential since minute quantities of chemicals are involved in the analysis.

Methods of producing known vapor concentrations are batch or static systems and dynamic or continuous flow systems. Most all of the instruments used by the field group at Sandia Laboratories can be calibrated by the static system so it will be the only one discussed here. In static systems, calculated amounts of gas or liquid are introduced into a 5-liter glass bottle or a 5-liter flexible inert plastic bag and then diluted with an appropriate amount of clean air. The instrument to be calibrated is then hooked up to the system and the meter reading is noted. The calculations for preparation of static mixtures are based upon the Perfect Gas Law.

$$\text{For gas concentrations, PPM} = \frac{\text{vol. of test gas in mixture in liters}}{\text{vol. of mixture in liters}} \times 10^6$$

$$\text{For volatile liquids, PPM} = \frac{(V_{ml})\,(\text{density})\,\frac{22.4}{\text{M.W.}} \times \frac{1}{273} \times \frac{760}{P} \times 10^6}{\text{vol. of containers in liters}}$$

where

t = temperature in degrees kelvin

P = pressure, torr

21

CALIBRATION OF J-W MODEL GPK COMBINED OXYGEN/ COMBUSTIBLE GAS DETECTOR

Johnson-Williams Products, Bacharach Instrument Company, 2300 Leghorn Street
Mountain View, California 94040. (See Figure 10)

The model GPK is a combined oxygen/combustible gas indicating detector. The oxygen meter reads directly in the range 0-25% oxygen. The combustibles meter reads 0-1.0 of the lower explosive limit (L.E.L.).

ANALYTICAL PROCEDURE

1. With instrument off, set both meter pointers to zero on the scales.
2. Turn the function switch to the Volt Test position. The oxygen and combustible meters should both deflect upscale and the integral sampling pump should come on.
3. Allow instrument to warm up for 5 minutes and then pull upwards on the Oxygen Calibrate knob and adjust meter pointer to indicate 21% oxygen on the scale.
4. Use the Volt Adjust Knob to set meter pointer on the combustibles scale on the green arrow ("Set Voltage Mark").
5. Turn the Function Switch on the ON position and use the ZERO ADJUST to set combustibles pointer to zero on the scale.
6. Prepare a known amount of the gas or vapor that is to be measured in the static system.
7. Connect the static system to the detector and observe the meter readings.
8. Repeat for 2 or 3 different gas or vapor concentrations and prepare calibration curves.

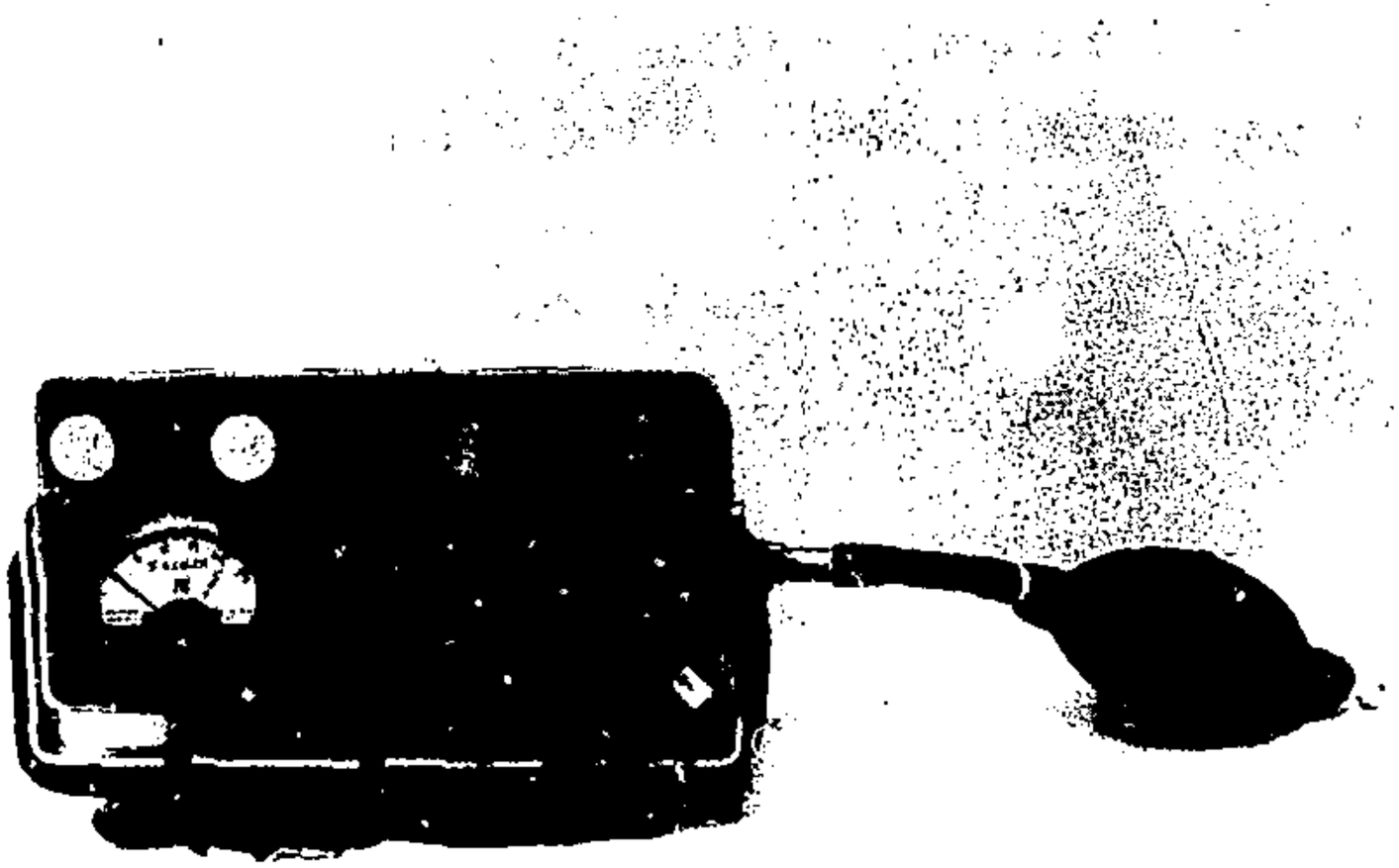

Figure 10. Model GPK Combined Oxygen/Combustible Gas Indicating Detector

CALIBRATION OF J-W MODEL SS-P SUPERSENSITIVE INDICATOR

Johnson-Williams Products, Bacharach Instruments Company, 2300 Leghorn Street, Mountain View, California 94040 (See Figure 11)

The model SS-P is a portable instrument for measuring combustible gas concentrations. On its 0-1000 PPM scale, it can measure concentrations at or below TLV levels. Concentrations in the explosive range can be measured on the 0-1.0 L.E.L. scale.

ANALYTICAL PROCEDURE

1. With instrument off, set meter pointer to zero on the scale.
2. Turn instrument on by turning selector switch to *VOLT CHK*. The pump should start and the meter will go upscale, giving an indication of battery voltage.
3. Allow instrument to warm up for 5 minutes and turn selector switch to EXPL position. Set meter to zero by means of the EXPL zero adjust control.
4. Prepare a known amount of the gas or vapor that is to be measured in the static system.
5. Connect the static system to the detector and observe the meter readings.
6. Repeat for 2 or 3 different gas or vapor concentrations and prepare a calibration curve.
7. For checking very low concentrations, purge detector and reset zero carefully. Move selector switch to PPM position and adjust to zero using PPM zero adjust control.
8. Repeat steps 4, 5, and 6 with low concentrations of gas or vapor to be tested.

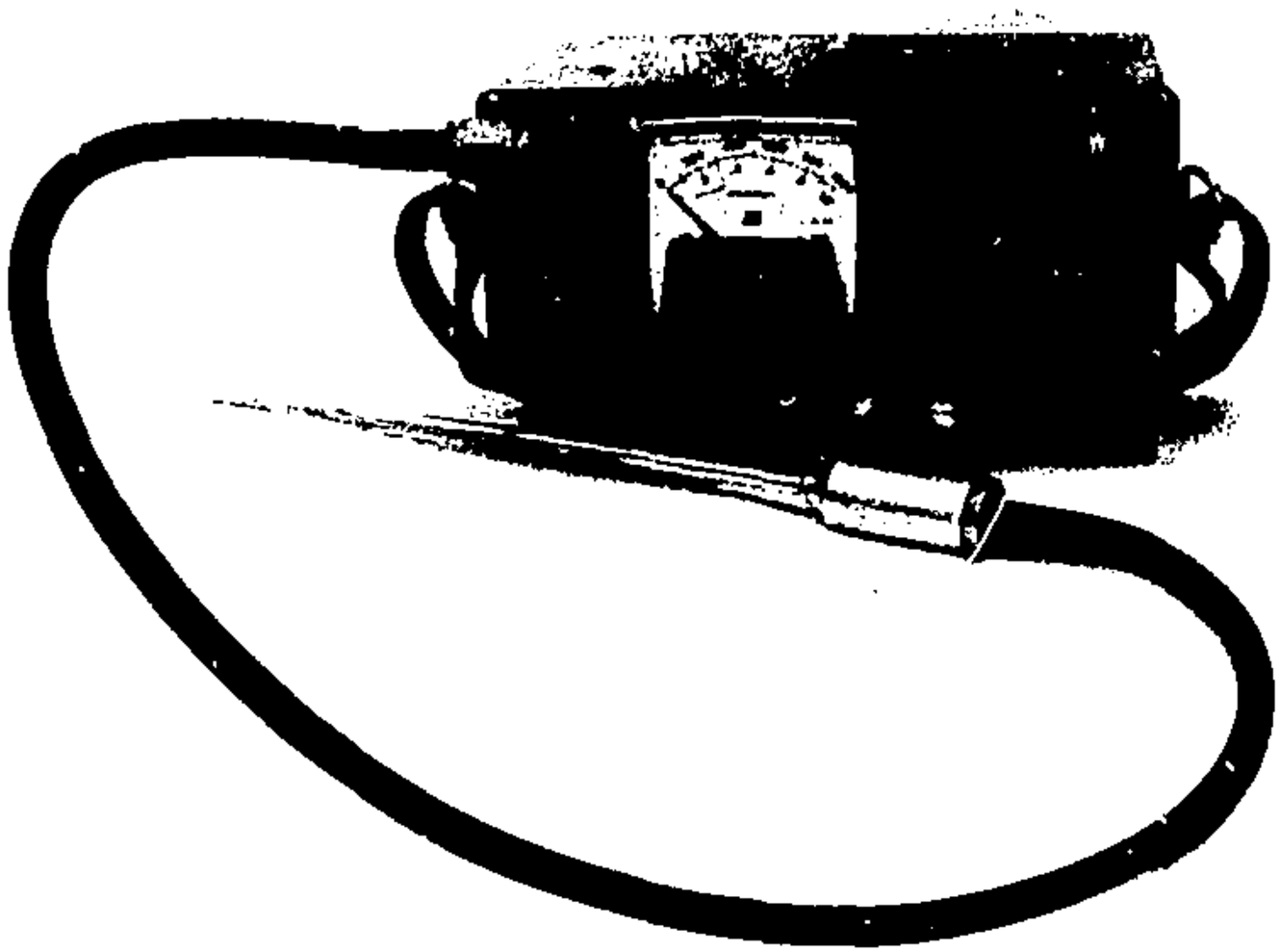

Figure 11. SS-P Supersensitive Indicator

CALIBRATION OF J-W SENTINEL INDICATOR-ALARM

Johnson-Williams Products, Bacharach Instruments Company, 2300 Leghorn Street,
Mountain View, California 94040

The Sentinel Indicator-Alarm is a portable instrument for measuring combustible gas concentration. It uses a diffusive type of detector, which is exposed to the ambient atmosphere. Concentration in the explosive range can be measured on the 0-1.0 L.E.L. scale. The sensing head can be operated at distances of up to 15 feet from the Sentinel, using an extension cable. It also contains an alarm circuit which activates an audible warning when the alarm setting is exceeded.

CALIBRATION OF MSA PORTABLE CARBON MONOXIDE INDICATOR

Mine Safety Appliance Company, 201 North Braddock Ave.,
Pittsburgh, Pennsylvania 15208 (See Figure 12)

The MSA's Portable Indicator is a battery-powered instrument designed to measure carbon monoxide in the atmosphere in a range of 0-500 PPM by volume. It also comes with a battery-operated alarm unit.

ANALYTICAL PROCEDURE

1. With instrument OFF, set meter pointer to zero on the scale.
2. *Turn instrument to ON position and allow the instrument to warmup* for 10 minutes.
3. During warmup, adjust the flowmeter to 4 on the scale.
4. After warmup, zero the meter by adjusting zero control with a small screwdriver.
5. Depress the sample inlet valve fitting. At the same time, slide the meter cover to the right, over the inlet fitting. The meter cover holds the inlet valve in SAMPLE position, while exposing the entire *meter scale ready for sample monitoring.*

   (NOTE: Readjust the sample flowmeter, if necessary, to keep the float control at 4 on the scale.)
6. Prepare a known amount of CO in the static system.
7. Connect the static system to the detector and observe the meter readings.
8. Repeat for 2 or 3 different CO concentrations and prepare a calibration curve.

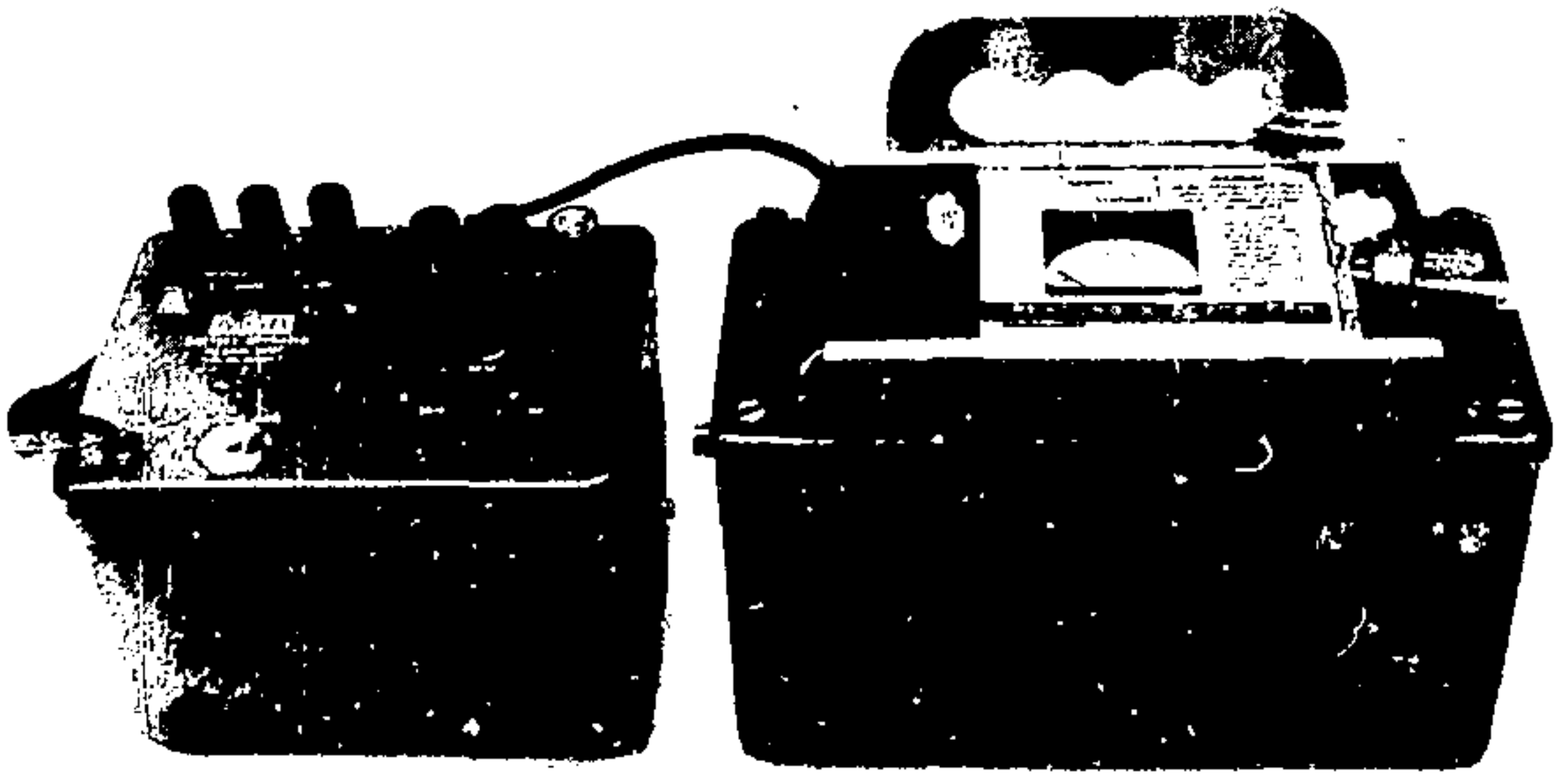

Figure 12, MSA Portable Carbon Monoxide Indicator

CALIBRATION OF J-W MERCURY VAPOR SNIFFER

Lacharach Instrument Company, 625 Alpha Drive, RIDC Industrial Park,
Pittsburgh, Pennsylvania (See Figure 13)

The J-W Model MV-2 Mercury Vapor Sniffer is a dual-range portable instrument for the detection and measurement of mercury vapor. The indicating meter is calibrated in 0-1.0 mg/m^3 and 0-0.2 mg/m^3.

ANALYTICAL PROCEDURE

1. With instrument OFF, set meter pointer to zero on the scale.
2. Turn control knob to "V" position.
3. Turn the "Ambient/Filtered Air" knob to the "Filtered Air" position.
4. Turn control knob to the "1.0" position and allow a 2-minute warmup period.
5. Unlock the clutch on the "Zero Adjust" knob and adjust meter pointer to zero. Use "Course Zero Adjust" if the pointer will not adjust to zero.
6. Turn "Ambient/Filtered Air" knob to "Ambient Air" position.
7. Prepare a known amount of mercury in the static system.
8. Connect the static system to the detector and observe the meter readings.
9. Repeat for 2 or 3 different mercury concentrations and prepare calibration curves for both meter ranges.

Figure 13. J-W Model MV-2 Mercury Vapor Sniffer

CALIBRATION OF DASIBI MODEL 1003AH O. ONE MONITOR

Dasibi Corporation, 3223 North Verdugo Road,
Glendale, California 91208 (See Figure 11)

The Dasibi ozone monitor continuously measures the ozone concentration in air at PPM levels which can be read directly on the front panel by a digital readout.

ANALYTICAL PROCEDURE

1. Turn on power switch and let instrument warmup for 15 to 30 minutes.
2. Open front panel door and move FUNCTION switch to SPAN.
3. Verify that the displayed number corresponds to the number which is set into the four AUTO SPAN SET switches in the access panel.
4. Return the FUNCTION switch to OPER.
5. Calibrate instrument by preparing a known ozone concentration and observing the displayed number. (A procedure for preparing a known concentration of ozone is listed on page 173).

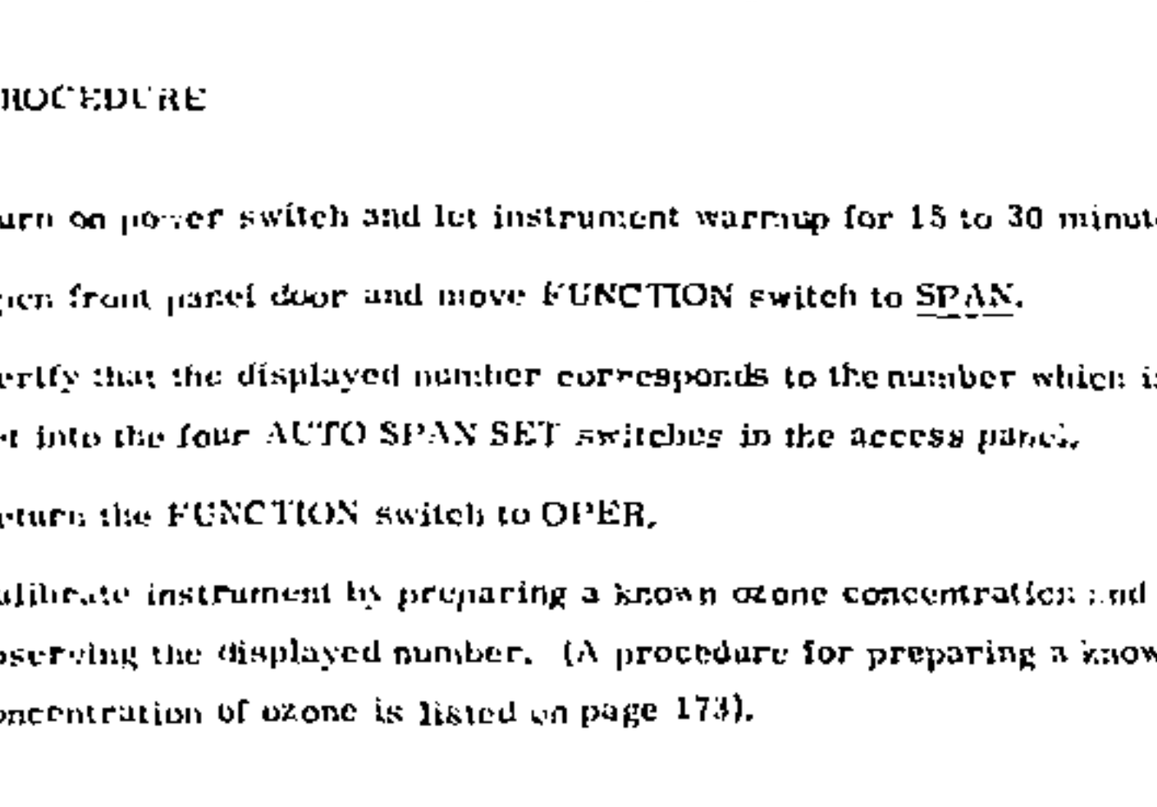

Figure 11. Dasibi Model 1003AH Ozone Monitor

23

CALIBRATION OF OZONE METERS
(Titration Method)

Abstract

Ozone is absorbed in potassium iodide and the iodine released is titrated with standard sodium thiosulfate.

APPARATUS

Midget bubbler, 10 ml volume, all glass (Figure 15)

Ozone Generator, commercial unit or equivalent (Figure 15)

Mixing flask, 1-liter flask with two inlets and one outlet (Figure 15)

Collecting Bags, Saran Plastic Bags - 1.5-liter capacity

Air-metering devices, glass rotameters capable of measuring a flow of 0 to 2 liters per minute, and from 0-100 ml per minute.

REAGENTS

Potassium iodide solution (5%) prepared fresh daily

Starch indicator solution - Dissolve 1 g soluble starch in 100 ml of boiling distilled water

Hydrochloric acid, 1:1 in distilled water

Sodium thiosulfate (0.01N) - Dissolve 2.5 g $Na_2S_2O_3 \cdot H_2O$ in 1 liter of distilled water. Standardize against I_2 or $K_2Cr_2O_7$.

Potassium dichromate, 0.1N, 5 g dried (130°C for 2 hours) $K_2Cr_2O_7$ dissolved in 1 liter of distilled water.

$$N = \frac{\text{wt } K_2Cr_2O_7}{49.04}$$

Double distilled water, used for all reagents. To distilled water in an all-glass still, add a crystal each of $KMnO_4$ and $Ba(OH)_2$, and redistill.

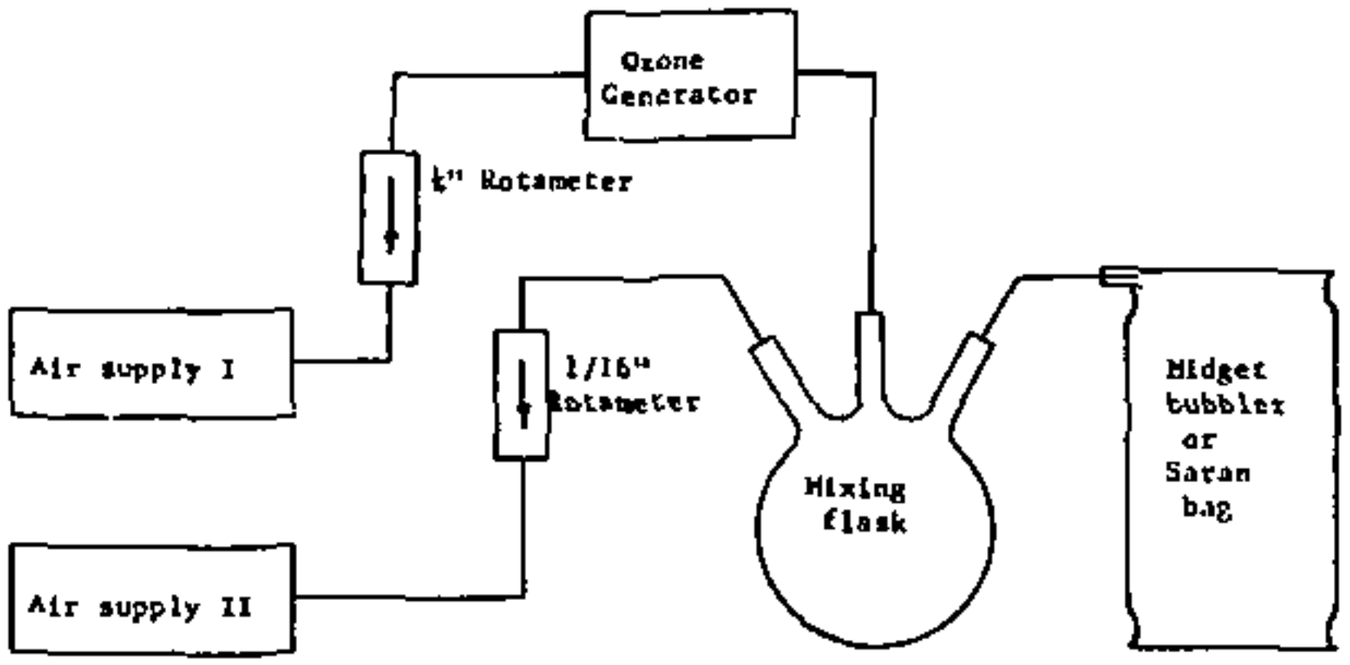

Figure 15. Schematic Of The Ozone Generation System

ANALYTICAL PROCEDURE

1. Allow ozone meter to reach operating conditions (30 minutes).
2. Set the voltage dial on ozone meter to 90. Adjust air supply I to read 800-900 ml per minute and air supply II to read 70-80 ml per minute.
3. Set pot dial at 0 and allow 5 minutes for generator to reach operating condition.
4. Collect a sample in 10 ml freshly prepared KI for 5 minutes, add teflon stirring bar, and place on magnetic stirrer.
5. Add 1 ml 1:1 HCl + 1 ml starch indicator.
6. Titrate with standard thiosulfate to the colorless end point.
   1 ml 0.01N $Na_2S_2O_3$ = 0.24 mg ozone.
7. With generator settings unchanged, connect Saran bag to outlet and collect for 5 minutes.
8. Use ozone in bag to calibrate ozone meter.
9. Set pot dial from 1-9 and repeat Steps 4 through 7.

STANDARDIZATION OF THIOSULFATE

Dissolve 5 g KI + 4 g $NaHCO_3$ in 300 ml H_2O; add slowly 1:1 HCl until no more CO_2 is released, then add 10 ml excess 1:1 HCL. Add 35 ml 0.1N $K_2Cr_2O_7$ and mix thoroughly. Add stirring bar and place on magnetic stirrer. With stirring,

titrate with thiosulfate to a light yellow. Add 1 ml starch indicator and titrate until the blue is replaced with the pale color of $CrCl_3$.

OTHER METHODS

H. H. Bovee, "Determination of Trace Concentration of Ozone by Use of P-Sodium Diphenylamine," Ind. Hyg. News Rept., 3, No. 7, July 1960.

Measurement of Air Pollutants, Division of Air Pollution, U.S. Public Health Services, Publication No. 99-AP-11, May 1965.

CALIBRATION OF DAVIS HALIDE INSTRUMENT

Scott Aviation-Davis Instruments, P.O. Box 751, Rt. 29 North,
Charlottesville, Virginia 22902

The Davis Halide Meter is used for field detection and measurement of halogenated hydrocarbons in the 0- to 500-PPM range.

ANALYTICAL PROCEDURE

1. With instrument OFF, set meter pointer to zero on the scale.
2. Turn AC switch to ON position and allow instrument to warmup for 15 minutes.
3. Adjust flow indicator to green or black line by means of "sample knob." Alternately depress and release "Arc" starter button if arc has not started.
4. Push "Key" down and turn filter valve to "Test."
5. Turn DC switch to "ON" and adjust meter pointer to zero using the "Zero Key Down" knob.
6. Release "Key" and adjust meter pointer to zero by using the "Zero Key Up" knob.
7. Turn filter valve to "Run."
8. Prepare a known amount of the gas or vapor that is to be measured in the static system.
9. Connect the static system to the detector and observe the meter reading.
10. Repeat for 2 or 3 different gas or vapor concentrations and prepare calibration curve.

CALIBRATION OF GASTECH HALIDE DETECTOR

Johnson Instrument Division, Gastech, Inc., 2560 Wyandotte Street,
Mountain View, California 94040 (See Figure 16)

The GasTech Halide Detector is a portable instrument for detection and measurement of all airborne halogen compounds.

ANALYTICAL PROCEDURE

1. With instrument OFF, set meter pointer to zero on the scale.
2. Put RANGE switch in the 10 position and turn instrument ON. Press SPARK ON button to start spark.
3. Adjust flowmeter to register within the light band and let instrument warm up for 15 minutes.
4. Insert sampling line into charcoal filter on back of case and adjust meter pointer to zero. Put range switch into 3 position and then into 1 position, carefully adjusting zero each time.
5. Prepare a known amount of the gas or vapor that is to be measured in the static system.
6. Connect the sampling line to the static system and observe the meter readings on each scale.
7. Repeat for 2 or 3 different gas or vapor concentrations and prepare calibration curve.

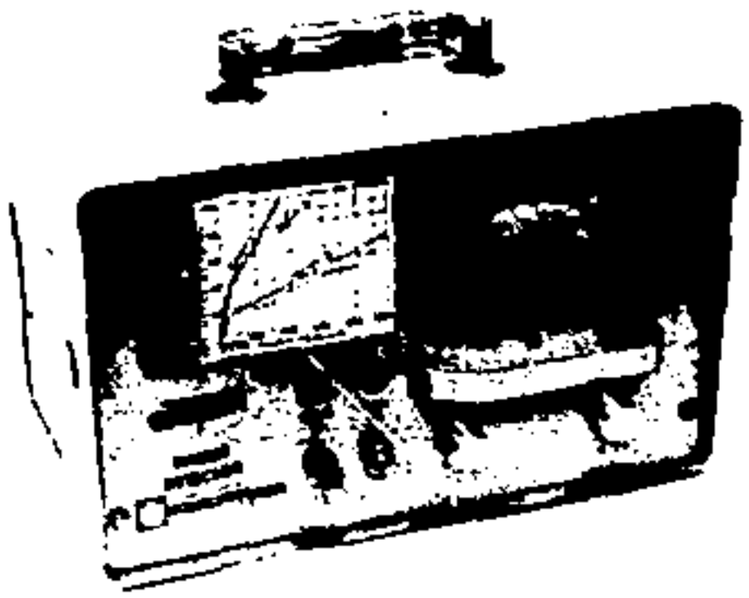

Figure 16. Gastech Halide Detector