EPA–670/2–74–007
March 1974

Environmental Protection Technology Series

Physical, Chemical, and Microbiological METHODS OF SOLID WASTE TESTING Four Additional Procedures

National Environmental Research Center
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

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Physical Chemical and Microbiological
METHODS OF SOLID WASTE TESTING

Four Additional Procedures

by Nancy S. Ulmer

Program Element No 1DB064

SOLID AND HAZARDOUS WASTE RESEARCH LABORATORY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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REVIEW NOTICE

The National Environmental Research Center, Cincinnati, U.S. Environmental Protection Agency, has reviewed this report and approved its publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment – air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In May 1973, the Solid and Hazardous Wastes Research Laboratory published a manual "Physical, Chemical, and Microbiological Methods for Solid Waste Testing" (EPA 6700-73-01). It was not intended to be a complete manual, but the first edition of a growing collection of methods used to characterize refuse, compost, incinerator residues and wastewaters, landfill leachates, and related water samples. This publication is the first manual supplement and presents for the first time procedures for determining (a) chloride in solid wastes, incinerator wastewaters, landfill leachates, and related water samples; (b) total phosphate in solid wastes; and (c) total and orthophosphate in refuse extracts, landfill leachates, and related water samples.

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LABORATORY PROCEDURE FOR DETERMINING THE CHLORIDE CONTENT OF INCINERATOR WASTEWATERS, LANDFILL LEACHATES, AND RELATED WATER SAMPLES

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DISCUSSION

The significance of chloride ion as a solid waste characteristic becomes apparent when one considers the impact of the discharge of highly reactive incinerator waters and landfill leachates to the environment. The direct effect of chloride on the receiving medium is, of course, a chemical degradation. Indirect effects, biological in nature, may also occur. Thus, a knowledge of the chloride content of incinerator scrubber, quench, and clarifier wastewaters; landfill leachates; and related water samples is of value to those persons developing and evaluating water treatment processes in solid waste management systems.

Chemists have employed a variety of titrimetric, potentiometric, and colorimetric methods for the determination of chloride in water and wastewater (1, 2). The procedure recommended here is a mercuric nitrate titration. In the pH range of 2.3 to 2.8, diphenylcarbazone indicates the end point of the titration by forming a deep purple complex with excess mercuric ion. The error in the titration is about 1 percent of the titrant volume used per change of 0.1 pH unit, in the pH range of 2.1 to 2.8.

EQUIPMENT

1. Balance, analytical, 0.1-mg readability
2. Bar, magnetic stirring, approximately 14 mm (9/16 inch) long
3. Beakers, Pyrex, 250-ml
4. Blender, e.g., Waring® no. 700
5. Bottles, liquid storage, Pyrex, amber, 1-gal (~ 3.8-liters), with screw-cap lid
6. Bottles, reagent, Pyrex, amber, 500-ml
7. Bottles, reagent, Pyrex, 250-ml and 1-liter
8. Bottle, weighing; low form; cylindrical with standard taper cap; height, 30 mm; inside diameter, 60 mm
9. Buret, 50-ml, with a fine tip, dispensing drops 0.025 ml or less in volume
10. Buret, micro, 5-ml, with a fine tip, dispensing drops 0.01 ml or less in volume
11. Desiccator, either Pyrex or small stainless-steel cabinet-type
12. Filters, cellulose ester, 0.45μ-pore size, 47-mm-diameter (e.g., Millipore Corp. type HA)
13. Filter holders, hydrosol stainless, (e.g., Millipore Corp. no. XX20-047-20)
14. Flasks, filtering, Erlenmeyer form with side arm, 250-ml
15. Flasks, volumetric, 500-ml, 1-liter, and 2-liter
16. Meter, pH (e.g., Corning, Model 7 with Corning pH electrode no. 476022 with triple-purpose glass membrane and Corning reference calomel electrode no. 476002 with asbestos junction; a silver electrode, Corning no. 476065, is suggested if the chloride concentration of the unknown solution is low)
17. Pipets, Pyrex, serological, 1-ml and 5-ml
18. Pipets, Pyrex, volumetric, 5-, 10-, 15-, and 20-ml
19. Spatula, stainless-steel (e.g., Scoopula,® Fisher Scientific Co. no. 14-357)
20. Stirrer, magnetic, round (e.g., Fisher Scientific Co. no. 14-511-1)
21. Support, buret
22. Tubing, vacuum (with internal diameter to fit both the side arm of the filtering flask and the vacuum source)
23. Vacuum source

REAGENTS

1. Chloride-free water· If necessary, redistill or deionize distilled water to remove chloride and any interferring ion, such as iron.
2. Diphenylcarbazone bromphenol blue indicator: Dissolve 2.5 g diphenylcarbazone and 0.25 g bromphenol blue in 375 ml 95 percent ethyl alcohol and dilute with same to 500 ml. Store in an amber reagent bottle. (Note: Some analysts employ a diphenylcarbazone indicator containing xylene cyanol FF (1, p. 98). The author prefers the bromphenol blue indicator because its color change (at pH 3) serves as a guide in the pH adjustment of the sample prior to titration, thus, the routine use of a pH meter is eliminated. The final yellow-pink-deep purple color change is generally easier to discern than the blue-purple change of the indicator containing xylene cyanol FF).
3. Nitric acid solution, approximately 3.9 N: To 375 ml chloride-free water, slowly add 125 ml concentrated nitric acid. Cool and store in a 1-liter reagent bottle. (Note: Some analysts recommend a less concentrated nitric acid solution. The use of a 3.9 N acid solution, however, minimizes the dilution of the sample during pH adjustment.)
4. Standard sodium chloride solution, 0.0141 N: Dissolve 0.8241 g analytical reagent grade NaCl (previously dried at 140 C for 1 hour) in chloride-free water and dilute with same to 1 liter.
5. Standard mercuric acid solution no. 1, (0.1410 N): Dissolve 50 g $Hg(NO_3)_2 \cdot H_2O$ in 1800 ml chloride-free water containing 5 ml concentrated nitric acid. Dilute with chloride-free water to 2 liters. Determine the normality of the solution as directed in the Standardization section of this Procedure.
6. Standard mercuric nitrate solution no. 2, (0.0141 N): Dissolve 5 g $Hg(NO_3)_2 \cdot H_2O$ in 200 ml chloride-free water containing 0.5 ml concentrated nitric acid, and dilute with chloride-free water to 2 liters. Determine the normality of the solution as directed in the Standardization section of this Procedure.
7. Buffer solution, pH 2.0 ± 0.02 at 25 C (e.g., Fisher Scientific Co. no. SO-B-96.)
8. Potassium chloride solution, saturated (e.g., Corning no. 477000).

SAFETY PRECAUTIONS

To avoid hazards associated with the titration

1. Wear safety glasses when handling concentrated nitric acid and mixtures thereof.
2. Exercise care in weighing, transferring, and disposing mercuric nitrate solutions because inhalation, ingestion, or contact with the compound may cause mercurial poisoning.

STANDARDIZATION

The normality of a mercuric nitrate solution is determined after titrating triplicate samples of both a water blank and a standard sodium chloride solution, as follows:

Procedure	Comments
1. Place 100 ml of the sample to be titrated with mercuric nitrate solution in a 250-ml beaker.	1. a) If titrating a water blank, use 100 ml of chloride-free water. b) If titrating a standard NaCl solution

with mercuric nitrate solution no. 1 (approximately 0.1410 N), use 25 ml 0.0141 N NaCl diluted to 100 ml with chloride-free water.

c) If titrating a standard NaCl solution with mercuric nitrate solution no. 2 (approximately 0.0141 N), use 5 ml 0.0141 N NaCl diluted to 100 ml with chloride-free water.

2. While gently stirring the contents of the beaker with a magnetic stirrer, add 1 ml diphenylcarbazone bromphenol blue indicator.
3. Slowly add 3.9 N nitric acid dropwise until a yellow color forms.
4. Using the mercuric nitrate solution that is to be standardized, titrate the contents of the beaker to a deep purple end point.

4. a) Use a 50-ml buret with mercuric nitrate solution no. 1 and a 5-ml micro buret with mercuric nitrate solution no. 2.
   b) The pH of the solution should be 2.5 ± 0.1 at the end point.

5. Calculate and record the average volume of titrant required to titrate 100 ml chloride-free water.
6. Calculate the normality of the mercuric nitrate solution as directed in the Calculations section of this Procedure. Average the calculations.

5. In our laboratory, 100 ml chloride-free water usually requires 0.02 ml 0.1410 N or 0.2 ml 0.0141 N mercuric nitrate.
6. The deviation of each individual observation of normality from the average should not exceed 0.0002.

SAMPLE PREPARATION

Physical

Process or tap water, well water, and other groundwater samples are generally analyzed directly without any physical preparation; however, landfill leachates containing soil particles are usually filtered through a Millipore® HA filter using a hydrosol filter holder. In this manner, iron particles, which can interfere with the titration, can be removed without loss of soluble chloride. Incinerator quench, scrubber, and clarifier waters containing insoluble particles of various sizes are usually homogenized in a Waring Blender® prior to analysis. (Filtration of incinerator wastewaters may be applicable, but has not been evaluated in our laboratory.)

Chemical

If a sample contains more than 10 mg sulfite or chromate or 20 mg ferric ion per liter (even after dilution with chloride-free water to an appropriate range of chloride concentration), the analyst should also chemically pretreat the samples as suggested by the American Society for Testing and Materials in Referee Method A of standard D512-67 (2, p. 26-27).

PROCEDURE

Duplicate determinations of a water blank; a standard solution; and an incinerator wastewater, or landfill leachate, or related water sample will be required. The chloride content of two 100-ml aliquots of chloride-free water should be determined as outlined in the Standardization section. The procedure, presented herein, is applicable for the determination of 250 mg (or less) chloride in 100-ml aliquots of a standard or aqueous solution. Smaller aliquots (5 to 50 ml) are generally used to attain measurable chloride concentrations and to avoid color and ionic interferences during titration. (See Method Evaluation section of this Procedure.)

Mercuric nitrate solution no. 1 (approximately 0.1410 N) can be used for titrating 100-ml aliquots containing up to 250 mg chloride. Those aliquots, containing less than 5.0 mg chloride, are best titrated, however, with mercuric nitrate solution no. 2 (approximately 0.0141 N).

Procedure	Comments
1. Place an appropriate aliquot of sample (100 ml or less) in a 250 ml beaker.	1. The aliquot must contain less than 250 mg chloride.
2. Dilute the sample to 100 ml, if necessary, with chloride-free water.	
3. While carefully stirring the contents of the beaker with a magnetic stirrer, add 1 ml diphenylcarbazone bromphenol blue indicator.	
4. Slowly add 3.9 N nitric acid dropwise until a yellow color forms.	
5. Using the appropriate mercuric nitrate solution, titrate the contents of the beaker to a deep purple end point. Record the volume of titrant used.	5. a) Use mercuric nitrate solution no. 1, contained in a 50-ml buret, for 100-ml samples containing 5.0 to 250 mg chloride. b) Use mercuric nitrate solution no. 2, contained in a 5-ml micro buret for 100-ml samples containing less than 5.0 mg chloride.
6. Calculate the concentration of chloride as instructed in the Calculations section immediately below.	

CALCULATIONS

The normality, (N), of either mercuric nitrate solution is calculated as follows:

$$N = \frac{N_1 V_1}{A\text{-}B}$$

where

N_1 = normality of the standard sodium chloride solution
V_1 = ml of standard sodium chloride solution diluted to 100 ml
A = ml of mercuric nitrate solution used to titrate the sodium chloride solution
B = ml of mercuric nitrate solution used to titrate 100 ml chloride-free water.

The concentration of chloride (mg Cl/l) in a sample is calculated as follows:

$$\text{mg Cl/l} = \frac{N(A-.01BC)\,(35.45)\,(1000)}{S}$$

where

N = normality of the mercuric nitrate solution used in the titration
A = ml of mercuric nitrate solution used in the titration
B = ml of mercuric nitrate solution used to titrate 100 ml of chloride-free water
C = ml of chloride-free water used to dilute the sample aliquot to 100 ml
S = ml undiluted sample titrated

METHOD EVALUATION

Interferences

Iodide and bromide are titrated with mercuric nitrate in the same manner as chloride. Zinc, lead, nickel, ferrous, and chromous ions affect the solution and end point colors but not the accuracy unless their individual concentrations exceed 10 mg per 100-ml sample. Only 5 mg copper can be tolerated in a similar volume of sample. Interferences will also occur when more than 1 mg of sulfite or chromate or 2 mg ferric ion is present in a 100-ml sample.

Accuracy

The accuracy of the method was first evaluated by determining the chloride concentration of two aqueous samples, which were provided by the Analytical Quality Control Laboratory, National Environmental Research Center-Cincinnati, U.S. Environmental Protection Agency. The average percent recovery of the chloride concentration of these samples was 100. (See Table 1.) The chloride content of 10-ml aliquots of 13 wastewater samples was also determined before and after adding 5 ml 0.0141 N NaCl. The percent chloride recovery from the Winston Salem, North Carolina, and Boone County, Kentucky, landfill leachates was 96.8 and 100, respectively. The average percent chloride recovery from the 11 Boone County, Kentucky, refuse extracts was 97.9.

Precision

The reproducibility of the observations of the chloride content of incinerator tap water and wastewater samples has been evaluated by calculating the standard deviation and coefficient of variation of the triplicate determinations of each of 20 samples (see Table 2). In each case, the coefficient of variation was 0.02 or less.

The reproducibility of the observations of the chloride content of the refuse extracts, landfill leachates, and related well-water samples was evaluated by calculating the pooled standard deviation and coefficient of variation of groups of duplicate observations. The groupings were based on sample type, and the subgroupings on range of chloride concentration. A review of the data, presented in Table 3, similarly reveals that the coefficient of variation never exceeded 0.02.

TABLE 1
ACCURACY OF THE METHOD

Sample type	Sample source	Lab. No.	% Recovery of added chloride
Aqueous solutions	Analytical Quality Control Lab. (NERC-Cincinnati, U.S. EPA)	Min. 1	100
		Min. 2	100.1
Landfill leachates	Winston Salem, N.C.	70-204	96.8
	Boone County, Ky. (Cell 2D)	73-8	100
Refuse extracts	Boone County, Ky. (Cell 1)	71-120	96.4
		71-173	96.4
		71-125	98.0
		71-128	96.8
		71-130	100.4
		71-133	96.4
		71-135	96.8
		71-138	100.4
		71-140	97.6
		71-145	97.6
		71-160	100

TABLE 2
PRECISION OF TRIPLICATE CHLORIDE DETERMINATIONS OF
WATER SAMPLES FROM INCINERATOR NO. 3, DELAWARE CO , PENNSYLVANIA

Type of sample	Lab. No.	Observed mean, mg Cl/l (M)	Standard deviation (S)	Coefficient of variation (S/M)
Tap or process water	70-56	63.83	1.20	0.02
	70-64	83.68	0.30	0.00
	70-72	75.05	1.36	0.02
	70-80	87.48	0.52	0.01
	70-88	88.16	1.50	0.02
Quench water	70-54	512.4	1.38	0.00
	70-62	1045	2.30	0.00
	70-70	1169	2.65	0.00
	70-78	729.8	1.79	0.00
	70-86	780.5	1.79	0.00
Scrubber water	70-52	1399	1.15	0.00
	70-60	1606	0.00	0.00
	70-68	1816	1.73	0.00
	70-76	1868	3.46	0.00
	70-84	2573	2.87	0.00
Clarifier water	70-50	1348	1.15	0.00
	70-58	1386	1.53	0.00
	70-66	1621	0.00	0.00
	70-74	1683	0.60	0.00
	70-82	2345	2.65	0.00

TABLE 3
PRECISION OF DUPLICATE CHLORIDE DETERMINATIONS OF REFUSE EXTRACTS, LEACHATES, AND WELL-WATER SAMPLES FROM THE RESEARCH LANDFILL OPERATION IN BOONE COUNTY, KENTUCKY

Type of sample	Sample source	Group	No. of samples in group	Range of chloride concentration in mg/l (>)	(≤)	Mean mg Cl/l (M)	Pooled standard deviation (S_p)	Coefficient of variation (S_p/M)
Refuse extracts*	Cell no. 1 refuse	Total	14	1	1000	64.86	0.39	0.01
		Subgroup A	1	1	10	5.90	0.14	0.02
		Subgroup B	11	10	100	52.74	0.39	0.01
		Subgroup C	2	100	1000	161.0	0.50	0.00
Leachates	Cell no. 1 upper pipe	Total	48	10	10000	694.8	4.35	0.01
		Subgroup A	1	10	100	90.00	0.00	0.00
		Subgroup B	44	100	1000	678.8	4.01	0.01
		Subgroup C	3	1000	10000	1123.	8.16	0.01
Leachates	Cell no. 1 lower pipe	Total	38	100	1000	495.8	3.95	0.01
Well water	Well no. 1	Total	18	10	10000	1621.	7.74	0.00
		Subgroup A	3	10	100	83.93	0.40	0.00
		Subgroup B	7	100	1000	417.0	4.31	0.01
		Subgroup C	8	1000	10000	3619.	10.89	0.00
Well water	Well no. 2A	Total	20	1000	100000	8458.	15.04	0.00
		Subgroup A	14	1000	10000	3936.	7.07	0.00
		Subgroup B	6	10000	100000	16800.	31.62	0.00

*Each extract was prepared in the laboratory by suspending 50 g ground, mixed refuse (particles 2 mm or less in diameter) in 750 ml distilled water. After occasional stirring over a 15-hour period, the mixture was filtered. The remaining solid was washed with several 200-ml portions of distilled water and the mixture refiltered each time. The combined filtrates were diluted to 2 liters with distilled water.

ACKNOWLEDGMENTS

The author wishes to thank the staffs of the Process and Disposal Division, Office of Solid Waste Management Programs, and the Landfill Disposal Project, Solid and Hazardous Waste Research Laboratory, NERC-Cincinnati, for supplying the incinerator and landfill water samples, respectively. Special thanks are also extended to Israel Cohen, Monitoring and Analysis Project, for preparing some of the incinerator water samples.

REFERENCES

1. American Public Health Association, American Water Works Association, and Water Pollution Control Federation. Chloride. In: Standard methods for the examination of water and wastewater. 13th ed. Washington, D. C., American Public Health Association, 1971. p. 95-99, 376-380.
2. American Society for Testing and Materials. Standard methods of test for chloride ion in industrial water and wastewater. In: 1969 Book of ASTM standards. pt. 23. D512-67. Philadelphia, 1969. p. 24-31.

LABORATORY PROCEDURE FOR DETERMINING THE CHLORIDE CONTENT OF SOLID WASTES

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DISCUSSION

The significance of chloride ion as a solid waste characteristic becomes apparent when one considers the impact it may have upon processing equipment and on the environment surrounding a processing or disposal site. P. D. Miller et al. have studied the corrosion, pitting, and cracking of incinerator boiler tubes, probes, and wet scrubbers (1). Their analyses clearly demonstrated the presence of ferrous chloride ($FeCl_2$), sodium chloride (NaCl), and potassium chloride (KCl) in boiler-tube deposits and up to 16 percent chloride in the scrubber fan deposits. Their investigations also revealed that the most corrosive salts at 600 F (~316 C) are potassium bisulfate ($KHSO_4$) and potassium pyrosulfate ($K_2S_2O_7$), whereas at 800 to 1000 F (~427 to 538 C) zinc chloride ($ZnCl_2$) and lead chloride ($PbCl_2$) accelerate the corrosion. Since chloride appears to enhance the corrosive action of sulfates, a knowledge of the concentration and distribution of chloride in solid wastes is important to the engineers and scientists responsible for the design, maintenance, and control of incinerator equipment.

The emission of hydrogen chloride gas from incinerator stacks and the leaching of highly reactive chloride ion from municipal refuse and residue in incinerators or landfills may result in environmental pollution. The direct effect of chloride is, or course, a chemical degradation of the receiving medium, but indirect effects, biological in nature, may also occur. Thus, a knowledge of the chloride content of municipal refuse, incinerator residue, wastewaters, stack emissions, and landfill leachates is also important to those persons developing and evaluating gaseous pollutant control measures and water treatment processes in solid waste management systems.

Chemists have employed a variety of analytical procedures to determine the chloride content of the individual components of solid wastes (2-13). Most of the methods recommend that first a sample be oxidized by either (a) wet digestion or (b) combustion in a muffle furnace, Parr Bomb, or Schöniger, Thompson-Oakdale, or similar glass apparatus. A potentiometric, titrimetric, or gravimetric determination of the chloride content then follows after absorption and solution of the products of oxidation.

Since paper is the primary component of solid wastes, the ASTM procedure for chloride in paper was considered (7). Briefly, it consists of ashing a dried sample at 600 C in a muffle furnace. After aqueous solution and dilution of the ash, the chloride content is determined by titration using $AgNO_3$ as titrant and $K_2Cr_2O_7$ as indicator. Since the sensitivity of this procedure is limited to 150 ppm (0.15 mg Cl/g sample) however, the technique is not applicable to solid wastes.

The procedure presented here, developed and evaluated in the Solid and Hazardous Waste Research Laboratory, represents a modification of the techniques used for the determination of chloride in mineral oils (14), epoxy resins (15), and wastewater (16). Briefly, it recommends that a 0.25- to 0.5-g solid waste sample, layered with mineral oil, be combusted under 30 atmospheres O_2 in a combustion cup suspended in a Parr Bomb that contains a carbonate solution. The products of combustion are absorbed by or dissolved in the carbonate solution, transferred with rinsing to a beaker, diluted to 200 ml with distilled water, treated with diphenylcarbazone bromphenol blue indicator, and acidified with dilute nitric acid until a yellow color (pH 3.0) forms. The chloride content is then determined by titrating with 0.0141 N mercuric nitrate until excess mercuric ions are indicated by the formation of a deep purple color (pH 2.5 ± 0.1).

EQUIPMENT

1. Balance, analytical, 0.1-mg readability
2. Bar, magnetic stirring, approximately 14 mm (9/16 inch) long
3. Beakers, Pyrex, 600-ml

4. Bottle, liquid storage, Pyrex, amber, 1-gal (3.8-liters), with screw-cap lid
5. Bottle, reagent, Pyrex, amber, 500-ml
6. Bottles, reagent, Pyrex, 1-liter
7. Bottle, washing-dispensing, polyethylene, 500-ml
8. Bottle, weighing; low form; cylindrical with standard taper cap, height, 30 mm; inside diameter, 60 mm
9. Buret, 25-ml, with fine tip, dispensing drops 0.025 ml (or less) in volume
10. Calorimeter, Parr Adiabatic, Series 1200; with a self-sealing, 360-ml stainless-steel, oxygen bomb with double valve (Parr no. 1101); an oxygen-filling connection (Parr no. 1823); stainless-steel capsules (Parr no. 43AS); and 26-gauge platinum fusion wire (Parr no. 43A); a platinum-lined or tantalum-lined bomb and nickel capsules are suggested if numerous determinations are to be performed over a long period of time.
11. Cloth, aluminum oxide, fine (e.g., Norton Alox®cloth, no. 120 or 150)
12. Cylinder, graduate, Pyrex, 25-ml
13. Desiccator, either Pyrex or small stainless-steel cabinet-type
14. Dishes, aluminum, moisture, 89- x 50-mm, with tightly fitting lids (e.g., Arthur H. Thomas Co., no. 3840-F30)
15. Flasks, volumetric, Pyrex, 2-liter, 1-liter, and 500-ml
16. Forceps, dissecting, with straight sharp points (e.g., Fisher Scientific Co., no. 8-880)
17. Meter, pH (e.g., Corning, Model 7, with Corning pH electrode no. 476022 with triple-purpose glass membrane and Corning reference calomel electrode no. 476002 with asbestos junction; a silver electrode, Corning no. 476065, is suggested if the chloride concentration of the unknown solution is low)
18. Oven, forced draft, capable of maintaining a set temperature within the 75- to 105-C range over a 4-hour period (e.g., Precision Scientific Co., Model 18)
19. Pipets, Pyrex, serological, 1-ml and 5-ml
20. Policemen, rubber, for glass rods, 4.8 mm (3/16 inch) in diameter
21. Press, pellet, with a 12- to 19-mm-(1/2- to 3/4-inch) diameter punch and dye set (e.g., Parr press no. 2811 with punch and dye set no. A33PR or Carver Lab Press, Model B, and a 19-mm-diameter punch and dye set, made in machine stop)
22. Rods, stirring, glass, 4.8 mm (3/16 inch) in diameter
23. Spatula, stainless-steel (e.g., Scoopula,® Fisher Scientific Co. no. 14-357)
24. Stirrer, magnetic, round (e.g., Fisher Scientific Co. no. 14-511-1)
25. Support, buret
26. Support, gas cylinder, safety (e.g., Fisher Scientific Co. no. 10-595)
27. Support, ringstand, with a cast-iron support ring having a 60-mm (2-3/8 inch) I.D.
28. Syringe, Luer, Tuberculin, Pyrex, 1-ml, with 1/100-ml subdivisions
29. Wool, steel, fine (gauge no. 0000)
30. Wrench, for opening hand wheel on oxygen tank

REAGENTS

1. p-Chlorobenzoic acid, M. P. 239-241 C, 22.64 percent chloride by weight: Dry the solid at 105 C for 1 hour and store in a desiccator until used as a standard in the evaluation of the entire procedure.
2. Squibb mineral oil, extra heavy
3. Chloride-free water: If necessary, redistill or deionize distilled water to remove chloride and any interferring ion, such as iron.

4. Sodium carbonate solution, 2 percent: Dissolve 40 g anhydrous Na_2CO_3 in chloride-free water and dilute with same to 2 liters. Store in two 1-liter reagent bottles.
5. Oxygen, produced by rectification of air, cylinder size 1A (244 cu. ft.)
6. Nitric acid solution, approximately 3.9 N: To 375 ml chloride-free water, slowly add 125 ml concentrated nitric acid. Cool and store in a 1-liter reagent bottle. (Note: Other procedures recommend a less concentrated nitric acid. The use of a 3.9 N acid solution will, however, minimize sample dilution during pH adjustment.)
7. Diphenylcarbazone bromphenol blue indicator: Dissolve 2.5 g diphenylcarbazone and 0.25 g bromphenol blue in 375 ml of 95 percent ethyl alcohol and dilute with same to 500 ml. Store in an amber reagent bottle. (Note: Some analysts employ an indicator containing 0.25 g s-diphenylcarbazone and 0.03 g xylene cyanol FF in 100 ml of 95 percent ethyl alcohol. The author prefers the indicator with bromphenol blue because the color change (at pH 3) serves as a guide in the pH adjustment of the sample before titration; thus, the routine use of a pH meter is eliminated. The final yellow-pink-deep purple color change (during the titration) is generally easier to discern than the blue-purple change of the indicator containing xylene-cyanol FF).
8. Standard sodium chloride solution, 0.0141 N: Dissolve 0.8241 g analytical reagent grade NaCl (previously dried at 140 C for 1 hour) in chloride-free water and dilute with same to 1 liter.
9. Standard mercuric nitrate solution, 0.0141 N: Dissolve 5 g $Hg(NO_3)_2.H_2O$ in 200 ml chloride-free water containing 0.5 ml concentrated HNO_3, and dilute with chloride-free water to 2 liters. Store in a 1-gal amber bottle. Determine the normality of the solution as directed in the Standardization section of this Procedure.
10. Buffer solution, pH 2.0 ± 0.02 at 25 C (e.g., Fisher Scientific Co., no. SO-B-96).
11. Potassium chloride solution, saturated (e.g., Corning No. 477000).

SAFETY PRECAUTIONS

The high pressure and explosive reaction employed in the combustion of the sample need not be hazardous if the analyst observes the following precautions:

1. Limit the total sample weight (solid waste plus oil) to 1 g; i.e., do not use a quantity of sample that will liberate more than 10,000 calories of heat. If the calorific value of a solid waste is unknown, determine the value before proceeding with the chloride determination.
2. Do not charge the bomb with more than 30 atmospheres of oxygen. If overcharging occurs, release the bomb pressure gently and recharge. Never fire an overcharged bomb.
3. Keep all parts of the bomb, especially the insulated electrode assembly, clean and in good repair. Do not fire a bomb if gas is leaking from the bomb when submerged in water.
4. Stand away from the calorimeter during and immediately after (15 seconds) firing the bomb.

To avoid the chemical hazards associated with the titration:

1. Wear safety glasses when handling concentrated nitric acid and mixtures thereof.
2. Exercise care in weighing, transferring, and disposing mercuric nitrate solutions because inhalation, ingestion, or contact with the compound may cause mercurial poisoning.

STANDARDIZATION

The normality of the mercuric nitrate solution is determined after titrating triplicate samples of both a water blank and a standard NaCl solution as follows:

Procedure	Comments
1. Place 200 ml of the sample to be titrated with mercuric nitrate solution in a 600-ml beaker.	1. a) Use 200 ml of chloride-free water for a water blank. b) For the standard solution, use 5 ml stock 0.0141 N NaCl solution diluted to 200 ml with chloride-free water.
2. While gently stirring the solution with a magnetic stirrer, add 1 ml of the diphenylcarbazone bromphenol blue indicator.	
3. Slowly add 3.9 N nitric acid dropwise until a yellow color forms.	
4. Using the mercuric nitrate solution, titrate the contents of the beaker to a purple end point. Record the volume of titrant used.	4. The pH of the solution should be 2.5 ± 0.1 at the end point.
5. Calculate and record the average volume of titrant required to titrate 200 ml chloride-free water.	5. In our laboratory, this volume is usually 0.04 ml.
6. Calculate the normality of the mercuric nitrate solution as directed in the Calculations section of this Procedure. Average the three calculations.	6. The deviation of each individual observation of normality from the average should not exceed 0.0002.

SOLID WASTE SAMPLE PREPARATION

A solid waste sample must undergo physical preparation before its characterization is initiated in the laboratory. The sample must be dried to constant weight, preferably in a forced-air or mechanically-convected oven. A temperature of 70 to 75 C should be used to dry municipal refuse or compost; incinerator residue may be dried at 100 to 105 C. The particle size of the dried sample should then be reduced to 0.5 mm (or less) using a hammermill, pulverizer, and laboratory mill. Since samples may absorb moisture during the grinding and mixing process, they should be redried for 4 hours at the previously specified temperature and then stored in a desiccator.

Immediately before initiating an analysis, prepare several 1.0-g pellets of the standard or solid waste sample. (A punch and dye set, 12 to 19 mm in diameter, can be used with a Model B, Carver Laboratory Press, capable of exerting a 7000-lb or 3175 kg load). Store the pellets in a desiccator and remove as required for the determinations.

PROCEDURE

Duplicate determinations of a water blank, an oil blank, and a standard or solid waste sample will be required. The volume of mercuric nitrate solution required to titrate two 200-ml aliquots of

chloride-free water should be determined, as outlined in the Standardization section, steps 1-5. The chloride content of the oil blank and the standard or solid waste sample should be determined as follows:

Procedure	Comments
1. Carefully weigh a steel combustion capsule to the nearest 0.0001 g.	1. a) A capsule should have been previously cleaned with fine steel wool, then rinsed with chloride-free water, dried, and stored in a desiccator until used. b) Use nickel capsules if many chloride determinations are planned over a period of time.
2. If performing a standard or solid waste analysis, add an appropriate portion of a pelletized sample to the capsule and then proceed to step 3.	2. a) Use 0.015 to 0.020 g p-chlorobenzoic acid (standard) or 0.25 to 0.50 g solid waste. b) If performing an oil blank analysis, omit steps 2 and 3 and proceed directly to step 4.
3. Weigh the capsule and solid sample to the nearest 0.0001 g. Determine and record the weight of the solid sample.	
4. Using a 1-ml, Pryex, Tuberculin syringe, flow approximately 0.5 to 0.7 ml extra heavy Squibb mineral oil directly into the capsule, wetting any solid sample present.	4. If performing a standard or solid waste analysis, limit the total weight of the sample plus oil to 1 g; i.e., do not use sample and oil quantities that will liberate more than 10,000 calories of heat.
5. Weigh the capsule and sample(s) to the nearest 0.0001 g. Determine and record the weight of the oil.	
6. Rinse the inner surfaces of the stainless-steel bomb with the 2 percent Na_2CO_3 solution.	6. a) Use 25 ml of solution for the bomb cylinder and 15 ml for the bomb head. b) Support the rinsed bomb head on a ring stand.
7. Place 25 ml fresh 2 percent Na_2CO_3 solution in the bomb cylinder.	
8. Attach the fuse wire to the 4A and 5A electrodes of the bomb head.	8. Detailed instructions are provided in the Parr Instrument Company Manual (17).
9. Place the capsule containing the sample in the base of the 5A electrode.	
10. Bend the fuse wire loop so that it either barely touches the oil-soaked pellet or lies just above the free oil (e.g., in the blank).	
11. Place the bomb head in the cylinder.	11. a) Keep the cylinder upright to prevent any sample loss from the capsule. b) Make sure the sealing ring is in good condition.
12. Screw the bomb cap down thoroughly by hand.	12. The outlet needle valve should be open during this step.

13. Close the outlet needle valve.
14. Remove the inlet valve thumb nut.
15. Attach the union nut of the oxygen-filling tube firmly by hand.
    15. a) Use Parr no. 1823 oxygen-filling connection.
    b) Detailed instructions are provided in the Parr Instrument Company manual (17, p. 20-22).
16. Open the oxygen-filling connection control valve slowly.
    16. a) The oxygen tank valve must have been opened previously with a special wrench.
    b) If the oxygen-filling connection valve is opened too quickly, some of the sample may be blown from the capsule and, thus, prevent complete combustion.
17. Allow the oxygen pressure to rise slowly until the gauge reads 30 atmospheres.
18. Close the oxygen-filling connection control valve.
19. Push the ball knob under the relief knob sideways.
    19. This relieves the gas pressure in the connecting tube.
20. Disconnect the oxygen-filling tube.
21. Replace the thumb nut in the inlet valve.
22. Place the bomb in the bucket so that its feet span the boss at the bottom of the bucket.
23. Attach the thrust terminal to the bomb head.
    23. The lead wire should not extend above the bucket.
24. Lower the bucket into the jacket.
    24. Position the bucket so that the stirrer and handle are in the rear.
25. Add 2000 ml distilled water, at room temperature, to the bucket.
26. Swing the calorimeter cover to the right and lower it using the cam lever.
27. Check to see if the pump and stirrer drive shafts are seated properly.
    27. a) The pump and stirrer shafts should be lowered as far as possible and the pulleys should move freely.
    b) The calorimeter's thermometers are not used in this test and can be removed.
28. With the water inlet tube attached to a cold water source and the discharge tube draining to a sink, open the appropriate valves and turn on the cold water.
    28. Excessive water pressure will cause seepage through the stirring shaft journal into the bucket chamber.
29. After the water begins to drain from the discharge tube, start the stirring motor.
30. WHILE STANDING TO THE SIDE OF THE CALORIMETER, press the ignition button.
    30. a) If ignition occurs, a red light near the ignition button will flash on briefly.
    b) If ignition fails to occur (no red light seen), proceed immediately to steps 32-35, 38-40, and then begin the determination again at step 8.

31. Allow the bomb to stand in the calorimeter for 10 minutes after ignition.
32. Turn off the stirring motor and allow the water to drain from the calorimeter cover.
33. Lift the cam lever, then the calorimeter cover, and swing the latter to the left.
34. Lift the bucket out of the jacket and disconnect the thrust terminal wire.
35. Remove the bomb and gently dry the exterior with a towel.
36. Tilt the bomb 75 to 80 degrees and rotate to wash the inner surfaces with the Na_2CO_3 solution.
37. Stand the bomb upright on a table for 10 minutes to allow the Na_2CO_3 solution to drain to the bottom of the cylinder.
38. Gently and slowly open the outlet needle valve to relieve the pressure.
39. Remove the screw cap.
40. Lift the bomb head and capsule slowly from the cylinder.
41. Inspect the capsule and cylinder for uncombusted sample.
42. Inspect the inner bomb head surface for formation of iron oxide.
43. Wash all interior bomb surfaces and all capsule surfaces with a fine stream of chloride-free water. Collect all washings in a 600-ml beaker.
44. While gently stirring the combined washings in the beaker, add 1.0 ml diphenylcarbazone bromphenol blue indicator.
45. Slowly add 3.9 N nitric acid dropwise until a yellow color forms.
46. Using 0.0141 N mercuric nitrate, contained in a 25-ml buret with a fine tip, titrate the contents of the beaker to a deep purple end point. Record the volume of titrant used.
47. Calculate the concentration of chloride as instructed in the Calculations section of this Procedure.

32. The flow from the discharge tube will return to normal when the cover is drained.

40. If the capsule fell down into the cylinder during step 36, do not remove it until step 43.

41. If the combustion was incomplete, discard the test and proceed to step 48. Repeat the determination beginning at step 1.

42. If a red color is noticeable, the analyst should suspect a high cloride concentration. The test may have to be repeated with a smaller sample.

43. a) A rubber policeman is useful in rinsing the surfaces of the cylinder.
    b) The total volume of all washings should be 200 ml.

44. Use a magnetic stirring device.

46. a) The buret should deliver 0.025-ml drops.
    b) The pH of the solution should be 2.5 ± 0.1 at the end point.

48. Rinse the interior surface of the bomb head and cylinder with additional chloride-free water and set them aside to drain.

49. For each determination, repeat steps 1-48.

50. At the end of a day (or a series of determinations), turn off the cold water.

48. a) Occasionally clean the inner surfaces of the bomb head with fine steel wool (gauge no. 0000) and then rinse with chloride-free water and place in a ring stand support to drain.

b) If the inner surface of the stainless-steel cylinder becomes pitted over a period of time, clean the surface with a fine aluminum cloth (e.g., Alox®cloth no 120 or 150). Rinse surface well with chloride-free water and drain.

CALCULATIONS

The normality (N) of the mercuric nitrate solution is calculated as follows:

$$N = \frac{N_1 V_1}{A\text{-}B}$$

where

N_1 = normality of the standard sodium chloride solution
V_1 = ml of standard sodium chloride solution diluted to 200 ml
A = ml of mercuric nitrate solution used to titrate the sodium chloride solution
B = ml of mercuric nitrate solution used to titrate 200 ml chloride-free water

The percent chloride (% Cl_o) in the oil blank sample is calculated as follows:

$$\% Cl_o = \frac{100\ (N)\ (C\text{-}B)\ (0.03545)}{W_o}$$

where

N = normality of the mercuric nitrate solution
B = ml of mercuric nitrate solution used to titrate 200 ml of chloride-free water
C = ml of mercuric nitrate solution used to titrate the total washings from the combusted oil sample
W_o = grams of oil sample used in this test

The percent chloride (% Cl_s) of a standard or solid waste sample is calculated as follows:

$$\% Cl_s = \frac{100\ N\ (D\text{-}B)\ (0.03545) - \% Cl_o\ (W_o)}{W_s}$$

where

N = normality of the mercuric nitrate solution
B = ml of mercuric nitrate solution used to titrate 200 ml of chloride-free water
D = ml of mercuric nitrate used to titrate the total washings from the combined oil and standard or solid waste sample
% Cl_o = percent chloride in the oil
W_o = grams of oil used in the test
W_s = grams of standard or solid waste used in the test

METHOD EVALUATION

Interferences

Iodide and bromide are titrated with mercuric nitrate in the same manner as chloride. Chromate and sulfite ions interfere when present in excess of 10 mg/l (16, p. 97-98). Concentrations of ferric ions up to 20 mg/l can usually be tolerated. Above that level, ferric ions interfere with the indicator and cause a sliding or delayed endpoint in the titration.

Accuracy

Five p-chlorobenzoic acid samples, ranging in weight from 12 to 25 mg and containing 3 to 6 mg chloride, respectively, were analyzed by using this procedure. The mean percent recovery of the theoretical chloride content was 98.1. Three aliquots of a Boone County, Kentucky, refuse sample (no. 71-130) were also analyzed before and after the addition of 15 to 23 mg p-chlorobenzoic acid. The mean percent recovery of the added chloride was 97.4.

Precision

The reproducibility of the method has been determined by calculating the standard deviation of the replicate determinations of the chloride content of a number of refuse samples. The data are presented in Table 1.

ACKNOWLEDGMENTS

The author wishes to thank Dirk Brunner and the staff of the Landfill Disposal Project for providing the Boone County, Kentucky, refuse samples. Special thanks are extended to Israel Cohen, Monitoring and Analysis Project, for preparing these samples.

Raymond Loebker, Thermal Degradation Project, kindly provided and prepared the Troy, Ohio, refuse samples for analyses.

TABLE I
REPRODUCIBILITY OF THE METHOD

Source of refuse sample	Lab. No.	Number of replicate determinations per sample	Observed mean % chloride	Standard deviation
Boone County, Kentucky	71-120	2	0.43	0.01
	71-123	2	4.48	0.17
	71-125	2	0.28	0.03
	71-128	2	0.12	0.03
	71-130	2	0.29	0.01
	71-133	2	1.16	0.01
	71-135	2	0.25	0.00
	71-138	2	0.36	0.01
	71-140	2	0.30	0.03
	71-142	2	0.20	0.03
	71-145	2	0.62	0.02
	71-155	2	0.92	0.03
	71-158	2	0.76	0.03
	71-160	2	0.49	0.01
Troy, Ohio	72-668	3	0.54	0.04
	72-669	2	0.44	0.01
	72-670	6	0.78	0.02
	72-671	2	0.70	0.01
	72-672	2	0.32	0.04
	73-19	2	0.37	0.01
	73-20	2	0.38	0.01

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LABORATORY PROCEDURE FOR DETERMINING THE TOTAL PHOSPHATE AND TOTAL ORTHOPHOSPHATE CONTENTS OF REFUSE EXTRACTS, LANDFILL LEACHATES, AND RELATED WATER SAMPLES

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DISCUSSION

Orthophosphates, condensed (pyro-, meta-, and poly-) phosphates, and organically-bound phosphorus may occur in natural water and wastewaters. Since phosphorus promotes the growth of algae, its discharge into receiving streams may contribute to the deterioration of water quality and the eutrophication of lakes. A knowledge of the form and concentration of phosphorus in solid waste leachates and other water samples, associated with landfill operations, is therefore important to the scientists and engineers responsible for developing and evaluating solid waste and water quality management systems.

Chemists have employed numerous methods to determine the various phosphorus forms present in water and wastewater (1-10). In general, the procedures are characterized by (1) a conversion of the phosphorus forms of interest to orthophosphate and (2),the determination of the latter by colorimetric, gravimetric, or atomic absorption techniques.

The amino reduction method (2 [sect. 13-21, p. 46-50]; 11) is recommended here for the determination of the orthophosphate content of water and wastewater samples. An aliquot of an unfiltered but appropriately diluted sample is first treated with a sulfuric acid reagent containing bismuth. Ammonium molybdate is then added to form molybdophosphate. The subsequent addition of 1-amino-2-naphthol-4-sulfonic acid results in the formation of molybdenum blue. The absorbance of the latter is measured at 650 nm against the absorbance of a similarly treated distilled water blank. The bismuth in the acid reagent increases the intensity of the blue color fourfold.

When a total phosphate determination is desired, an unfiltered but appropriately diluted sample, contained in an Erlenmeyer flask, is similarly treated with the sulfuric acid bismuth reagent. After the addition of potassium persulfate, the sample is heated to convert the condensed phosphates and organically-bound phosphorus to orthophosphate. The molybdenum blue color of the cooled and appropriately diluted digest is then developed after the addition of ammonium molybdate and amino solutions as previously described. The absorbance of the solution is measured against that of a similarly processed distilled water blank. The observed total orthophosphate concentration serves as a measurement of the total phosphate.

SAFETY PRECAUTIONS

To avoid hazards associated with the maintenance of the glassware and the performance of each analysis:

1. Wear safety glasses when handling concentrated acids or mixtures thereof.

2. Perform all acid digestions in a hood to avoid inhaling acid fumes.

3. Wear asbestos glove while handling hot digestion flasks.

4. Place hot digestion flasks on asbestos mats while cooling their contents.

5. Exercise care in weighing, transferring, and disposing 1-amino-2-naphthol-4-sulfonic acid as its toxological properties have not been fully evaluated.

6. Avoid inhalation of SO_2 vapors during disposal of the final color-reaction mixtures. The sink area should be well ventilated and the tap water running during disposal of the solutions.

EQUIPMENT

Requirements

1. Balance, analytical, 0.0001-g readability
2. Bottles, reagent, 250-ml and 1-liter
3. Bottle, reagent, Pyrex, amber, 1-liter
4. Bottle, washing-dispensing, polyethylene, 500-ml
5. Bottle, weighing; low form; cylindrical with standard taper cap; 30 mm high and 60 mm in diameter
6. Cuvettes, spectrophotometer, matched with 1-cm pathlength
7. Cylinders, graduate, Pyrex, 100-ml, with standard taper stopper; A 105-ml volume mark should be etched on each cylinder with a glass-marking pencil.
8. Desiccator, Pyrex or small stainless-steel cabinet-type
9. Filler, pipet (e.g., Will Scientific Co. no 22105)
10. Flasks, Erlenmeyer, Kimax or Pyrex, 250-ml, with wide mouth
11. Flasks, volumetric, 100-ml and 2-liter
12. Foil, aluminum
13. Gloves, asbestos
14. Hood, capable of removing acid fumes
15. Hot plate, electric (230 volts), rectangular, 12 x 20 inches (~ 30 x 51 cm), with input proportioner and 79- to 510-C temperature range (e.g., Lindberg Hevi-duty hot plate, type H-2, Matheson Scientific Co. no. 28650-20)
16. Mats, asbestos, 12 x 12 inches (~ 30 x 30 cm)
17. Meter, pH (e.g., Corning Model 7, with Corning pH electrode no. 476022 with triple-purpose glass membrane and Corning reference calomel electrode no. 476002 with asbestos junction)
18. Pencil, diamond, for marking glass
19. Pipets, serological, class A accuracy, 5-ml
20. Pipets, volumetric, Pyrex; 1-, 5-, and 10-ml
21. Spatula, stainless-steel (e.g., Scoopula®, Fisher Scientific Co. no. 14-357)
22. Spectrophotometer, operative at 650 nm, with matched cuvettes having a 1-cm pathlength (e.g., Beckman model B spectrophotometer)

Preparation

Soak all glassware in the special cleaning solution (See Reagents section below). Rinse well with distilled water, and dry before using. Avoid contact of glassware with soaps or detergents as they contain phosphates.

REAGENTS

1. Cleaning solution for glassware: Slowly add 250 ml concentrated hydrochloric acid to 750 ml distilled water. Cool before using.
2. Stock organic phosphate solution (21.98 mg PO_4/l): As needed, dissolve 0.1 g anhydrous *beta* sodium glycerophosphate (e.g., $C_3H_7Na_2O_6P \cdot 5\frac{1}{2}\ H_2O$, Fisher Scientific Co. no. 314, previously heated for 1 hour at 105 C to drive off water) in distilled water and dilute with same to 2 liters.

3. Stock inorganic phosphate solution no. 1 (1000 mg PO_4/l): Dissolve 1.433 g KH_2PO_4 (previously dried for 1 hour at 105 C) in distilled water and dilute with same to 1 liter. Store in a 1-liter reagent bottle.
4. Stock inorganic phosphate solution no. 2 (10 mg PO_4/l): Prepare as needed by diluting 10 ml stock inorganic phosphate solution no. 1 to 1 liter with distilled water.
5. Sulfuric acid solution containing bismuth: Slowly add 370 ml concentrated sulfuric acid (S.G. 1.84) to 600 ml distilled water. While the solution is warm, add 4.8 g $Bi(NO_3)_3 \cdot 5H_2O$. Cool the solution to room temperature, and dilute with distilled water to 1 liter. Store in a 1-liter reagent bottle.
6. Potassium persulfate, A.C.S., anhydrous ($K_2S_2O_8$).
7. Ammonium molybdate solution: Dissolve 48 g $(NH_4)_6MO_7O_{24} \cdot 4H_2O$ in 800 ml distilled water. Add 2.5 ml concentrated NH_4OH (S.G. 0.90), and dilute with distilled water to 1 liter.
8. Amino solution: In 500 ml distilled water, dissolve (in order specified) 18.5 g sodium sulfite (Na_2SO_3), 0.500 g 1-amino-2-naphthol-4-sulfonic acid, and 31 g sodium metabisulfite (sodium pyrosulfite, $Na_2S_2O_5$). Store in an amber reagent bottle, wrapped in aluminum foil to exclude light. Prepare fresh once a month.
9. Buffer solution, pH 2.0 ± 0.02 at 25 C (e.g., Fisher Scientific Co. no. SO-B-96).
10. Potassium chloride solution, saturated (e.g., Corning no. 477000).

STANDARDIZATION

The calibration of the method is initiated by developing the molybdenum blue color in eight standard inorganic phosphate solutions that range in concentration from 0.5 to 5.0 mg PO_4/l. After measuring the absorbance of each standard solution against that of a similarly treated water blank, a calibration graph is prepared.

The steps of the calibration procedure are as follows:

Procedure	Comments
1. Prepare a blank sample by transferring 100 ml distilled water to a 100-ml glass-stoppered cylinder.	
2. Prepare eight calibration standards by individually transferring a 2-, 5-, 10-, 15-, 20-, 25-, 30-, 40-, and 50-ml aliquot of standard inorganic solution no. 2 to an appropriately labelled 100-ml glass-stoppered cylinder. Then dilute each with distilled water to 100 ml.	2. The calibration standards contain 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 mg PO_4/l, respectively.
3. Add 5 ml sulfuric acid reagent containing bismuth to each of the nine cylinders. Stopper and invert several times to mix the contents.	3. Use a pipet filler and a clean serological pipet to add each reagent in steps 3-5.
4. Add 5 ml ammonium molybdate reagent to each cylinder. Restopper and invert to mix the contents.	4. A yellowish color forms.

5. Without delay, add 5 ml amino solution to each cylinder. Restopper and invert to mix the contents. Note the time.

6. Fifteen minutes after mixing the samples in step 5, transfer an aliquot of each solution to a spectrophotometer cuvette having a 1-cm pathlength.
7. Measure at 650 nm the absorbance of each standard solution against that of the water blank, set at zero.
8. Prepare a calibration graph (i.e., on regular graph paper plot the absorbance values as ordinates and the phosphate concentrations as abscissas; connect the points).

5. Molybdenum blue begins to form directly upon the addition of this reagent to a standard solution. The color intensity increases within the first few minutes and appears stable after 15 minutes.
6. The color remains stable for at least 25 minutes (i.e. from 15 to 40 minutes after mixing the samples in step 5).

7. The final pH of each developed solution should be 0.65 ± 0.05.

8. The graph should be linear.

SAMPLE PREPARATION

Since the total phosphate and total orthophosphate determinations are performed on aliquots of the total aqueous sample, no sample preparation is required. It is advantageous, however, to minimize the oxidation of a sample (particularly its ferrous iron content) during its collection and delivery to the laboratory. If the collection vessel is quickly and completely filled and then tightly sealed, sample oxidation will be minimized. In this way, the ferric iron concentration may be prevented from rising to the level of interference. (See Method Evaluation Section of this Procedure.)

PROCEDURES

The procedures recommended here are applicable for the direct determination of the total phosphate and total orthophosphate contents of refuse extracts, landfill leachates, and related water samples containing up to 5 mg PO_4/l. The range of applicability has routinely been extended to 100 mg PO_4/l by diluting an appropriate aliquot of the sample to 100 ml before initiating the analysis.

Duplicate determinations of the total phosphate and total orthophosphate contents of a standard or wastewater sample should be performed. A reagent blank should also be processed with each set of samples. The blank for the total phosphate analysis (reagent blank no. 1) measures the color produced by all the reagents and is therefore subjected to both the digestion and the color development. The blank for the total orthophosphate analysis (reagent blank no. 2) measures only the color produced by the reagents used in the color development.

Determination of Total Phosphate

Procedure	Comments
1. Prepare reagent blank no. 1 by transferring 100 ml distilled water to a labelled, wide mouth 250-ml Erlenmeyer flask.	

2. Transfer an appropriate aliquot of a standard solution or wastewater to a labelled wide-mouth 250-ml Erlenmeyer flask.	2. a) An appropriate aliquot contains less than 0.5 mg PO_4. b) A 10-ml aliquot of the stock organic phosphate solution can be used for the standard analysis. c) A pipet filler and clean volumetric pipet should be used to transfer each sample.
3. If necessary, dilute the sample aliquot in the flask to 100 ml with distilled water.	
4. Process a second aliquot of the standard solution or wastewater as directed in steps 2 and 3.	
5. Add 5 ml sulfuric acid reagent containing bismuth to each flask. Mix the contents of the flask by swirling.	5. a) Wear safety glasses while handling acids and mixtures thereof. b) Use a pipet filler and clean serological pipet to add the reagent. c) A sample, containing sulfide, will turn brown on addition of this reagent. If this occurs, modify the procedure as suggested by ASTM. (See Method Evaluation section of this procedure.)
6. Add 0.8 g potassium persulfate to each flask. Mix the contents of the flask by swirling.	6. Previously weighed glassine paper may be used as support while weighing and transferring the potassium persulfate to each flask.
7. Place each flask on a previously heated hot plate.	7. a) Turn hot plate on to maximum heating position 30 minutes prior to use. b) The directions concerning the hot plate apply to the apparatus specified in the Equipment section of this procedure.
8. Using maximum heating, boil the contents of each flask for 40 minutes.	8. a) The sample volume normally decreases to about 10 to 15 ml during the 40-minute digestion. A white precipitate forms if the volume falls below 10 ml. b) If the sample volume falls below 25 ml during the first 35 minutes of the digestion, add distilled water to the sample to maintain a volume between 25 and 100 ml.
9. After digestion is completed, remove each flask from the hot plate.	9. a) Wear asbestos gloves while handling hot flasks. b) Support hot flasks on asbestos mats.
10. Wash down the inner surface of each flask with a fine stream (10 ml) of distilled water.	10. A dispensing-washing bottle can be used to dispense the distilled water.
11. Cool the contents of each flask to room temperature (25 C ±5 C).	11. Cooling is usually completed after 45 to 60 minutes.
12. Transfer the contents of each flask to a correspondingly labelled, 105-ml marked, glass-stoppered cylinder.	

13. Using a fine stream (10 ml) of distilled water, rinse each flask several times. Add each rinse to its corresponding sample, contained in a cylinder.
14. Dilute the contents of each cylinder to 105 ml with distilled water. Stopper and invert to mix the contents.
15. Add 5 ml ammonium molybdate solution to each cylinder. Restopper and invert to mix the contents.
16. Without delay, add 5 ml amino addition to each cylinder. Restopper and invert to mix the contents. Note the time.
17. Fifteen minutes after mixing the samples in step 16, transfer an aliquot of each solution to a spectrophotometer cuvette with a 1-cm pathlength.
18. Measure at 650 nm the absorbance of each standard solution or wastewater against that of reagent blank no. 1, set at zero.
19. Obtain the orthophosphate concentration (mg PO_4/l) of each solution from the calibration graph.
20. If the sample aliquot (used in step 2) was less than 100 ml, calculate the phosphate concentration of the original (undiluted) standard solution or wastewater as directed in the Calculations section of this Procedure.
21. Report the observed total orthophosphate concentration as the total phosphate.

14. Mixing of insufficiently cooled samples may result in excessive generation of heat, expansion of flask contents, and expulsion of both the stopper and acidic solution.
15. a) Use a pipet filler and clean serological pipet to add each reagent in steps 15 and 16.
    b) A yellowish color forms on addition of this reagent.
16. Molybdenum blue begins to form upon the addition of this reagent to the standard solution or wastewater. The color intensity increases within the first few minutes and appears stable after 15 minutes.
17. The color remains stable for at least 25 minutes (i.e., from 15 to 40 minutes after mixing the samples in step 16.)
18. The final pH of each developed solution should be 0.65 ± 0.05.

Determination of Total Orthophosphate

Procedure	Comments
1. Prepare reagent blank no. 2 by transferring 100 ml distilled water to a labelled, 100-ml glass-stoppered cylinder.	
2. Transfer an appropriate aliquot of the standard solution of wastewater to a labelled, 100-ml glass-stoppered cylinder.	2. a) An appropriate aliquot contains less than 0.5 mg PO_4. b) A 10-ml aliquot of stock inorganic phosphate solution no. 2 can be used for the standard analysis. c) A pipet filler and clean volumetric pipet should be used to transfer each sample.

3. Dilute the contents of each cylinder, if necessary, to 100 ml with distilled water. Stopper and invert to mix the contents.	
4. Process a second aliquot of the standard solution or wastewater as directed in steps 2 and 3.	
5. Add 5 ml sulfuric acid reagent containing bismuth to each cylinder. Stopper and invert to mix the contents.	5. a) Wear safety glasses while handling acids or mixtures thereof. b) Use a pipet filler and a clean serological pipet to add each reagent in steps 5-7. c) A sample, containing sulfide, will turn brown on addition of this reagent. If this occurs, modify the procedure as suggested by the American Society for Testing and Materials (ASTM). (See Method Evaluation section of this Procedure).
6. Add 5 ml ammonium molybdate solution to each cylinder. Restopper and invert to mix the contents.	6. A yellowish color forms when this reagent is added.
7. Without delay, add 5 ml amino solution to each cylinder. Restopper and invert to mix the contents. Note the time.	7. Molybdenum blue begins to form upon the addition of this reagent to the standard solution or wastewater. The color intensity increases within the first few minutes and appears stable after 15 minutes.
8. Fifteen minutes after mixing the samples in step 7, transfer an aliquot of each solution to a spectrophotometer cuvette with a 1-cm pathlength.	8. The color remains stable for at least 25 minutes (i.e., from 15 to 40 minutes after mixing the samples in step 7).
9. Measure at 650 nm the absorbance of each standard solution or wastewater against that of reagent blank no. 2, set at zero.	9. The final pH of each developed solution should be 0.65 ± 0.05.
10. Obtain the orthophosphate concentration (mg PO_4/l) of each solution from the calibration graph.	
11. If the sample aliquot (used in step 2) was less than 100 ml, calculate the orthophosphate concentration of the original (undiluted) standard solution or wastewater sample as directed in the following section.	

CALCULATIONS

Since the total phosphate concentration is reported in terms of the total orthophosphate concentration of a sample, the following formula suffices for the calculation of either the total phosphate or total orthophosphate concentration of the original (undiluted) standard solution or wastewater sample.

$$\text{mg } PO_4/l = 100\frac{C}{V}$$

where:

C = mg PO_4/l obtained from the calibration graph

V = ml of sample used in the test

METHOD EVALUATION

Interferences

Studies performed in the Solid and Hazardous Waste Research Laboratory have demonstrated that the color development of a 100-ml sample is not affected by the presence of 100 mg chloride or 50 mg calcium. Ferric iron may delay the color development for a few minutes, but the maximum color intensity is always attained within 15 minutes in the presence of 20 mg ferric iron. The ASTM has reported only a 2 percent error in the analyses of solutions containing silica concentrations fifty times larger than their phosphate concentrations (2, sect. 15, p. 47). Nitrite, several mg sulfide, and >75 mg chromate per liter, however, will interfere with the test. The analyst should use the modifications proposed by ASTM to overcome these interferences (13).

Accuracy

Total phosphate method.

The accuracy of the total phosphate procedure was first evaluated by analyzing four aliquots of three standard solutions of organic phosphates: *beta* sodium glycerophosphate, 3-adenylic acid, and barium fructose 6-phosphate. The average percent recoveries of the theoretical phosphate concentrations of the three solutions were 99.6, 91.3, and 86.3, respectively (See Table 1). Although the phosphate recoveries from the 3-adenylic acid and barium fructose 6-phosphate solutions were lower than the recovery from the *beta* sodium glycerophosphate solution, the observations compare favorably with those of Gales, Julian and Kroner (4).

Four diluted leachate samples were also analyzed before and after the addition of an aliquot of one of the organic phosphate solutions. The percent recovery of phosphate added as 3-adenylic acid (3AA) to two landfill leachates was 92.6 whereas the percent recovery of phosphate added as barium fructose 6-phosphate (BF6P) to the same leachates was 86.7. When aliquots of the *beta* sodium glycerophosphate (BSG) solution were added to four leachates, the percent phosphate recovery varied from 97.1 to 99.1; the average was 98.6. The excellent recovery of phosphate from two leachates, (namely, nos. 71-303 and 73-49) was particularly significant because these samples contained substances that prevented the determination of their total phosphate content by the vanadomolybdophosphoric acid and stannous chloride methods (7, p. 78-93).

Total Orthophosphate method.

The accuracy of the total orthophosphate method was first evaluated by analyzing an inorganic phosphate standard obtained from the Analytical Quality Control Laboratory, National Environmental Research Center-Cincinnati, U.S. Environmental Protection Agency. The percent recovery of the theoretical phosphate concentration was 102. (See Table 2.)

Two diluted leachate samples were also analyzed before and after adding an aliquot of a standard solution of monobasic potassium phosphate (KH_2PO_4). The percent phosphate recovery was 100 in each case. The excellent phosphate recovery from leachate no. 73-49 was particularly significant in view of the 290 mg iron (ferrous and ferric) present in the aliquot analyzed.

Precision

The reproducibility of the observations of the total phosphate and total orthophosphate contents of refuse extracts and landfill leachates was evaluated by calculating the pooled standard deviation and coefficient of variation of groups of duplicate observations. The groupings were based on sample type and source, and the subgroupings, on range of phosphate concentration. A review of the data, presented in Tables 3 and 4, reveals that the coefficient of variation never exceeded 0.03.

ACKNOWLEDGMENTS

The author wishes to thank Dirk Brunner and the staff of the Landfill Disposal Project, Solid and Hazardous Waste Research Laboratory, for supplying the refuse and landfill leachate samples. Special thanks are also extended to Israel Cohen, Monitoring and Analysis Project, for preparing the refuse extracts.

TABLE 1
ACCURACY OF THE TOTAL PHOSPHATE METHOD

Sample Identity	mg PO_4/l diluted sample	Added standard mg PO_4/l	% Recovery standard	
			Observed	Avg.
Standards				
Beta sodium	2.198		100.0	
glycerophosphate	2.198		99.1	
(BSG)	2.198		100.0	
	1.099		99.1	99.6
3-Adenylic acid	1.367		91.4	
(3AA)	1.367		91.4	
	1.367		91.4	
	0.684		91.2	91.3
Barium fructose	1.200		85.6	
6-phosphate	1.200		88.3	
(BF6P)	1.200		84.9	
	0.600		86.6	86.4
Boone Co., Ky., Landfill Leachates				
no. 71-303	2.10			
with BSG		1.099	99.1	
with BSG		1.099	100.0	99.6
no. 72-125	2.59			
with BSG		1.099	99.1	
with 3AA		0.684	92.6	
with BF6P		0.600	86.7	
no. 72-126	1.40			
with BSG		1.099	97.3	
with 3AA		0.684	92.6	
with BF6P		0.600	86.7	
no. 73-49	1.01			
with BSG		2.198	99.1	

TABLE 2
ACCURACY OF THE TOTAL ORTHOPHOSPHATE METHOD

Sample Identity	mg PO_4/l diluted sample	Added standard mg PO_4/l	%Recovery standard
Standard			
Analytical Quality Control Lab. nutrient soln. no. 2	0.975		102
Boone Co., Ky., Landfill Leachates			
no. 73-9	0.170		
with KH_2PO_4		1.100	100
no. 73-49	0.645		
with KH_2PO_4		1.100	100

TABLE 3
PRECISION OF DUPLICATE TOTAL PHOSPHATE DETERMINATIONS OF REFUSE EXTRACTS AND LEACHATES FROM THE RESEARCH LANDFILL OPERATION IN BOONE COUNTY, KENTUCKY

Type of sample	Sample source	Group	No. of samples in group	Range of total PO_4 conc. in mg/l		Mean mg PO_4/l (M)	Pooled standard deviation (S_p)	Coefficient variation (S_p/M)
				>	≤			
Refuse extracts*	Cell no. 1 refuse	Total	14	1	100	20.66	0.25	0.01
		Subgroup A	4	1	10	7.30	0.14	0.02
		Subgroup B	10	10	100	26.00	0.29	0.01
Leachates	Cell no. 1 upper pipe	Total	39	1	100	29.94	0.23	0.01
		Subgroup A	3	1	10	8.43	0.22	0.03
		Subgroup B	36	10	100	31.73	0.24	0.01
Leachates	Cell no. 1 lower pipe	Total	33	1	100	14.41	0.19	0.01
		Subgroup A	9	1	10	6.87	0.13	0.02
		Subgroup B	24	10	100	17.25	0.22	0.01

*Each extract was prepared in the laboratory by suspending 50 g ground, mixed refuse (particles, 2 mm or less in diameter) in 750 ml distilled water. After occasional stirring over a 15-hour period, the mixture was filtered. The remaining solid was washed with several 200-ml portions of distilled water and the mixture refiltered each time. The combined filtrates were diluted to 2 liters with distilled water.

TABLE 4
PRECISION OF DUPLICATE TOTAL ORTHOPHOSPHATE DETERMINATIONS OF LEACHATES FROM THE RESEARCH LANDFILL OPERATION IN BOONE COUNTY, KENTUCKY

Sample source	Group	No. of samples in group	Range of total PO_4 conc. in mg/l		Mean mg PO_4/l (M)	Pooled standard deviation (S_p)	Coefficient of variation (S_p/M)
			>	≦			
Cell no. 1 upper pipe	Total	23	10	100	31.50	0.12	0.00
Cell no. 1 lower pipe	Total	18	1	100	11.53	0.20	0.02
	Subgroup A	10	1	10	6.26	0.14	0.02
	Subgroup B	8	10	100	18.12	0.25	0.01

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LABORATORY PROCEDURE FOR DETERMINING THE TOTAL PHOSPHATE CONTENT OF SOLID WASTES

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DISCUSSION

The significance of phosphorus as a solid waste characteristic becomes apparent when one considers that it is an essential nutrient. Along with nitrogen, phosphorus promotes the growth of algae in streams. Discharging incinerator wastewater and landfill leachates containing phosphorus into receiving streams will contribute to the deterioration of stream water quality and the eutrophication of lakes. A knowledge of the concentration and distribution of phosphorus in solid wastes and related water samples is, therefore, important to the engineers and scientists responsible for the development and evaluation of solid waste and water quality management systems.

Analysts have employed a variety of methods to determine the phosphorus content of solid wastes and related materials (1-11). The condensed phosphates and organically bound phosphorus present in a sample must first be converted to orthophosphate by either ashing or digesting the sample. The total orthophosphate content of the treated and diluted sample is then determined with the use of volumetric, gravimetric, colorimetric, or atomic absorption technique.

The technique outlined here recommends the digestion of 1-g solid waste samples with sulfuric and nitric acids. After the digestion is completed, the sample is cooled, filtered, and carefully diluted. The orthophosphate concentration of an appropriate aliquot of solution is then determined colorimetrically using the amino reduction method (2, p. 46-50). The solution is therefore treated with a sulfuric acid reagent containing bismuth. Ammonium molybdate is added to form molybdophosphate. The latter, in turn, is reduced to molybdenum blue with 1-amino-2-naphthol-4-sulfonic acid. The bismuth salt in the acid reagent provides a fourfold increase in the intensity of the blue color.

SAFETY PRECAUTIONS

To avoid the physical and chemical hazards associated with the maintenance of the glassware and the performance of each analysis:

1. Wear safety glasses when handling concentrated acids and mixtures thereof.
2. Perform all acid digestions in a hood to avoid inhalation of fumes.
3. Wear asbestos gloves while handling hot flasks.
4. Avoid contact of skin, clothing, metal, and painted surfaces with the molybdate reagent as it is corrosive.
5. Exercise care in weighing, transferring, and disposing 1-amino-2-naphthol-4-sulfonic acid as its toxicological properties have not been fully evaluated.
6. Avoid inhalation of SO_2 vapors when disposing of the final color-reaction mixtures. The sink area should be well ventilated and tap water should be running during disposal of the solutions.

EQUIPMENT

Requirements

1. Apparatus, digestion, micro-Kjeldahl, with six individual heaters and controls (e.g., Fisher Scientific Co. no. 21-131-5)
2. Balance, analytical, 0.0001-g readability
3. Bottles, reagent, Pyrex, 250-ml and 1-liter

4. Bottle, reagent, Pyrex, amber, 1-liter
5. Bottle, washing-dispensing, polyethylene, 500-ml
6. Bottle, weighing, low form, cylindrical with standard taper cap, 30 mm high and 60 mm in diameter
7. Cuvettes, spectrophotometer, matched, with 1-cm pathlength
8. Cylinders, graduate, Pyrex, with standard taper stopper, 100-ml
9. Desiccator, Pyrex or small, stainless-steel, cabinet-type
10. Dishes, aluminum, moisture, 89- x 50-mm, with tightly fitting lids (e.g., Arthur H. Thomas Co., no. 3840-F30)
11. Dispenser, tilting, with 25-ml reservoir, for use with 500-ml Erlenmeyer flask (e.g., Lab. Glass, Inc., no. LG-7915)
12. Filler, pipet (e.g., Will Scientific Co. no. 22105)
13. Flask, Erlenmeyer, 500-ml, with 20/40 ground glass neck to receive tilting dispenser
14. Flasks, Kjeldahl, micro, 100-ml (e.g., Scientific Glass Blowing Co. no. SGB-16350)
15. Flasks, volumetric, 100-ml and 1-liter
16. Foil, aluminum
17. Funnel, filtering, Pyrex, 65 mm in diameter, with 60° angle and short stem
18. Gloves, asbestos
19. Hood, capable of removing acid fumes
20. Meter, pH (e.g., Corning Model 7 with Corning pH electrode no. 476022 with triple-purpose glass membrane and Corning reference calomel electrode no. 476002 with asbestos junction)
21. Oven, forced-draft, capable of maintaining a 70- to 75-C temperature over a 4-hour period
22. Paper, filter, Whatman no. 7, 12.5-cm diameter
23. Paper, glassine
24. Pipets, serological, Pyrex, class A accuracy, 5-ml
25. Pipets, volumetric, Pyrex, 1-, 5-, and 10-ml
26. Spatula, stainless-steel (e.g., Scoopula®, Fisher Scientific Co. no. 14-357)
27. Spectrophotometer, operative at 650 nm; with cuvettes having a 1-cm pathlength (e.g., Beckman model B spectrophotometer)
28. Support for funnels, 65 mm in top diameter

Preparation

Soak all glassware in the special cleaning solution (see Reagent section in this Procedure). Rinse well with distilled water, and dry before using. Avoid contact of glassware with soaps and detergents as they contain phosphates.

REAGENTS

1. Cleaning solution for glassware: Slowly add 250 ml concentrated hydrochloric acid to 750 ml distilled water. Cool before using.
2. *Beta* sodium glycerophosphate, ACS. Heat $C_3H_7Na_2O_6P.5\text{-}1/2\ H_2O$ (e.g., Fisher Scientific Co. no. S-314) for 1 hour at 105 C to drive off water. Store in a desiccator. The dried solid contains 43.96 percent phosphate (PO_4) by weight.

3. Stock inorganic phosphate solution no. 1 (1000 mg PO_4/l): Dissolve 1.433 g KH_2PO_4 (previously dried for 1 hour at 105 C) in distilled water and dilute with same to 1 liter. Store in a 1-liter reagent bottle.
4. Stock inorganic phosphate solution no. 2 (10 mg PO_4/l): Prepare as needed by diluting 10 ml stock inorganic phosphate solution no. 1 to 1 liter with distilled water.
5. Sulfuric acid, concentrated, ACS. (S.G. 1.84).
6. Nitric acid, concentrated, ACS.
7. Sulfuric acid reagent containing bismuth: Slowly add 370 ml concentrated sulfuric acid (S.G. 1.84) to 600 ml distilled water. While the solution is warm, add 4.8 g $Bi(NO_3)_3 \cdot 5H_2O$. Then cool the solution to room temperature and dilute with distilled water to 1 liter. Store in a 1-liter reagent bottle.
8. Ammonium molybdate solution: Dissolve 48 g $(NH_4)_6MO_7O_{24} \cdot 4H_2O$ in 800 ml distilled water. Add 2 5 ml concentrated NH_4OH (S.G. 0.90), and dilute with distilled water to 1 liter.
9. Amino solution: In 500 ml distilled water, dissolve (in order specified) 18.5 g sodium sulfite (Na_2SO_3), 0.500 g 1-amino-2-naphthol-4-sulfonic acid, and 31 g sodium metabisulfite (sodium pyrosulfite, $Na_2S_2O_5$). Store in an amber reagent bottle that has been wrapped in aluminum foil to exclude light. Prepare fresh once a month.
10. Buffer solution, pH 2.0 ± 0.02 at 25 C (e.g., Fisher Scientific Co. no. SO-B-96).
11. Potassium chloride solution, saturated (e.g., Corning no. 477000).

STANDARDIZATION

The calibration of the method is initiated by developing the molybdenum blue color in eight standard inorganic phosphate solutions, ranging in concentration from 0.5 to 5.0 mg PO_4/l. After measuring the absorbance of each standard solution against that of a similarly treated water blank, a calibration graph is prepared.

The steps of the calibration procedure are as follows:

Procedure	Comments
1. Prepare a blank sample by transferring 100 ml distilled water to a 100-ml glass-stoppered cylinder.	
2. Prepare eight calibration standards by individually transferring a 2-, 5-, 10-, 15-, 20-, 25-, 30-, 40-, and 50-ml aliquot of standard inorganic phosphate solution no. 2 to an appropriately labelled 100-ml glass-stoppered cylinder. Then dilute each with distilled water to 100 ml.	2. The calibration standards contain 0.2, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 mg PO_4/l, respectively.
3. Add 5 ml sulfuric acid reagent containing bismuth to each of the nine cylinders. Stopper and invert several times to mix the contents.	3. Use a pipet filler and a clean serological pipet for each of the three reagents added in steps 3-5.
4. Add 5 ml ammonium molybdate reagent to each cylinder. Restopper and invert to mix the contents.	4. A yellowish color forms.

5. Without delay, add 5 ml amino solution to each cylinder. Restopper, invert to mix, and note the time.	5. Molybdenum blue begins to form upon the addition of this reagent to a standard solution. The color intensity increases within the first few minutes and appears stable after 15 minutes.
6. Fifteen minutes after mixing the sample in step 5, transfer an aliquot of each solution to a spectrophotometer cuvette having a 1-cm pathlength.	6. The color remains stable for at least 25 minutes (i.e., from 15 to 40 minutes after mixing the sample in step 5).
7. Measure at 650 nm the absorbance of each standard solution against that of the water blank, set at zero.	7. The final pH of each developed solution should be 0.65 ± 0.05.
8. Prepare a calibration graph (i.e., on regular graph paper, plot the absorbance values as ordinates and the phosphate concentrations as abscissas. Connect the points.)	8. The graph should be linear.

SOLID WASTE PREPARATION

A solid waste sample must undergo physical preparation before its characterization is initiated. First, most of the glass and the metallic and magnetic iron particles are removed manually. Then the waste is dried to a constant weight in a forced-air or mechanically convected oven. A temperature of 70 to 75 C is used to dry municipal refuse or compost. The particle size of the dried sample is then reduced to 2 mm (or less) using a hammermill, pulverizer, and laboratory mill. Finally, since samples may absorb moisture during the grinding and mixing process, they are redried for 4 hours at the previously specified temperature and stored in a desiccator until the analyses are completed.

PROCEDURE

Duplicate determinations of the total phosphate content of a solid standard or waste sample should be performed. Initially, two different reagent blanks should also be processed. Reagent blank no. 1 measures the color produced by all the reagents and is therefore subjected to both the digestion and the color development (steps 1-34). Reagent blank no. 2 measures only the color produced by the three reagents used in the final color development (steps 28-34). If the initial analyses demonstrate that the absorbance of reagent blank no. 1 equals that of blank no. 2, the analyst can conclude that phosphate is not present in the sulfuric and nitric acids used to digest the samples. Thereafter the preparation of reagent blank no. 1 can be omitted and blank no. 2 used as the reference solution.

The steps of the analytical procedure are as follows:

Procedure	Comments
1. Label a 100-ml micro-Kjeldahl flask as reagent blank no. 1, and place on a cold-heater unit of a micro-Kjeldahl digestion apparatus located in a well-ventilated hood.	
2. Transfer an appropriate quantity of a solid sample to a preweighed piece of glassine paper and determine the sample weight to the nearest 0.0001 g.	2. Use 0.025 g dried *beta* sodium glycerophosphate (organic standard) or 1 g of prepared solid waste

3. Quantitatively transfer the solid to an appropriately labelled micro-Kjeldahl flask. Place the latter on a cold-heater unit of the micro-Kjeldahl digestion apparatus.
4. Select and process a second aliquot of the solid sample as directed in steps 2 and 3.
5. Carefully flow 10 ml concentrated sulfuric acid down the side of each micro-Kjeldahl flask.
   a) Wear safety glasses when handling acids and mixtures thereof.
   b) Use a pipet filler with a serological pipet to add the acid to each flask.
6. Gently swirl each flask to wet the solid and mix the contents.
   Wear asbestos gloves while handling the flasks in steps 6-8; heat will be generated as the acids react with the sample.
7. Carefully add 5 ml concentrated nitric acid to each flask.
   Avoid inhaling the brown fumes that will evolve from samples.
8. Gently swirl the contents of each flask and return the latter to a cold heater unit.
9. Turn the control knob of each heater to position 1.
   The directions concerning the heater control knobs apply only to the apparatus specified in the Equipment section of this Procedure.
10. After the brown fumes have evolved from each flask, turn each heater control knob to position 3.
    Samples, containing organic matter will turn dark brown.
11. As the heat increases, swirl each flask to mix its contents.
    Wear asbestos gloves while handling hot flasks.
12. After heating 5 to 10 minutes at control knob position 3, turn each control knob to position 5 and digest each sample for 1-1/2 to 2 hours.
    Do not allow the sample volume to drop below 3 ml.
13. Turn off heater units and cool samples.
14. Examine each sample for completeness of digestion.
    a) The solution of a completely digested solid sample will appear colorless on cooling. A white precipitate may be present in a flask containing a digested solid waste.
    b) An incompletely digested sample will be brown or tan in color.
15. If the sample is completely digested, proceed to step 17.
16. If the sample is incompletely digested, carefully add 1 ml concentrated nitric acid, and continue digestion until the solution clears. Then turn off the heater and cool the sample.
    a) Continue digestion using heater control knob position 5.
    b) This additional step is required for only an occasional sample.
17. After the contents of each flask have cooled, carefully flow 25 ml distilled water down the side of each flask.
    a) Use a 25-ml tilting dispenser attached to a 500-ml Erlenmeyer to add the water.
    b) Minimize the spattering of acid while adding water to each flask.

18. Return each flask to a heater unit and boil its contents for 10 minutes

18. a) Use heater control knob position 5.
    b) This treatment helps to drive off excess nitric acid.

19. After boiling is completed, turn off each heater. While waiting for the digested samples to cool to room temperature, proceed to step 20.

20. Set up a filtering apparatus for each sample, including reagent blank. no. 1, as follows: Place a clean, 100-ml volumetric flask, containing 25 ml distilled water, beneath a supported funnel containing Whatman no. 7 filter paper recently washed with four 20-ml portions of distilled water.

20. a) At least 30 minutes are required for sample cooling.
    b) Discard the filtrate from the four washings of each filter paper.

21. Quantitatively transfer the cooled contents of each micro-Kjeldahl flask to its respective filtering apparatus.

21. a) If the filter paper is wet, it will not rupture when the acidic sample is slowly added.
    b) Filtering the sample into a volumetric flask containing distilled water reduces the generation of heat on further dilution in step 25.

22. Rinse each micro-Kjeldahl flask several times with 5- to 10-ml portions of distilled water. Add the rinsings to the appropriate funnel.

22. A washing-dispensing bottle can be used to dispense the rinses in steps 22 and 23.

23. After the material in each funnel is completely filtered, rinse the filter paper down with a gentle stream (10 ml) of distilled water.

23. Allow the rinse to filter through the paper into the flask.

24. Allow the contents of each 100-ml volumetric flask to cool to room temperature (25 ± 5 C).

25. Carefully dilute the contents of each volumetric flask to 100 ml with distilled water. Stopper tightly and invert to mix. Each solution, thus prepared is labelled Solution A.

25. BEWARE: Mixing of insufficiently cooled samples may result in excessive generation of heat, expansion of flask contents, and expulsion of both the stopper and acidic solution.

26. Dilute a 10-ml aliquot of each solution A to 100 ml with distilled water. Each new solution is labelled Solution B.

26. The specified dilution of Solution A suffices for the analysis of 0.025-g *beta* sodium glycerophosphate samples and for 1-g solid waste samples containing up to 5 percent total phosphate (PO_4).

27. To initiate the color development, transfer a 10-ml aliquot of each Solution B to an appropriately labelled, 100-ml glass-stoppered cylinder.

28. Similarly prepare reagent blank no. 2 by transferring 10 ml distilled water to an appropriately labelled 100-ml glass-stoppered cylinder.

29. Dilute each cylinder to 100 ml with distilled water. Each solution, thus prepared, is identified as Solution C.

30. Add 5 ml sulfuric acid reagent containing bismuth to each of the cylinders. Stopper each cylinder and invert several times to mix the contents.

30. a) Use a pipet filler and a clean serological pipet for each of the three reagents added in steps 30-32.
    b) Although 10-ml aliquots of the B solutions may theoretically contain up to 0.1 ml residual concentrated sulfuric acid (from the digestion), an adjustment in the added volume of the sulfuric acid – bismuth reagent does not appear necessary. The final pH of developed solutions of digested samples has not varied significantly from those of undigested inorganic standards.

31. Add 5 ml ammonium molybdate reagent to each cylinder. Restopper and mix the contents.

31. A yellowish color forms

32. With delay, add 5 ml amino solution to each cylinder. Restopper and mix the contents. Note the time.

32. Molybdenum blue begins to form directly upon the addition of this reagent to the standard or waste solution. The color intensity increases within the first few minutes and appears stable after 15 minutes.

33. Fifteen minutes after mixing the samples in step 32, transfer an aliquot of each solution to a spectrophotometer cuvette with a 1-cm pathlength.

33. The color remains stable for at least 25 minutes (i.e., from 15 to 40 minutes after mixing the sample in Step 32).

34. Measure at 650 nm the absorbance of reagent blank no. 2 and each standard and solid waste solution against that of reagent blank no. 1, set at zero. Record the observations.

34. a) If the initial analyses reveal that the two blanks have equal absorbance, reagent blank no. 2 can henceforth be used as a reference solution.
    b) The final pH of each developed solution should be 0.65 ± 0.05.

35. Obtain the orthophosphate concentration (mg PO_4/l) of each C solution from the calibration graph.

36. Calculate the percent total phosphate in the original solid standard or waste sample according to the instructions in the Calculations section below.

CALCULATIONS

The percent total phosphate (% total PO_4) of a solid standard or waste sample, analyzed as recommended in the Procedure section, is calculated as follows:

$$\% \text{ total } PO_4 = \frac{M}{W}$$

where

M = mg orthophosphate (PO_4) observed per liter of solution C of the digested sample
and W = g of standard or solid waste digested in the test

This formula is based on the presence of 1 ml of solution A (or 1/100 of the solid sample) in 100 ml solution C. When any other volume of solution A is diluted to 100 ml and the color is developed as outlined, the formula must be modified as follows:

$$\% \text{ total } PO_4 = \frac{M}{V(W)}$$

where

M = mg orthophosphate (PO_4) observed per liter of the developed solution
V = ml of solution A in the 100 ml of developed solution
W = g standard or solid waste digested in the test

METHOD EVALUATION

Interferences

Studies performed in the Solid and Hazardous Waste Research Laboratory have demonstrated that the color development of a 100-ml sample is not affected by the presence of 100 mg chloride or 50 mg calcium. Ferric iron may delay the color development for a few minutes, but the maximum color intensity is always attained within 15 minutes in the presence of 20 mg ferric iron. The American Society for Testing and Materials (ASTM) has reported only a 2 percent error in the analyses of solutions containing silica concentrations fifty times larger than their phosphate concentrations (1, p. 47). Nitrite, several mg sulfide, and 75 mg chromate per liter, however, will interfere with the test. The analyst should use the modifications proposed by ASTM to overcome these interferences (1, p. 47).

Accuracy

Duplicate 0.025-g samples of *beta* sodium glycerophosphate, 0.1-g samples of 3-adenylic acid, and 0.1-g samples of barium fructose-6-phosphate were all analyzed using the recommended procedure. The average percent recoveries of the theoretical total phosphate of the three standards were 99.1, 94.0, and 89.8, respectively. Although the average percent recoveries from 3-adenylic acid and barium fructose-6-phosphate were less than the average recovery from the *beta* sodium glycerophosphate, the observations compare favorably with the data reported by Gales, Julian, and Kroner (12).

The concentration of total phosphate in duplicate aliquots of a Boone County, Kentucky, refuse sample (no. 71-142) was also determined before and after the addition of 0.025 g *beta* sodium glycerophosphate. The average percent recovery of the added phosphate was 99.1. Additional studies also revealed that the chloride, calcium, and iron concentrations in the C solutions of the 14 analyzed Boone County refuse samples were all very low and, hence, noninterfering.

Precision

The reproducibility of the method has been determined by calculating the standard deviation of the duplicate determinations of 14 Boone County, Kentucky, refuse samples. The data are presented in Table 1.

TABLE I
PRECISION OF THE DUPLICATE TOTAL PHOSPHATE DETERMINATIONS OF BOONE COUNTY, KENTUCKY, REFUSE SAMPLES

Sample No.	Observed mean % total phosphate	Standard deviation
71-120	2.22	0.09
71-123	0.51	0.02
71-125	0.44	0.01
71-128	0.34	0.04
71-130	0.50	0.04
71-133	1.02	0.02
71-135	0.24	0.02
71-138	0.26	0.01
71-140	0.18	0.02
71-142	0.20	0.01
71-145	0.44	0.00
71-155	0.44	0.01
71-158	0.58	0.03
71-160	0.20	0.00

ACKNOWLEDGMENTS

The author wishes to thank Dirk Brunner and the staff of the Landfill Disposal Project, Solid and Hazardous Waste Research Laboratory, for providing the Boone County, Kentucky, refuse samples. Special thanks are extended to Israel Cohen, Monitoring & Analysis Project, Solid and Hazardous Waste Research Laboratory, for preparing these samples. The calcium and iron analyses, mentioned in the Method Evaluation section, were kindly performed by Michael Fluharty while he was associated with the Laboratory.

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