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Analytical Abstracts -- Fertilizers

Selected from *Fertilizer Abstracts*, January 1968-June 1972

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Tennessee Valley Authority
National Fertilizer Development Center
Fertilizer Abstracts
Muscle Shoals, AL 35660

FOREWORD

Developing and introducing new fertilizer technology are primary goals of the National Fertilizer Development Center. A key need in the program is to keep abreast of new developments in many areas. To help in this effort, TVA began publishing a monthly abstract journal *Fertilizer Abstracts* in 1968. It has carried more than 10,000 abstracts from hundreds of journals around the world. Articles are selected by specialists in technology, analytical techniques, agronomy, marketing and other areas. The journal is available on an annual subscription basis.

This book is a collection of material from *Fertilizer Abstracts* from January 1968 through June 1972 dealing with analytical work with fertilizers. Its purpose is to make recent analytical work available to laboratory researchers. It should be especially useful to persons wishing to establish a laboratory as they select methods and equipment.

Abstracts from *Chemical Abstracts* are used with the permission of the publisher, The American Chemical Society.

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NITROGEN

1

Comparison of the Automatic Dumas and Kjeldahl Methods for the Determination of Total Nitrogen in Fertilizers.

G. F. Morris, R. B. Carson, and W. T. Jopkiewicz (Canada Dept. Agr., Central Exp. Farm, Ottawa, Ontario, Canada).

J. Assoc. Offic. Anal. Chem. 52 (5), 943-6 (Sept. 1969).

Representative N-P-K fertilizers were analyzed for total N by the automatic Dumas method, using a catalyst-assisted combustion at 900°C., and by the macro Kjeldahl method. The precision and accuracy of both methods were considered to be adequate for this type of material and compared favorable. The automatic Dumas method gave slightly higher results than the Kjeldahl method and a statistical evaluation of the experimental data showed that the Kjeldahl method was generally more precise.

2

Automatic Procedure for Determination of Total Nitrogen in Inorganic Fertilizers.

T. Niedermaier (Badische Anilin & Soda-Fabrik A.-G., Ludwigshafen, Ger.).

Z. Anal. Chem. 223 (5), 336-43 (1966) (Ger).

Anal. Abstr. 15 (2), 1120 (Feb. 1968).

The ground sample (2 g) is dissolved in 40 ml of 1:1 HCl and the solution is diluted to 2 l. and fed into an AutoAnalyzer system, where NO_3^- is reduced by VSO_4 solution and the total NH_4^+ is determined photometrically by the indophenol blue reaction. When 10 determinations are made/hr at levels of 10-13% N, a difference of less than ±0.15% is obtained between this method and the conventional method.

3

Total Nitrogen in Fertilizers.

P. R. Rexroad and G. F. Krause (Univ. Missouri, Columbia).

J. Ass. Offic. Anal. Chemists 51 (4), 851-7 (July 1968).

A three-laboratory collaborative study (Univ. Missouri, Tennessee Valley Authority, and Purdue University) was made of the comprehensive N method and the new Raney catalyst powder method for total N in fertilizers. Both methods worked quite well and, with minor modifications, they should provide the basis for a broader collaborative study to provide an official method for total N in fertilizer applicable to all samples. The limitations of method 2.045 are reviewed and a rephrasing of the official applications of the method is recommended. Further work is recommended toward adoption of a new method and possible deletions or change of status in current official methods.

4

A New Approach to the Raney Catalyst Powder Method for Total Nitrogen in Fertilizers.

J. A. Brabson and T. C. Woodis (Tennessee Valley Authority, Muscle Shoals, Ala.).

J. Assoc. Official Analytical Chemists 52 (1), 23-30 (Jan. 1969).

Further study of the title method established conditions in which commercial alloy containing 50% Ni and 50% Al was a more efficient reductant for nitrates than an experimental alloy that contained 10% Co. Errors in measurement were decreased, accuracy was increased, and time was saved by adding all the H_2SO_4 and part of the K_2SO_4 as a single dilute solution and heating the mixture immediately to promote the reduction. Changes in the amounts of reagents, including use of the contents of a Kel-Pak without the polyethylene envelope, resulted in smoother and more effective Kjeldahl digestions. The method is "rugged" and is equally applicable to the refractory compound nicotinic acid, mixtures of nitrates and organic materials, and the simplest inorganic fertilizers. The time required for an analysis can be further shortened by using "autopettes" for dispensing the standard acid, and a "Titralyzer" for back titrations.

5

Total Nitrogen Methods—Applicable to All Fertilizer Samples.

P. R. Rexroad and G. F. Krause (Agr. Exp. Sta., Univ. Missouri, Columbia).

J. Ass. Offic. Anal. Chem. 53 (3), 450-6 (1970).

An extensive collaborative study was conducted to evaluate a comprehensive N method and a Raney powder method for acceptance as official methods. Twenty-nine laboratories participated; 10 samples were used and the new methods were compared to the official method, 2.045 (sulfuric-salicylic acid). Evaluation of the data and overall consideration lead to the recommendation that both new methods be adopted as official. It is recommended that 2.047 (reduced iron) and 2.049 (chromium powder) be deleted as official methods.

6

Determination of Total Nitrogen.

H. D. Drew (Southern Illinois Univ., Edwardsville).

Anal. Chem. Nitrogen Its Compounds. Part I, pp. 1-27 (1970). Edited by C. A. Streuli, Interscience: New York, N.Y.

Measurement techniques for molecular N are discussed. Methods for converting the total N in samples of NH_3, molecular N, CN^-, and NO_2 to forms suitable for quantative analysis are reviewed. (175 ref)

7

Effect of Chloride Nitrate Ratios on Total Nitrogen Determinations.

P. R. Rexroad (Agr. Exp. Sta., Univ. Missouri, Columbia).

J. Ass. Offic. Anal. Chem. 54 (4), 990 (1971).

A study is reported on the effect of various $Cl^-:NO_3^-$ ratios on percent N recovered in fertilizer analysis. The comprehensive and Raney methods were not affected. The salicyclic acid method gave decreasing recoveries with the higher ratios.

8

Semiautomatic Determination of Total and Ammonium Nitrogen in Fertilizers.

P. H. Janssen.

Proc. Fert. Soc. No. 104, 5-16 (Oct. 1968).

A coulometric analytical method is given for the determination of total and ammonium N in fertilizers. The equipment, principles, and results are discussed. The standard deviation was 0.05-0.1% of N in the range of 10-25% N in the sample. The method is most suitable for analyzing 10-20 samples or more in series.

9

Missouri Automated Method for Total Nitrogen in all Fertilizers.

C. W. Gehrke *et al* (Univ. Missouri, Columbia).

J. Ass. Offic. Anal. Chem. 54 (3), 651-7 (1971).

An automated spectrophotometric method, utilizing Technicon AutoAnalyzer modules, was developed for the analysis of N in fertilizers. The continuous digestor, which was found to effectively digest organic materials in solution after the reduction step, is coupled with an automated colorimetric system. This colorimetric system employs the ammonia-

phenate-hypochlorite reaction. The fertilizer samples are reduced manually by the comprehensive N method (CNM). The sampling rate chosen is 30 cups/hr (6 reference standards included) which yields an effective analysis rate of 24 samples/hr. Mn^{2+} at a concentration of 5.0 ppm introduced into the color development manifold as a catalyst gives a significant increase in sensitivity. When commercial fertilizer samples were analyzed with the automated system, consistently low results were obtained for some samples as compared to results obtained by the AOAC CNM. However, 0.01 *M* K Na tartrate in the color development manifold provides sufficient complexing potential to eliminate the effect of interfering ions. One hundred commercial fertilizer samples including solid, liquid, and suspension fertilizers were analyzed by the Missouri automated N method. The results agreed well with the results obtained by multiple independent analyses by the AOAC CNM. Details of the automated system, sample preparation, reagent concentrations and preparation, and experimental data are given.

10

Determination of Nitrogen in Nitro-Chalk and Ammonium Nitrate.

Edward Chromiak (Inst. Ciezkiej Syn. Org., Blachownia Slaska, Pol.).

Chem. Anal. (Warsaw) 15 (4), 789-94 (1970) (Pol).
CA 74, 38042.

The N content in NH_4NO_3 was calculated from the determination of NH_4^+ by conductometric titration with 0.5*N* NaOH in aqueous Me_2CO medium. The N content of nitro-chalk was calculated on the basis of the titrimetric determination of NH_4^+ and NO_3^- after passing the solution through a column filled with Dowex 50 WX4 cation exchanger (in H^+ form). Ammonium ion can also be determined by the formaldehyde method. The differences in N content were <2%. Thus, all three methods can be used for its determination.

11

Determination of Water-Insoluble Nitrogen in Mixed Fertilizers.

S. E. Katz, C. A. Fassbender, and Merril Greenstein (Rutgers State Univ. New Brunswick, New Jersey).

J. Ass. Offic. Anal. Chem. 53 (4), 808-11 (July 1970).

A procedure is given for the determination of water-insoluble N which does not require alteration of the sample by grinding. Samples of the fertilizer are washed in a column with the equivalent of 100 m. of water. The residual N is then determined by conventional Kjeldahl procedures. The procedure is as reproducible as the present official method but is applicable to all types of sources of water-insoluble N. Since grinding is eliminated, particle size-solubility relationships and coatings are not affected.

12

Automatic Determination of Nitrogen.

R. L. Martin and R. J. Flannery (Standard Oil Co., Indiana).

Fr. 1,516,307, Mar. 8, 1968, U. S. Appl. Feb. 21, 1966; 6 pp.
CA 70, 120869.

The N is converted into NH_3 by passing the sample over a catalyst (Ni on MgO) in a H stream. The NH_3 is titrated automatically in a microtitrating cell (coulometrically). The method permits the determination of 1 ppm N.

13

New Automation to Determine Nitrogen in Fertilizers and Foods.

W. Merz (Untersuchungslabor, Bad. Anilin- und Sodafabr. A.-G., Ludwigshafen/Rhein, Ger.).

Landwirt. Forsch., Sonderh 26 (1), 311-19 (1971) (Ger).
CA 76, 33129.

The two basic sources of error in the Dumas method are low values due to incomplete decomposition of thermally stable compounds and high values due to incompletely oxidized, volatile gases; these are avoided by the use of pure O_2 to give explosive-like combustion in a tube of dimensions suitable for the higher flow velocity. The combustion gases are passed with CO_2 over CuO and Cu into an automatic azotometer and N is determined volumetrically. Nitrogen volumes can be read directly, printed out, or fed directly into a computer. An electronic balance and an electromagnetic charging valve are essential for complete automation. Actual analysis time is 2.5 min, 30 sec for combustion and 2 min for flushing with CO_2.

14

Automated Distillation Procedure for the Determination of Nitrogen.

John Keay and P. M. A. Menage (C.S.I.R.O., Wembley, Aust.).

Analyst (London) 94 (1123), 895-9 (1969).

A distillation step was incorporated into the automated determination of NH_3 by the indophenol method. Interference from metal ions and the need of dialysis of turbid solutions were eliminated, and accuracy was improved.

15

Automated Spectrophotometric Method for Nitrogen in Fertilizers.

C. W. Gehrke, F. E. Kaiser, and J. P. Ussary (Univ. Missouri, Columbia).

J. Ass. Offic. Anal. Chem. 51 (1), 200-11 (1968).

An automated spectrophotometric method utilizing the Technicon AutoAnalyzer has been developed to determine N in fertilizer digests in the range from 5 to 15 ppm N at a rate of 40 analyses/hr. Ammonium was determined by reacting it with phenol and hypochlorite in an alkaline medium to form a blue compound closely related to indophenol. Optimum reagent concentrations for the colored reaction were determined, and several ions were investigated to determine if they interfered with the reaction. Comparison of results obtained by the automated method and the comprehensive N method in primary standard grade $(NH_4)_2SO_4$ and KNO_3, Magruder check samples, and several commercial fertilizers showed that the automated method was accurate and precise. The automated method resulted in considerable saving of analysis time, especially in laboratories analyzing large numbers of samples.

16

Determination of Microgram Amounts of Nitrogen Using Distillation, Flow Spectrophotometry, and Data Acquisition by Computer.

J. W. Frazer *et al* (Lawrence Radiation Lab., Univ. California, Livermore).

Anal. Chem. 41 (11), 1485-7 (1969).

An automated method is described for determination of microgram-amounts of NH_3 in solutions containing high Li^+ concentrations. NH_3 was separated by distillation from NaOH media and determined colorimetrically by reacting with HClO and NaOPh, similarly to an earlier method (P. G. Scheurer and F. Smith, 1955). A computer was used to integrate the colorimetric signal. The relative standard deviation was 1.5% for a 0.5-g Li metal sample analyzed to contain 5.43 micrograms N.

17

Modification of the Kjeldahl Nitrogen Determination Method.

W. C. Urban (Jacksonville, Fla.).

Anal. Chem. 43 (6), 800-1 (1971).

A *p*-hydroxybenzoic acid solution (~ 7 g/l. of pH 2.9 at 25°) was an especially suitable distillate receiving solution for the Kjeldahl N determination, since the low ionization constant of *p*-hydroxybenzoic acid made negligible any pH differences between the blank comparison and the receiving solution due to small differences in the distillate vol and made negligible any pH increase in the receiving solutions due to a vol increase during the titration. The pH of a second aliquot of the receiving solution after dilution with H_2O to the final vol of the sample receiving solution after distillation was used as the end-point pH for the titration. An $(NH_4)_2SO_4$ standard theoretically containing 21.20% N was analyzed to contain 21.15% N.

18

Preparing Gas Samples for ^{15}Nitrogen Determination.

P. J. Ross and A. E. Martin (Div. Soils, C.S.I.R.O., St. Lucia, Aust.).

Analyst (London) 95 (1134), 817-22 (1970).

An apparatus is described for the rapid conversion of dry $(NH_4)_2SO_4$ to N for the mass spectrometric determination of ^{15}N. The sample is both stored and oxidized (with BrO^- in vacuo) in a simple vial to eliminate time-consuming sample transfer and degassing procedures. Air contamination of a 0.5-mg sample is generally <0.1%.

19

Optical ^{15}Nitrogen Analysis of Small Nitrogen Samples Using a Noble Gas to Sustain the Discharge.

G. B. Cook, J. A. Goleb, and V. Middelboe (IAEA, Vienna, Austria).

Nature 216 (5114), 475-6 (Nov. 4, 1967).

Research was conducted on the analysis of ^{15}N by optical emission spectroscopy. The sensitivity of the method has been improved. The smallest detectable amount of excess ^{15}N (above the natural ^{15}N concentration) was reduced from 10-100 nanograms to about 0.5 nanogram. A noble gas (Kr or A) at 1 mm Hg pressure was used as a sustainer in an electrodeless discharge tube with a quartz capillary tube of 2 mm bore and 3 in. long.

20

Analysis of ^{15}Nitrogen Abundance in Biological Samples by Means of Emission Spectrometry.

H. Perschke and G. Proksch (Int. At. Energy Ag., Vienna, Austria).

Proc. ^{15}Nitrogen in Soil-Plant Studies, held Sofia Dec. 1-5, 1969; pp. 157-64. Int. At. Energy Ag., Vienna (1971).

The ratio of $^{15}N/^{14}N$ was analyzed in a modified Hilger Watts quartz spectrograph adapted with a RCA 1P 28 Photomultiplier tube. The sample is prepared in an electrodeless quartz tube with a pressure of about 2 Torr and is excited with a 100 Mc generator operating at approximately 50 W. The light from the tube is focused and resolved in the spectrograph. The Bandheads $^{14}N\,^{14}N$ at 2977Å, $^{14}N\,^{15}N$ at 2983Å, and $^{15}N\,^{15}N$ at 2989Å are used for the $^{14}N/^{15}N$ ratio determination. The light corresponding with the N_{29} and N_{28} bands is collected by a photomultiplier, amplified, and recorded. The ^{15}N is calculated from the peak heights of N_{29} and N_{28}.

21

Recovery System for Mercury Catalyst Used in Kjeldahl Analysis.

P. L. Dillon, M. J. Caldwell, and A. J. Gehrt (Moorman Mfg. Co., Quincy, Ill.).

J. Ass. Offic. Anal. Chem. 55 (1), 101-2 (Jan. 1972).

A simple system was developed for recovering Hg used as a catalyst in Kjeldahl analysis. The equipment consists of two 55 gallon stainless steel drums connected by an overflow. Mercuric sulfide sludge settles in the first drum and clear, essentially Hg-free effluent passes to the second drum, which is periodically discharged to the sewer. Analyses show over 99.99% removal of Hg from the effluent.

22

New Sensitive Method for the Detection and Quantitative Analysis of Ammonia and Aliphatic Amines.

D. N. Kramer and J. M. Sech (Edgewood Arsenal, Md.).

U.S. Clearinghouse Fed. Sci. Tech. Inform., AD, No. 713556, 12 pp. (1969).

A direct, one-step method is given for the determination of NH_3 (and aliphatic amines) The rate of the reaction is so rapid that instantaneous determinations may be made of the NH_3 concentrations being sampled. The method requires collection of NH_3 in a suitable neutral solvent (for example, dioxane) containing the reagent, *o*-(benzenesulfonamido)-*p*-benzoquinone, and measuring the absorption of light at 480 nm. A proposed reaction sequence is given.

23

Highly Productive Apparatus for the Distillation of Ammonia.

M. Sh. Shaimukhametov (Pochv. Inst. im. Dokuchaeva, Moscow, U.S.S.R.).

Agrokhimiya, No. 4, 131-4 (1971) (Russ).

CA 75, 34511.

The modified distillation apparatus for the determination of NH_3 is described. The apparatus is small, simple, and gives highly reproducible results. Nearly 10 distillations may be carried out per hr.

24

Gas Stream Ammonia Analysis System.

J. J. McKinley (to Monsanto Co.)

U. S. 3,545,931, Dec. 8, 1970, Appl. Aug. 28, 1968; 5 pp.

A system for the continuous determination of NH_3, for example in gas streams, is described in which NH_3 is collected from the sample via a NH_3-permeable membrane, such as a poly(tetrafluoroethylene) membrane, and is catalytically decomposed into H and N for detection and measurement of the H, for example with a katharometer An Fe oxide-based, K_2O-promoted catalyst is suitable for the NH_3 decomposition.

25

Conductometric Determination of Ammonia in Boric Acid Solutions.

Imre Sarudi and Elemer Siska (Chem. Res. Office, Rejer Veszprem State Disto, Szekesfehervar, Hung.).

Zentralbl. Pharm., Pharmakotherapie Laboratoriumsdiagnostik 109 (7), 675-80 (1970) (Ger).

CA 74, 60639.

Ammonia was separated from samples by distillation, collected in H_3BO_3 solution, and determined by measuring the specific conductance of the solution, which was related linearly to the NH_3 concentration. Suitable distillation procedures are those used conventionally in analysis of NH_4^+ salts, protein analysis by the Kjeldahl N method, and NO_3^- determinations after reduction. Relative errors were $\leq$1.4% for determinations of 4.6–36.6 mg NH_3 in H_3BO_3 solutions.

26

Phenol-Hypochlorite Reactions as Applied to Ammonia Analysis.

J. E. Harwood and D. J. Huyser (Natl. Inst. Water Res., South Afr. Counc. Sci. Ind. Res., Pretoria, S. Africa).

Water Res. 4 (7), 501-15 (1970).

The effects of changes in PhOH, hypochlorite, and catalyst concentrations on the indophenol blue reaction to determine ammonia-N was studied by using Me_2CO and $Na_2[Fe(CN)_5NO]$ as catalysts. The effect of pH on the color intensity, stability, and rate of development was also investigated by using the AutoAnalyzer. $Na_2[Fe(CN)_5NO]$ was generally far superior to Me_2CO, providing a stable color and rapid color development. Increasing the pH increased both the final color obtained and the rate of development. With excess caustic present, the color became unstable and sensitivity decreased.

27

Determination of Ammonia Nitrogen in Agricultural Chemicals with Sodium Hypobromite.

M. L. Tsap, O. A. Leonchik, and I. K. D'yachenko-Okladnyuk (Ukrainian Agricultural Academy).

Fr. 1,545,030, Nov. 8, 1968, Appl. Nov. 20, 1967; 3 pp.

CA 71, 90413.

Ammonia-N of the soil and fertilizers was determined by titration with NaBrO in the presence of $Na_2B_4O_7$ and NaBr buffer solutions according to: $(NH_4)_2SO_4 + 3NaBrO + 2NaOH \rightarrow N_2 + 3NaBr + Na_2SO_4 + 5H_2O$. The end point was determined amperometrically. The described method did not have the inconveniences of Kjeldahl and Nessler methods.

28

Sampling and Analysis of Fertiliser-Quality Anhydrous Ammonia.

R. A. Hoodless and R. E. Weston.

Chem. Ind., pp. 374-6 (1969).

J. Sci. Food Agr. 20 (7), ii-10 (July 1969).

The procedure described avoids the difficulties inherent in the Institute of Petroleum and A.O.A.C. methods; provided no neutral volatile matter, such as, gaseous N, is present, it gives reliable results and an indication of the degree of contamination by mineral oil or water. The sampling apparatus (mainly of steel) comprises an injection head fitted with needle valves, bleeding tube, and a nylon injection tube; the head is connected to the source by a flexible coupling having a non-return valve. Samples are collected in 1-l polyethylene bottles containing a known wt of water, and aliquots of the solution are taken, quickly weighed, and then (after dilution) titrated with H_2SO_4. The necessary precautions are detailed.

29

Electrochemical Cell for Ammonia Determination.

C. H. Beebe and Allan Strickler (to Beckman Instruments Inc.).

Ger. Offen. 2,009,937, Sept. 10, 1970, US Appl. Mar. 3, 1969; 21 pp.

CA 73, 137109.

An electrochemical cell for the determination of the NH_3 content in gases and liquids has a glass electrode covered with thin cellophane or filter paper and a poly (vinylidene fluoride) (Metricel VF-6) membrane permeable to NH_3, a AgCl-Ag reference electrode and an electrolyte containing 0.1*M* NH_4Cl. The NH_3 concentration can be measured linearly and independent of impurity traces affecting the pH.

30

Enhancement of Zirconium Atomic Absorption by Nitrogen-Containing Compounds and its Use in the Determination of Ammonia.

A. M. Bond (Univ. Melbourne, Victoria, Australia) and J. B. Willis (CSIRO Chem Res. Labs., Victoria, Australia).

Anal. Chem. 40 (14), 2087-90 (Dec. 1968).

The absorption of Zr atoms in the N_2O-C_2H_2 flame is enchanced in the presence of many N-containing compounds which can act as Lewis bases. For NH_3 the magnitude of this enhancement is proportional to the concentration of the base over the range 1×10^{-4} to $5 \times 10^{-3}M$ and can be used to determine NH_3 in the absence of phosphate and of certain N-containing compounds. When interfering species are present the method can be used, after prior distillation of the NH_3, to replace spectrophotometric methods requiring considerable time for color development. The method is useful for the determination of NH_3 in biological materials.

31

Determination of Ammonia in Boiler Feed-Water with an Ammonium-Selective Glass Electrode.

G. I. Goodfellow and H. M. Webber (Central Electricity Res. Lab., Leatherhead, Surrey, England).

Analyst (London) 97 (1151), 95-103 (Feb. 1972).

An investigation was made into the accuracy of ammonium-selective (ammonium-responsive) glass electrodes for determining NH_3 (10-1000 $\mu g\ l.^{-1}$) in boiler feed-water and similar high-purity water samples from power stations. The electrode potential follows the Nernst equation in samples containing up to 10,000 mg $l.^{-1}$ of NH_3, the pH of which is controlled between 8.0 and 8.4 by the addition of triethanolamine-HCl buffer solution. However, interfering species in the buffer solution cause a detectable deviation from Nernstian response at low NH_3 concentrations (less than 1000 $\mu g\ l.^{-1}$). By use of a calomel - 0.1 *N* HCl reference electrode, reproducible results have been obtained in static buffered solutions containing 10-10,000 $\mu g\ l.^{-1}$ of NH_3. Of the other impurities likely to be present in power-station waters only Na caused a serious effect (100 $\mu g\ l.^{-1}$ of Na is equivalent to 25 $\mu g\ l.^{-1}$ of NH_3). The within-batch standard deviations of analytical results were 2, 7, 17, and 33 $\mu g\ l.^{-1}$ at concentrations of 10, 100, 500, and 1000 $\mu g\ l.^{-1}$ of NH_3, respectively. Details of a recommended analytical procedure for discrete samples are given, and the application of the ammonium-selective electrode to continuous on-stream analysis is briefly discussed.

32

Determination of Ammonia Nitrogen in Organic Fertilizers.

V. M. Perepelitsa (Beloruss. Nauchno-Issled. Inst. Zemledel., U.S.S.R.).

Khim. Sel. Khoz. 9 (12), 940-2 (1971) (Russ).

CA 76, 58113.

A detailed description of a distillation apparatus is given. To 12.5 g organic fertilizer in a 500 ml flask 250 ml 0.05 *N* HCl is added. The mixture is either agitated for 30 min or left standing for 60 min with 5-6 agitations and filtered through a NH_3-free filter. The extract (25 ml) and 200-250 ml H_2O are placed in the distillation flask of the apparatus. The collecting glass is filled with 35-40 ml 4% H_3BO_3 50-60 ml H_2O, and 4-5 drops of Groac indicator; the mixture is a light-violet color. The glass is placed in a container filled with 0.5-0.6 l. tap water. About 1 g MgO in filtering paper is placed in the distillation flask. A drop collector joints the ends of the distillation flask and collecting glass. Distillation lasts 25 min. The liquid in the collecting glass is titrated with 0.02 *N* H_2SO_4.

33

Determination of the Free Nitric Acid and Free Ammonia in Ammonium Nitrate Solutions.

J. Fiker and J. Soukup.

Czech. 128,309, July 15, 1968, Appl. Apr. 5, 1966; 4 pp. *CA 70*, 120871.

A potentiometric sensing element, featuring a measuring Pt electrode and a reference AgCl or Ag_2SO_4 electrode, is very sensitive to all concentration changes. In the presence of HNO_3, the Pt electrode becomes coated, in proportion to the acid concentration and temperature, with an oxide layer which provides a reversible equilibrium between the electrode metal and the hydroxonium ions in the solution. The signal change is 120 mv for a concentration change in the range 1-7 g HNO_3/liter, in comparison with 63 mv which is obtained with a glass electrode. The concentration of free NH_3 is read from a graph plotting voltage against the NH_3 concentration.

34

Determination of Nitrous Acid in Solution by Spectrophotometry.

J. J. Perez (Commissariat a l'Energie Atomique).

Fr., 1,545,682, Nov. 15, 1968, Appl. Aug. 2, 1967; 5 pp. *CA 72*, 18272.

A sample solution containing HNO_2 is extracted with *sec*-octyl alcohol to remove the HNO_2, the extract is washed with an equal volume of 2*N* H_2SO_4 or with a mixture of 2*N* HNO_3 and *N* oxalic acid, and the spectral absorption of the alcohol extract at 372 millimicrons, which is proportional to the concentration of octyl nitrite, is determined. This method of determining the HNO_2 concentration is sensitive to HNO_2 concentrations>0.0005*M* and is especially useful for determining the amount of excess HNO_2 present after the oxidation of Pu^{3+} to Pu^{4+}. This excess HNO_2 must be destroyed in order to prevent contamination of the Pu obtained by this known recovery and purification method.

35

Investigation of Alkali and Ammonium Tetraphenylborates by Infrared Spectrophotometry.

Klara Kiss-Eross, I. Buzas, and Laszlo Erdey (Inst. Gen. Anal. Chem., Tech. Univ., Budapest, Hung.).

Proc. Anal. Chem. Conf., 3rd, 2,, 47-54 (1970) (Eng). Edited by Ilona Buzas, Akad. Kiado, Budapest, Hung. *CA 74*, 38071.

Ammonium and alkali metal ions were precipitated by BPh_4^+ after which the NH_4^+ was determined, without separation, by ir photometry of the 1405 cm^{-1} band. Standard deviation varied from ± 2.42 with a 10% concentration of NH_4BPh_4 present to ± 0.47 with 84% NH_4BPh_4 and in the presence of K, Rb, and Cs ions.

36

New Spectrophotometric Determination of Ammonium with a Mercury (II)–Methyl Thymol Blue Complex.

Sumio Komatsu *et al* (Shinshu Univ., Matsumoto, Japan).

Nippon Kagaku Zasshi 91 (9), 865-8 (1970) (Japan). *CA 74*, 38070.

Mercury (II)–methylthymol blue complex (bluish green) forms a 1:1 complex (indigo-blue) with NH_4^+ at pH 7.5 (phosphate plus borax buffer). The absorbance at 610 nm is proportional to the NH_4^+ concentration in the range 0-55 μg/50 ml, and the molar absorptivity is 5.84 x 10^3. The relative standard deviation is ~1% for 72 and 144 μg of NH_4^+. Nickel, Mn^{2+}, Ag, Cu, Fe^{3+}, Cl^-, CN^-, and SCN^- interfere seriously. These anions can be removed by anion exchange.

37

Solid Ammonium Ion-Selective Electrode.

R. E. Cosgrove, C. A. Mask, and I. H. Krull (Beckman Instruments, Inc., Fullerton, Calif.).

Anal. Lett. 3 (9), 457-64 (1970).

A new NH_4^+ selective electrode was developed and is capable of measuring NH_4^+ in the presence of other cations. The selectivity of the electrode over other cations is reported as well as its response time to step changes in NH_4^+ activity.

38

Spectrophotometric Determination of Ammonium Nitrogen by Using Thymol.

Hiroshi Hashitani and Hideyo Yoshida (Japan Atomic Energy Institute, Tokai, Japan).

Bunseki Kagaku 17 (9), 1136-9 (1968) (Japan). *CA 72*, 18238.

The method reported by Roskam and de Langen (1964) was examined and the following was made clear. (1) The pH of the sample solution should be adjusted to 9.8-10.3 when the NaClO solution is added. (2) The thymol solution should be added within 30 seconds after the addition of the NaClO solution. (3) The pH of the colored solution is kept at 11.5-11.9. The maximum color intensity is attained after 60 minutes and remained constant for five hours when the solution is kept in a dark place. No effect of temperature is observed in the range of 5-30°. The molar absorptivity at 660 millimicrons is 1.16 x 10^4. Thus the recommended procedure was established.

39

Estimation of Ammonium Salts in Fertilizers by Conductometric Titrations.

A. D. Pandey, K. K. Mallick, and A. K. Roy (Plann. Develop. Div., Fertilizer Corp. India, Ltd., Sindri, India).

Technology 5 (3), 174-80 (1968).

A quick and reasonably accurate analysis of ammonium salts in commercial fertilizers is described. A Hungarian conductivity meter, a bell-type electrode with three Pt rings, a hand-driven glass stirrer, a thermostatic water bath at a temperature of 30 ± 0.1°C., and a 10 ml microburette are used. An appropriate sample solution is prepared in absolute ethyl alcohol-water medium and titrated with NaOH (0.1–0.05*N*). The reagent is added until an appreciable excess is introduced. The conductance reading taken after each addition of titrant is plotted against volume of reagent added and the end point determined from the plots. Four systems were studied: (1) ammonium nitrate, (2) ammonium sulfate, (3), monoammonium phosphate, and (4) diammonium phosphate. The error does not exceed 2.5% in a complex system.

40

Determination of Ammonium Nitrogen in Fertilizers Containing Urea or Urea-Aldehyde Condensate.

T. Niedermaier (Anal. Lab., Bad. Anilin- und Soda-Fabrik A.-G., Ludwigshafen/Rh., Ger.).

Landwirt. Forsch., Sonderh. 23 (11), 182-91 (1969) (Ger). *CA 72*, 89286.

The reaction mixture contained the homogenized fertilizer sample dissolved in distilled water and made alkaline with a saturated K_2CO_3 solution. NaOH and KOH solutions were less effective because of saponification of urea. The receiver was 0.1 *N* H_2SO_4. The evolving NH_3 was removed in a stream of air (3 l./min). Three hr was sufficient for the quantitative transfer. The liberated NH_3 was determined titrimetrically.

41

Determination of Ammonium (Total) Nitrogen in Agricultural Materials.

M. L. Tsap, O. A. Leonchik, and I. K. Okladnyuk.

U.S.S.R. 185,104, Jan. 10, 1969, Appl. Mar. 25, 1965; From *Otkrytiya, Izobret., Prom. Obraztsy, Tovarnye Znaki 46* (4), 178 (1969).

CA 71, 2641.

To determine ammonium (total) N in agrochemical materials such as plants and soils, the samples to be analyzed are degraded by a mixture of H_2SO_4 and $HClO_4$. The resulting extracts are neutralized by NaOH in the presence of methyl red and are titrated by a hypobromite solution with an electrometric indication of the titration end point.

42

Ion-Selective Electrodes for Nitrate Analysis.

S. E. Manahan (Univ. Missouri, Columbia).

Trace Subst. Environ. Health-3, Proc. Univ. Mo. Annu. Conf, 3rd 1969, pp. 353-7 (Pub. 1970). Edited by D. D. Hemphill, Univ. Missouri, Columbia.

Nitrate (5×10^{-5}–$1 \times 10^{-2}M$) can be determined with ± 1% relative error and 0.5% relative standard deviation by using a NO_3^- selective electrode and a F^- selective reference electrode in solutions spiked with low concentrations of F^-. Equations are given for calculating the NO_3^- concentration from potential data.

43

An Evaluation of the Performance of the Nitrate-Selective Electrode.

Susan S. Potterton and W. D. Shults (Oak Ridge Natl. Lab., Oak Ridge, Tenn.).

Anal. Lett. 1 (2), 11-22 (1967).

CA 68, 45889.

The performance of the Orion nitrate-selective electrode was evaluated with respect to its working range, accuracy, precision, response time, and memory. The effects of temperature, type of reference electrode, and mode of operation have also been considered. The device makes possible the measurement of free nitrate activity with about the same accuracy as standard colorimetric methods, but with about the same ease as a pH measurement.

44

Determination of Nitrate in Waters with the Nitrate-Selective Ion Electrode.

D. R. Keeney, B. H. Byrnes, and J. J. Genson (Univ. Wisconsin, Madison).

Analyst (London) 95 (1129), 383-6 (Apr. 1970).

An evaluation of the Orion selective-ion nitrate electrode for the determination of nitrate-N in waters is presented. The results obtained showed that interferences from other anions were not great at levels commonly found in waters. Recovery of added nitrate-N ranged 83-105%. However, nitrate-N values obtained by the electrode method on ground and surface-water samples were lower than those obtained by phenoldisulphonic acid and steam-distillation procedures. The specific-ion electrode appeared to be suited for routine analysis of well and surface waters with nitrate-N concentrations near or above the tolerance limit (10 mg $l.^{-1}$ of nitrate-N).

45

Potentiometric Nitrate Analysis: A Flow-Through Electrode Unit.

P. J. Milham (New South Wales Dep. Agr., Rydalmere, Australia).

Analyst (London) 95 (1133), 758-9 (Aug. 1970).

A flow-through electrode unit for use with a liquid ion-exchange nitrate electrode is described. Temperature control to within ± 0.5°C. at 25°C, and reproducible stirring of the test medium give a mean coefficient of variation of 0.36% for standards and 0.63% for plant extracts. The average time for each nitrate concentration measurement is halved.

46

Fluorimetric Determination of Nitrate.

C. R. Sawicki (National Environ. Res. Center, Research Triangle Park, North Carolina).

Anal. Lett. 4 (11), 761-75 (1971).

A sensitive fluorimetric method was developed for the determination of nitrate based on the reduction of nitrate to nitrite with hydrazine sulfate and the subsequent determination of the nitrite formed with 2,3-diaminonaphthalene. Solvent effect on fluorescence intensity, optimum reaction conditions, and sensitivity of the method are discussed.

47

Phosphate Interference in the Devarda's Alloy Reduction Method for Nitrate.

J. R. Freney (CSIRO, Cranberra, Australia).

Commun. Soil Sci. Plant Anal. 2 (6), 479-84 (1971).

Nitrate determinations on phosphate extracts of soil by using Devarda's alloy distillation method demonstrate severe interference by phosphate. Interference can be eliminated by precipitation of the phosphate with a slight excess of Ca^{2+} and extending the distillation time.

48

The Determination of Nitrate Nitrogen in Mixed Fertilisers Using 1,2,4 Phenol-Disulphonic Acid.

B. Ripp and E. W. Schwehr.

Fertiliser Soc. Symp. on Fertilizer Analytical Methods, No. 104, 17-24 (held London, England, Oct. 24, 1968).

Details are given for a method based on the colorimetric estimation of the alkaline salt of 6 nitro–1,2,4 phenol-disulphonic acid. The final colored solution obeys Beer's Law over a broad wavelength with maximum sensitivity at 410 millimicron. The method was shown to give accurate results, a high degree of reproducibility and to be free of interference from materials normally found in fertilizers.

49

Gravimetric Determination of Nitrate in Compound Fertilisers Using N-(4-chlorobenzyl)-1-Naphthylmethylamine.

W. C. Hanson (Fisons Ltd.-Fertilizer Div., Levington Res. Sta., Ipswich, Engl.).

Proc., Fert. Soc., No. 104, 29-44 (1968).

It is desirable to be able to determine nitrate in presence of other forms of N. The reagent, N-(4-chlorobenzyl)-l-naphthylmethylamine (CBNMA) developed by Hutton, Salam, and Stephen has been used with synthetic fertilizer solutions of known nitrate content. For comparison, results obtained by the use of nitron reagent are given. The average recovery given by the final version of the method using CBNMA reagent was 102% for chloride/nitrate concentration ratios of 0.53–1.15. With a ratio of 2.04, the recovery was 101-105%. These high recoveries are due to co-precipitation of the reagent caused by the presence of chloride. They compare with an average of 99% using nitron. The reagent has no advantage over nitron.

50

Comparison of Permeation Devices and Nitrite Ion as Standards for the Colorimetric Determination of Nitrogen Dioxide.

F. P. Scaringelli, Ethan Rosenberg, and K. A. Rehme (National Air Pollution Control Administration, Cincinnati, Ohio).

Environ. Sci. Technol. 4 (11), 924-9 (Nov. 1970).

The most commonly used procedure for determination of the oxides of N in air is the colorimetric method of Saltzman. The ratio of the quantity of dye produced from NO_2 to that produced from NO_2^- has been the subject of considerable controversy. Permeation tubes were used to prepare standard atmospheres at realistic levels 0.02 - 1.8 ppm of NO_2. Precautions are enumerated for the use of permeation devices in preparing standard concentrations of NO_2 in air. It was established that 1 mole of NO_2 is equivalent to 0.764 ± 0.005 mole of NO_2^- with use of the unmodified Saltzman reagent. Earlier, the stoichiometric factor ranged from 0.5 to 1.0.

51

Determination of Nitrite Ion Using the Reaction with *p*-Nitroaniline and Azulene.

E. E. Garcia.

Anal. Chem. 39 (13), 1605 (Nov. 1967).

A sensitive, rapid method for the determination of nitrite ion is described. Nitrite is reacted with *p*-nitroaniline to form a diazonium ion, which is then coupled with azulene to form a purplish pink azo dye. The absorbance of the dye is measured at 515 mμ. Diazotization and coupling are very fast and no controls of pH and temperature are necessary. The sensitivity of the method (expressed as the amount of nitrite corresponding to an absorbance of 0.010 at 515 mμ in a 1-cm cell) is 0.22 μg of nitrite. The molar absorptivity is 5.2×10^4 $mole^{-1}$ cm^{-1} l. The precision is also satisfactory; the relative standard deviation at the 10-μg level is ±1.6%. The procedure's simplicity has permitted its use in remote analyses of highly radioactive solutions. Iron (III) is the only ion tested that interfered seriously. Large amounts of nitrate and nitric acid do not interfere.

52

Determination of Nitric Oxide and Nitrogen Dioxide in Flue Gases. Part II. Continuous Instrumental Methods.

C. J. Halstead, G. H. Nation, and L. Turner (Egham Res. Lab., Shell Research Ltd., Egham, Surrey, England).

Analyst (London) 97 (1150), 64-9 (Jan. 1972).

Continuous instrumental methods based on nondispersive infrared spectroscopy and on coulometry were evaluated for the determination of nitric oxide and nitrogen dioxide. Instrument modifications were made when necessary to increase sensitivity in the 0 to 100 ppm concentration range. The interference caused by the presence of other components of the flue gas were investigated.

53

Determination of Nitric Oxide and Nitrogen Dioxide in Flue Gases. Part I. Sampling and Colorimetric Determination.

C. J. Halstead, G. H. Nation, and L. Turner (Egham Res. Lab., Shell Research Ltd., Egham, Surrey, England).

Analyst (London) 97 (1150), 55-63 (Jan. 1972).

Methods for the determination of nitric oxide and nitrogen dioxide were evaluated for the analysis of flue gases from natural gas combustion systems: these methods were modified where necessary. The study included both manual and continuous instrumental methods of analysis; manual sampling and colorimetric methods are described.

54

Continuous Determination of NO_2 and (NO + NO_2) Concentration in Production Plants.

H. K. Hofmeister, H. Hummel, and R. Kohlhaas (Farbwerke Hoechst AG, Frankfurt/Mainz-Hochst).

Chimie Ingenieur Technik, No. 1-2, 61-4 (1968) (Ger).

An apparatus for continuous determination of NO_2 and/or (NO + NO_2) concentration in gas streams of production plants has been developed. A photometer appropriate for this operation serves to measure the NO_2 directly. In order to ascertain the total concentration of NO and NO_2, the NO is oxidized by I_2O_5 at 110° to NO_2 and the total NO_2 quantity is determined. Since the determination of the degree of oxidation for attaining higher concentrations of N gases creates extraordinary difficulties, a dilution process has been developed. The described apparatus has been tested in a potassium nitrate absorption installation.

55

Gas Chromatographic Determination of Nitric Oxide on Treated Molecular Sieve.

R. N. Dietz (Brookhaven Natl. Lab., Upton, N. Y.).

Anal. Chem. 40 (10), 1576-8 (Aug. 1968).

The use of a temperature-programmed molecular sieve column to eliminate subambient temperatures in the analysis of several inorganic gases is described.

56

The Simultaneous Automated Determination of Urea, Ammonia, and Ammonium Nitrate.

Karl Wrightman.

Advances in Automated Analysis-Industrial Analysis Technicon Int. Congr. 2, 61-7 (1969) Pub. 1970 Mediad Corp., White Plains, N. Y.

An analytical system capable of a very high order of precision and accuracy to measure the various components in liquid nitrogen fertilizers is given. The precision and accuracy of this system will enable the manufacturer to accurately and quickly analyze very large batches of material where 0.1-0.2% error represents many pounds of raw material. It is not inconceivable that a statistical analysis of each batch be performed, since 10 to 20 samples can be evaluated in about one and one-half hr. If mated to a continuous in-line sampler this system would also have extensive value in monitoring blending rates.

57

Urea, Its Derivatives, and Related Compounds.

P. P. L. Ho and M. M. Marsh (Eli Lilly Co., Indianapolis, Ind.).

Anal. Chem. Nitrogen Its Compounds. Part II, pp. 459-94 (1970). Edited by C. A. Streuli, Interscience: New York, N.Y.

A review is given of analytical methods for urea and its closely related compounds. (209 ref)

58

High Precision Spectrophotometry. Part II. The Determination of Ammelide, Ammeline, and Melamine in the Thermal Decomposition Products of Urea.

S. G. Farrow, S. R. Hill, and J. M. Skinner (Imperial Chem. Ind. Ltd., Billingham, Teeside, England).

Analyst (London) 97 (1150), 42-51 (Jan. 1972).

An automatic ultraviolet spectrophotometric method is described for the determination of ammelide, ammeline, and melamine in the thermal decomposition products of urea;

prior separation of the components is unnecessary. A Unicam SP3000 spectrophotometer is used to make absorbance measurements at several different wavelengths and at two pH values. From the absorbance values obtained the concentrations of the amino-*s*-triazines are calculated by using a computer to solve the appropriate simultaneous equations. The constants required in these equations are obtained by calibration of the spectrophotometer with solutions of the pure compounds. A semiquantitative estimation of triuret is also possible. Interferences caused by biuret and cyanuric acid can normally be ignored, but corrections are required if large amounts are present.

59

Polarographic Studies on the Urea-Cu^{2+} System. Indirect Method for Estimation of Urea.

S. S. Chatterjee, M. B. Mishra, and B. K. Banerjee (Fert. Corp. India Ltd., Sindri, India).

Technology 7 (4), 319-21 (1970).

Urea in the presence of biuret is estimated by a polarographic method based on the irreversible reduction of a 2:3 urea-Cu^{2+} complex at a dropping Hg electrode in a medium of NH_4OAc + HOAc (pH 5.8). The error of the determination is well within ± 1.0% for mg and g amounts. At extremely low concentrations (trace amounts) the urea concentration vs Cu^{2+} wave height plot is not linear. The transfer coefficient α is 0.941 and the forward reaction rate is 5.712×10^{-4} moles/l. sec, which indicates the high irreversibility of the reduction reaction.

60

Determination of Biuret in Urea and Mixed Fertilizers.

J. J. Geurts, J. E. Van Stelle, and E. G. Brinkman (N. V. Nederlandse Staatsmijnen, Geleen, Netherlands).

Anal. Chim. Acta 41 (1), 113-20 (Apr. 1968).

A new method for the determination of biuret is described, based on the separation of the Cu-biuret complex with the aid of an anion exchanger, followed by titration of the bound Cu with EDTA. The method can be used directly for the determination of biuret in solutions and in end-products of a urea plant, even with biuret contents as low as 0.001%. The well-known photometric method cannot be used for less than 0.1% biuret; corrections are needed for urea interference, and NH_3 and insoluble products have to be removed. Both methods are suitable for the determination of biuret in mixed fertilizers down to 0.5%, provided that the cations are first removed on a cation exchanger. However, the photometric determination requires special precautions with regard to acidity when phosphates are present.

61

Estimation of Low Content of Biuret in Urea by Atomic Absorption Spectrophotometry.

K. C. Singhal, R. C. P. Sinha, and B. K. Banerjee (Fertilizer Corp. India Ltd., Sindri, Bihar, India).

Technology 6 (2-3), 95-7 (1969).

A suspension of $Cu(OH)_2$ is prepared by shaking 20% $CuSO_4 \cdot 5H_2O$ solution (80 ml) with 30% KOH solution)100 ml), and is set aside for 5 hr. A 1% urea solution (2.5 ml) is added to the suspension (20 ml), and, after 5–10 min., the solution is centrifuged and the Cu in solution is determined by atomic absorption spectrophotometry. Standards are prepared containing known amounts of biuret, or an addition method may be used. The standard deviation for 20 ppm of biuret was ± 1.2%. The method is applicable to fertilizers.

SEE ALSO the following numbered abstracts in other sections: 340-42, 344-50, 352-53, 356, 358, 393, 396, 406, 409-12, 416, 455.

PHOSPHORUS

62

Determination of Large Amounts of Phosphorus by a Differential Photometric Method.

G N. Sharapova.

Tr. Ural. Nauch.-Issled. Khim. Inst., No. 19, 177-9 (1970) (Russ).

CA 74, 119711.

The content of P in the samples, containing <33% of P_2O_5, in superphosphate production was determined by using the phosphomolybdenum blue method. The absorbances of the sample solutions containing 0-4.5 mg P_2O_5 in 100 ml of the colorimetric solution were measured against a standard solution of 2 5 mg P_2O_5/100 ml. The results were evaluated from a calibration curve.

63

Determination of Phosphorus by Means of Reduced Molybdophosphoric Acid in an Aqueous Solution.

V. G. Goryushina, N. V. Esenina, and K. A.Snesarev (State Sci.-Res. Des. Inst. Rare Metal Ind., Moscow, USSR).

Zh. Anal. Khim. 24 (11), 1699-703 (1969) (Russ).

CA 72, 50626.

Several variants of the photometric method for determining trace amounts of $\leq$ 1 microgram P with reduced molybdophosphoric acid were compared. The best variant is the one where ascorbic acid and K antimonyl tartrate are used in a H_2SO_4 and HCl medium. The lower determinable amount is 0.05 micrograms with a 10% variation coefficient. The Mo (*V*)/Mo(*VI*) reagent gives less reproducible results and is less sensitive, besides taking much longer. The use of $SnCl_2$ as a reducing agent or a mixture of $SnCl_2$ with hydrazine sulfate cannot be recommended, as it is not sensitive for the determination of 0.1 microgram P. The variation coefficient is also higher when 1 microgram P is determined.

64

Determination of Phosphorus as Molybdenum Blue in the Presence of Nitric Acid.

N. G. Polyanskii, G. A. Akopov, and G. Ya. Isaeva (Tambov Inst. Chem. Mach. Build., Tambov, U.S.S.R.).

Zh. Anal. Khim. 26 (9), 1854-6 (1971) (Russ).

CA 76, 41688.

Phosphorus can be determined as molybdenum blue in the presence of small amounts ($\leq$6.3 mg/ml) of HNO_3 by using Mohr's salt as reducing agent. At higher HNO_3 concentrations the oxidizers present in the acid should be decomposed by boiling. The method was used for studying thermal stability of phosphate cation exchangers in HNO_3 solutions.

65

The Extractability of Phosphorus from Some Phosphorus Compounds by Methods for the Determination of Available Phosphorus.

J. Pirkl and I. Novozamsky.
Rostl. Vyroba 16 (43), 493-8 (1970).
Phosphorus Agr., No. 58, 38 (Dec. 1971).
Egner's reagent, calcium lactate, extracted all the P from superphosphate and dicalcium phosphate, and 19% from Rhenania phosphate. Addition of Fe^{2+} had a negative effect on extractability. Bray's reagent extracted P quantitatively only from superphosphate; it extracted 71% of the P from dicalcium phosphate and 21% from Rhenania phosphate. Addition of Al^{3+} had a positive influence, but addition of Fe^{2+} decreased extraction. Olsen's reagent extracted 10% of the P from superphosphate, 31% from dicalcium phosphate and very little from Rhenania phosphate. Al^{3+} and Fe^{2+} decreased extractability.

66
The Determination of Phosphate in Detergents by Cool-Flame Emission Spectroscopy.
W. N. Elliott and R. A. Mostyn (Quality Assurance Directorate, Royal Arsenal, London, Engl.).
Analyst 96 (1143), 452-6 (June 1971).
The total phosphate content of detergent materials is determined by measurement of the emission of the HPO molecular species at wavelength 528 nm in a cool H-N diffusion flame. Preliminary treatment with cation-exchange resin is necessary to remove interference by metals. Analytical results on detergent samples containing up to 20% phosphates (expressed as P_2O_5) indicate a precision of the order of 2-4% for the method.

67
Selected Comparisons Between Atomic Absorption and Flame Emission, With Emphasis on the Determination of Phosphorus.
J. D. Kerber, W. B. Barnett, and H. L. Kahn (Perkin-Elmer Corp., Norwalk, Conn.).
Abstr. Pittsburgh Conf. on Anal. Chem. and Appl. Spectrosc. 1970, March 1-6, 107.
At. Absorption Flame Emission Spectrosc. 2 (4), 224 (Abstr. No. 600) (July-Aug. 1970).
With improved instrumentation, flame emission spectroscopy is becoming more favored than atomic absorption, as it often has better detection limits, and interferences are less severe. The advantages for certain elements, and particularly in the measurement of P at the meta-stable 213.5nm line, are critically compared for both techniques.

68
Molecular-Emission Spectroscopy in Cool Flames. Part II. The Behavior of Phosphorus-Containing Compounds.
R. M. Dagnall, K. C. Thompson, and T. S. West (Imperial College, London).
Analyst 93 (1103), 72-8 (Feb. 1968).
A sensitive and selective molecular-emission method for the determination of P is described, in which the intense green emission obtained by nebulizing H_3PO_4 solution into a cool N-H diffusion flame is measured at 528 mμ. The limit of detection in aqueous solution is 0.1 ppm of P. Most cations produce a depressive matrix effect that can be readily overcome by a preliminary ion-exchange separation. Molar excesses of 50-fold of acetic, HBr, HCl, HNO_3, H_2SO_4, oxalic, and tartaric acids do not interfere. [For Part I, see *Analyst 92*, p. 506 (1967)]

69
Flame Spectrophotometric Determination of Phosphorus.
R. K. Skogerboe, A. S. Gravatt, and G. H. Morrison.
Anal. Chem. 39 (13), 1602 (Nov. 1967).
Flame conditions which permit the excitation of the atomic spectrum of P are reported. The analytical utilities of the atomic spectra and the PO bands are compared for different flame types and detection limits are given. Interference effects are evaluated and a simple batch ion exchange separation is given for the elimination of these effects. The results are shown to compare favorably with colorimetric results.

70
Determination of Phosphorus by Atomic Absorption and Flame Emission Spectroscopy.
J. D. Kerber, W. B. Barnett, and H. L. Kahn (Perkin-Elmer Corp., Norwalk, Conn.).
At. Absorption Newslett. 9 (2), 39-42 (1970).
The atomic absorption determination of P, with excitation and emission at 2136.20 and 2135.47 Å, respectively, did not exhibit interferences due to Al, Ca, Cu, Fe, Na, and K, as did the flame emission determination of P at 5262 Å. The detection limits for the atomic absorption and flame emission methods were 130 and 0.2 μg P/ml, respectively. The Ar-H-entrained air flame was generally preferable to the air-H flame for the flame emission determination of P, due to improved sensitivity and reduced background emission.

71
High Precision Spectrophotometry. Part I. Assessment of the Performance of the Unicam SP3000 Spectrophotometer and Its Application to the Determination of Phosphate in Fertilizers and Related Materials.
A. C. Docherty, S. G. Farrow, and J. M. Skinner (Imperial Chem. Ind. Ltd., Billingham, Teeside, England).
Analyst (London) 97 (1150), 36-41 (Jan. 1972).
By using conventional, single-beam spectrophotometers the ultimate precision that can be achieved by direct absorbance measurements is about 0.5% relative. Greater precision can be obtained if measurements are made differentially Recently, more advanced spectrophotometers have become available that enable measurements to be carried out directly with a precision comparable with that obtained by use of differential techniques. The performance of such an instrument, the Unicam SP3000, is discussed and its application to the precise determination of phosphate in fertilizers and intermediates is described.

72
Spectrophotometric Determination of Traces of Phosphorus by an Extraction Method.
P. Pakains (Australian Atomic Energy Comm. Res. Establishment, Lucas Heights, N.S.W.).
Anal. Chem. Acta 40 (1), 1-12 (Jan. 1968).
A general method is described for the spectrophotometric determination of P at trace levels. It involves extraction of the yellow molybdophosphoric acid with isobutyl acetate and subsequent reduction to heteropoly blue. The method covers the range 0.2-20.0 μg P. A comprehensive study of interferences using standard additions of 10.0 and 20.0 μg P was carried out and modifications are described to permit the determination of P in a wide variety of metals and salts.

73
Indirect Ultraviolet Spectrophotometric and Atomic Absorption Spectrometric Methods for Determination of Phosphorus and Silicon by Heteropoly Chemistry of Molybdate.
T. R. Hurford and D. F. Boltz (Wayne State Univ., Detroit, Mich.).
Anal. Chem. 40, (2), 379-82 (Feb. 1968).

The feasibility of effecting a selective extraction separation of molybdophosphoric and molybdosilicic acid followed by quantitation either by ultraviolet spectrophotometry and/or atomic absorption spectrometry was investigated. The molybdophosphoric and molybdosilicic acids are formed in acidic solution by the addition of an excess of molybdate. Molybdophosphoric acid is extracted with diethyl ether from an aqueous solution which is approximately 1*M* in HCl. After adjusting the HCl concentration of the aqueous phase to approximately 2*M*, the molybdosilicic acid is extracted with a 5:1 diethyl ether-pentanol solution. The extracts of molybdophosphoric acid and molybdosilicic acid are subjected to acidic washings to remove excess molybdate. Each extract is then contacted with a basic buffer solution to strip the heteropoly acid from the organic phase. The molybdate resulting from decomposition of the heteropoly acid in the basic solution is then determined either by measurement of the absorbance at 230 mμ using an ultraviolet spectrophotometer or by measurement of the absorbance at 313.3 mμ resonance line of Mo using an atomic absorption spectrometer. The optimum concentration ranges are approximately 0.1-0.4 ppm of P or Si for the indirect ultraviolet spectrophotometric method and 0.1-1.2 ppm for the indirect atomic absorption spectrometric method.

74

Atomic-Absorption Determination of Phosphorus in a Graphite Cuvette.

B. V. L'vov and A. D. Khartsyzov.

Zh. Prikl. Spektrosk. 11 (1), 9-12 (1969) (Russ).

CA 71, 119344.

Relative intensities and analytical sensitivities are given for nine lines of P between 2135 and 2555 Å. Martin's data (*CA 54*: 1066i), which differ, are believed to have been affected by self-absorption. By using a high-frequency Ar discharge lamp containing red P as light source and a C cuvette at 2700°K under three atmospheres Ar for the sample, $\geq 2 \times 10^{-10}$ g P can be determined by atomic absorption at the 2135-2136 Å doublet ($^2D^o_{3/2,5/2} - 4s\ ^2P_{3/2}$), even though the population of the $^2D^o_{5/2}$ level is only 0.004 of the total number of P atoms. H_3PO_4 samples should be neutralized before analysis.

75

Atomic Absorption Determination of Phosphorus Using Molybdenum Hollow Cathode Lamps.

T. Kumamaru, Y. Otani, and Y. Yuroka (Hiroshima Univ., Hiroshima, Japan).

Bull. Chem. Soc. Jap., 40, 429-30 (1967) (Japan).

A method for the determination of P by atomic absorption spectroscopy has been developed comprising forming phosphoric acid-molybdate complex in aqueous media, extracting it with an organic solvent, and determining the Mo-content of the latter by its atomic absorption, at the line 313.3 nm. Butyl acetate is used as the organic solvent. The butyl acetate extract is introduced into an air (6 l./min)-N_2O (3.4 l./min)-acetylene (2.1 l./min) flame. Jarrell-Ash apparatus was used. The results are comparable with the photometric determination of P. Silicon, As, and Ge are not extracted with the phosphate-molybdate complex and, hence, do not interfere. Various materials can be analyzed by converting their P content into phosphoric acid.

76

Direct Determination of Phosphorus by Atomic Absorption Spectroscopy.

D. C. Manning and Sabina Slavin (Perkin-Elmer Corp., Norwalk, Conn.).

At. Absorption Newslett. 8 (6), 132 (1969).

The absorption of 1% P (as $(NH_4)_2HPO_4$) in a N_2O-C_2H_2 flame is ~8 times that in an air-C_2H_2 flame. Lines at 2135.47, 2136.20, and 2149.11 Å arise from two metastable levels. A calibration curve is shown. The absorption sensitivities of Na_3PO_4, K_3PO_4, and H_3PO_4 are about equal. Since P interferes with many cations, it is likely that many cations will interfere with the determination of P by atomic absorption spectroscopy.

77

Atomic Absorption Adaptation of the Quinolinium Molybdophosphate Method for Phosphorus.

J. R. Melton *et al* (Texas A & M Univ., College Station).

J. Ass. Offic. Anal. Chem. 54 (2), 373-5 (Mar. 1971).

A method employing a modification of the quinolinium molybdophosphate method is proposed whereby total P may be indirectly determined by atomic absorption of Mo. Only routine instrumentation procedures are required. The official gravimetric method is followed until the quinolinium molybdophosphate precipitate is formed. The precipitate is dissolved in NH_4OH, and Mo is determined by atomic absorption. Phosphorus analyses of Magruder collaborative fertilizer samples determined by the AOAC and proposed methods compare favorably.

78

Alkalimetric Quimociac Method for Phosphorus in Fertilizers: Collaborative Study.

P. R. Caudill (Univ. Kentucky, Lexington).

J. Assoc. Offic. Anal. Chem. 52 (3), 587-92 (May 1969).

The alkalimetric variation of the quimociac method was shown by collaborative testing to be accurate and precise for determining total P, citrate-insoluble P, or available P by the direct method. The method is recommended for adoption as official, first action.

79

Direct Determination of Elemental Phosphorus by Gas-Liquid Chromatography.

R. F. Addison and R. G. Ackman (Halifax Laboratory, Halifax, Nova Scotia, Canada).

J. Chromatogr. 47 (3), 421-6 (Mar. 1970).

A rapid and sensitive method for the analysis of elemental P is described. Phosphorus is extracted into a suitable organic solvent, isolated by gas-liquid chromatography, and measured in a highly sensitive and specific flame photometric detector. Phosphorus levels as low as 10^{-12} g (corresponding to sensitivities of about two parts in 10^{12} in concentrated extracts) can be measured in a few minutes. Application of this method to the analysis of water, mud and biological samples is described.

80

Determination of Total Phosphate and Identification of Acid-Insolubles in Superphosphoric Acid.

A. B. Carel and D. E. Jordan (Cont. Oil Co., Ponca City, Okla.).

J. Assoc. Offic. Anal. Chem. 52 (3), 577-81 (May 1969).

Discrepancies in the analysis of superphosphoric acid for Fe, Al, and P are found to be directly related to the digestion procedure used for sample preparation. Various acid digestions and combined acid-base digestion data are discussed. Chemical and atomic absorption data are combined to confirm the

structure of the acid-insoluble material identified by x-ray diffraction analysis. Recommended digestion procedures are included for the quantitative analysis of superphosphoric acid for Fe, Al, and P.

81

Determination of Total Phosphate and Identification of Acid-Insolubles in Superphosphoric Acid.

A. B. Carel and D. E. Jordan (Continental Oil Co., Ponca City, Okla.).

J. Ass. Offic. Anal. Chem. 53 (2), 375 (Mar. 1970).

Correction of the title paper (*FA 2*, 1798), p. 580, right column, lines 16 and 21-23 and p. 581, left column, line 12, change "$H_2P_3O_{11}$" to "$H_2P_3O_{10}$."

82

Automated High Precision Determination of Phosphorus at Concentrations of 0.01 to 7.5 mg P_2O_5/ml.

D. E. Jordan (Cont. Oil Co., Ponca City, Okla.).

J. Assoc. Offic. Anal. Chem. 52 (3), 581-7 (May 1969).

An automatic P_2O_5 method of wide concentration range which analyzes phosphate from 0.01–7.5 mg P_2O_5/ml without range expansion and with *in situ* dilution is described. Parameters involving elimination of sample-wash crossmixing and modification of known published technology are described. Precision at 40 samples/hour throughout the concentration range from 0.1–75% P_2O_5 is better than ±0.3% relative and accuracy is better than ±0.4% relative.

83

Microdetermination of the Terminal Phosphate Groups in Esters of Pyrophosphoric Acid.

Marek Gniazdowski and Wladyslaw Wieckowski (Akad. Med., Lodz, Poland).

Chem. Anal. (Warsaw) 14 (4), 877-82 (1969) (Pol).

CA 72, 18247.

To determine total P, mineralize the sample in 0.5 ml H_2SO_4 at 200-20°, dilute to 8 ml, add 0.5 ml 5% $(NH_4)_2MoO_4$ and 0.5 ml of a solution containing 0.2 g Na 1-amino-2-naphthol-4-sulfonate dissolved in 100 ml solution 12% with respect to $Na_2S_2O_5$ and 1.2% with respect to Na_2SO_3, dilute to 10 ml, heat 20 minutes on a boiling water bath, cool, and measure the absorbance at 820 millimicrons. To determine labile P hydrolyze the sample in *N* H_2SO_4 and determine P similarly.

84

Determination of Phosphorus in Air.

Janina Pruszynska (Fabryka Polprzewodnikow, Warsaw).

Chem. Anal. (Warsaw) 12 (5), 1129-32 (1967) (Pol).

CA 68, 32958.

Air (in a semiconductor plant) was passed at a flow rate 100 l./hr through a moist filter paper, the filter was extracted with hot H_2O, and P was determined in the extract colorimetrically as Mo blue. The method permits the determination of 25 γ P/m^3.

85

New Spectrophotometric Method for the Determination of Phosphate with Complexon III: (Disodium Salt of EDTA).

S. R. Trivedi and G. S. Johar (V.S.S.D. Coll., Kanpur, India).

Labdev, Part A 8 (1), 19-21 (1970).

CA 72, 139382.

PO_4^{3-} ($\gtrsim$0.30 mg/ml) can be determined indirectly by precipitation with excess Bi(III) at pH ~0.5 ($NaOAc$-HNO_3 buffer). Heat the reaction mixture before filtering and determine Bi(III) in the filtrate by titration with Na_2H_2L (H_4L = EDTA). By using Fe salicylate as the indicator, monitor the titration spectrophotometrically at 500 nm in 20% EtOH. The relative error is ±0.5%.

86

An Automated Fast Reaction-Rate System for Quantitative Phosphate Determinations in the Millisecond Range.

A. C. Javier, S. R. Crouch, and H. V. Malmstadt (Univ. Illinois, Urbana).

Anal. Chem. 41 (2), 239-43 (Feb. 1969).

A new approach has been developed for precise and accurate quantitative determinations of phosphate with analysis times in the millisecond range. The method utilizes a completely automated stopped-flow system with direct digital readout of initial reaction rates to measure the initial rate of formation of 12-molybdophosphoric acid from phosphate and Mo (VI) in acid medium. This rapid reaction yields digital rate data proportional to the phosphate concentration about 100 milliseconds after the reagents are automatically mixed. The phosphate concentration from 1.0 ppm and up can be read out directly on the digital meter or a printer. With the automatic sampling system to deliver phosphate samples to the mixing chamber several thousand samples or standards can be analyzed per hour. An average of ten results can be read out in about 10 seconds, including all sample handling, and the relative standard deviations of the averages are less than 1%. Results are presented to demonstrate the relative freedom from interferences, the high sensitivity, and the general applicability of the technique.

87

Activity of Phosphate Ions Measured with Phosphate Electrodes of the Second Kind.

A. Statkay (Weizmann Inst. Sci., Rehovoth, Israel).

Anal. Biochem. 29 (2), 311-22 (1969).

Phosphate electrodes of the second kind were used to measure the activity of phosphate ions in aqueous solutions of orthophosphoric acid. The equation relating the emf with the activity of the various phosphate ions, which has been previously assumed to apply only under limited experimental conditions, is developed rigorously, and shown to be of general validity. The calculated results obtained by the use of the approximate equations developed agree well with the experimental values in the range of concentrations of phosphoric acid of 10^{-2} to $10^{-1}M$. In the range of concentrations of phosphoric acid of 10^{-4} to $10M$ the activity of HPO_4^{--} appears to be constant, and the change of emf between the phosphate electrodes and the H^+ electrodes is due only to the change in the activity of the H ions. The value of the phosphate electrodes of the second kind described in the literature appears to be limited, and considerable additional evaluation is necessary before they can be employed as reliable ion-specific reference electrodes.

88

Potentiometric Microdetermination of Phosphate with An Ion-Selective Lead Electrode.

Walter Selig (Lawrence Radiation Laboratory, Livermore, Calif.).

Mikrochim. Acta, No. 3, 564-71 (1970).

Phosphate (0.1-2.5 mg) was determined with 99-104% mean recoveries by direct potentiometric titration with $Pb(ClO_4)_2$ at pH 8.25-8.75, without interference from NO_3^- or SO_4^{2-}. A Pb-selective indicating electrode, a double-junction reference electrode, and an expanded-scale pH meter were used. Chlorine and F^- can interfere slightly, and the silicate content must not exceed that of P. Also, anions forming insoluble Pb

salts (solubility product $pK_{sp}>8$) interfered.

89

Titrimetric Method for the Determination of Phosphate.

B. C. Sinha, S. D. Gupta, and S. Kumar (Central Glass and Ceramic Res. Inst., Calcutta, India).

Analyst 93, 409-12 (1968).

Anal. Abstr. 17 (4), Abstr. No. 2066 (Oct. 1969).

The PO_4^{3-} is precipitated as zirconium phosphate with a known amount of Zr, and the excess of Zr is titrated with EDTA. There is no interference from Fe^{III}, Ti^{IV}, Th, or Bi^{III}, but F forms a strong complex with Zr^{IV}; if > 1.4 mg of F is present, removal by treatment of the sample with $HClO_4$ and H_3BO_3 is necessary. The solution (0.7 to 88 mg of P_2O_5) is treated with 125 ml of 4*M* HNO_3, and diluted to ≃200 ml. A known volume (10 to 30 ml) of 0.05*M* $ZrO(NO_3)_2$ in ≃1.1*M* HNO_3 is added, and the mixture is heated on a steam bath for ≃30 minutes, cooled and made up to 250 ml with *M* HNO_3. The liquid is filtered through paper and, after discarding the first portion of the filtrate, 100 ml is diluted to 200 ml with water and heated to boiling point to remove oxides of N; the Zr is then titrated slowly with 0.02*M* EDTA (xylenol orange as indicator). The temperature of the solution during titration should be 90° or higher, and near the end-point the EDTA solution should be added at 1 drop/second. Application of the method to phosphate fertilizers gave satisfactory results.

90

Application of Displacement Reactions in Flame Photometry: I. The Determination of Phosphate by a Flame Emission Method.

E. Szebenyi-Gyory *et al* (Queen's Univ., Belfast, Ireland).

Talanta 17 (12), 1167-74 (Dec. 1970).

Phosphate ions decrease the flame emission of Ca, but this effect can be partly offset by adding a second metal which partly displaces Ca from the non-excitable species. For the determination of phospnate the sample solution is divided into four equal parts; to each of these, various amounts of Ca and Ba ions are added such that the total (molar) concentration of the metals is constant. Plotting the intensity measured at 630 nm vs the Ca content of the solution gives a straight line, the slope of which depends on the concentration of phosphate ions present. The method is suitable for rapid determination of phosphate. Accuracy and precision are within the usual limits characteristic of flame photometric methods.

91

Divalent Phosphate Electrode.

Irving Nagelberg, L. I. Braddock, and G. J. Barbero (Hahnemann Medical College, Philadelphia, Pa.).

Science 166 (3911), 1403-4 (Dec. 12, 1969).

Divalent phosphate ion activities can be measured in dilute aqueous solutions in the physiological pH range (7.0-7.5) with a liquid ion-exchange membrane electrode system. The organic ion exchanger consists of an amine chloride membrane. Reference solutions may be either aqueous chloride or bicarbonate solutions. An essentially Nernstian slope is obtained.

92

A Selective Amplification-Titration Procedure for the Determination of Microgram Amounts of Phosphate.

G. F. Kirkbright, A. M. Smith, and T. S. West (Imperial College, London).

Analyst 93, 224-7 (Apr. 1968).

In the title determination phosphate is converted into phosphomolybdic acid, which is separated from excess molybdate by extraction. The phosphomolybdate is back-extracted into aqueous solution, and the 12 molybdate ions accompanying each phosphate ion are reduced on a Ag reductor column and titrated with 10^{-3}*M* Ce(IV) by the use of a 50 ml burette. Other heteropoly acid-forming elements (for example, As, Sb, Ge, and Si) do not interfere, nor do a wide range of other ions. The method is precise and rapid, and has been applied to the submicro determination of P in a standard organic compound.

93

Rapid Analysis for Phosphorus Pentoxide Content in Apatite Concentrates by a Nuclear Magnetic Resonance Method.

M. A. Slutskin.

Zap. Leningrad. Gorn. Inst. 56 (1), 39-42 (1968) (Russ).

CA 71, 56376.

The JNM-3H-60 N.M.R. spectrometer is suitable for rapid (time of one analysis four minutes) and accurate (error ≦0.04%) determination of P_2O_5 in apatite concentrate. The apatite standards contained 38.23–40.09% P_2O_5. Effective volume of the sample was 3 ml. Results were compared with the conventional oxalate method.

94

Evaluation of the Reproducibility and Sensitivity of a Determination of Phosphorus Based on Intralaboratory Control Data.

N. S. Valeev and V. I. Titov.

Tr., Tsent. Nauch.-Issled. Gornorazved. Inst., No. 82, 260-3 (1968) (Russ).

CA 73, 52025.

The average square deviation of the determination of P in rocks by the molybdophosphate method was calculated from results of basic and control analysis of 1195 industrial samples. The sensitivity is 0.1% P_2O_5 at 30% coefficient of variation.

95

A Rapid Visuo-Colorimetric Method for the Determination of Phosphate in Phosphatic Rocks.

P. D. Malhotra and J. K. Sacher (Geological Survey of India, Lucknow).

Am. Mineralogist 54 (1-2), 113-17 (Jan.-Feb. 1969).

The title method was developed for quick determination of the P_2O_5 content, even under field conditions, in evaluating the potential of phosphate rock deposits. To 0.1 g finely powdered sample in a dry test tube add 3 ml of 1:1 HNO_3. Heat to boiling and gently simmer for 30 minutes. If the solution is colorless, dilute to 20 ml, shake, and allow to settle. Transfer a suitable aliquot (0.1-2 ml) to a clean 16 x 150 mm test tube. Add 2 ml of molybdivanadate reagent from an automatic pipette. Shake and dilute to 10 ml. Let stand for 10 minutes. Compare the color with that of standards similarly prepared. If the digestion solution is not colorless the color must be removed: add $KMnO_4$ solution dropwise until the $KMnO_4$ color persists. Then destroy excess $KMnO_4$ with a few drops of Na_2SO_3 solution, followed by boiling for 2 or 3 minutes. A 3-man team can analyze 120-150 samples daily under field conditions. The results may deviate by 1-2% from the actual P_2O_5 content.

96

Indirect Estimation of Phosphorus in Rock Phosphate by Atomic Absorption Spectrophotometer Using Ion-Exchange Decomposition Technique.

K. C. Singhal and B. K. Banerjee (Plann. & Develop. Div., Fertilizer Corp. India Ltd., Sindri, India).

Technology 5 (3), 239-41 (1968).
P has been estimated by employing its depressing effect on Ca absorption. The samples were prepared by shaking the powdered rock phosphate with cation-exchange resin and water. The ion-exchange decomposition technique was found ideal for the estimation of P by atomic absorption spectrophotometer, because it eliminates the interfering anions which are added in the acid digestion technique and thus saves one step. The results are in good agreement with those of the chemically analyzed samples.

97
Indirect Method of Estimation of Phosphorus by Atomic Absorption Spectrophotometry.
K. C. Singhal, A. C. Banerji, and B. K. Banerjee (Fertilizer Corp. of India Ltd., Sindri, Bihar).
Technology (Sindri) 5 (2), 117-19 (Apr.-June 1968).
A quick and accurate method for P determination in rock phosphate has been developed by atomic absorption spectrophotometry. P is determined by observing the depression in absorbance of Sr caused due to its presence.

98
Rapid X-Ray Fluorescence Determination of Phosphorus in Geologic Samples.
B. P. Fabbi (U. S. Geological Survey, Menlo Park, California).
Appl. Spectrosc. 25 (1), 41-3 (Jan. 1971).
Calcium $K\beta_1$ and $K\beta_5$ both have second order (II) lines that interfere spectrally with the phosphorus $K\alpha_1$ first order (I) analytical line in the x-ray fluorescence determination. By combining maximum pulse height discrimination with a mathematical correction for peak overlap, P can be accurately determined in a wide variety of geologic samples.

99
Use of N.M.R. for Monitoring the Phosphorus Content in an Apatite Concentrate.
E. S. Krichevskii and M. A. Slutskin (Leningrad. Gorn. Inst. im. Plekhanova, Leningrad, U.S.S.R.).
Zavod. Lab. 34 (4), 435-6 (1968) (Russ).
CA 69, 53241.
The monitoring of P_2O_5 content in an apatite containing 38-40% P_2O_5 was examined. The results show that the N.M.R. method can be used as the absolute error is $\leqslant$0.5%.

100
Amperometric Determination of Phosphorus Pentoxide.
L. S. Rumyantseva.
Fiz.-Khim. Issled. Glinist. Miner. Silikat. Mater., pp. 113-14 (1970) (Russ).
CA 76, 67802.
A buffer containing glycocoll + $NaNO_3$ + HNO_3 is the best supporting electrolyte for amperometric titration of PO_4^{3-} with Bi salt solution. In determination of 5-20 mg P_2O_5, the mean square error was ±1.33%. PO_4^{3-} can also be determined by back-titration of excess MoO_4^{2-} (after precipitation of ammonium molybdophosphate) with Complexon III according to the oxidation current on a rotating Ta anode; for obtaining a constant composition precipitate, an additional electrolyte (NH_4NO_3) was added to the solution. The method is useful for determination of P_2O_5 in fertilizers and phosphorites.

101
Differential Photometric Method for Determining Phosphorus Pentoxide in Phosphorus Fertilizers and Phosphorites.
E. P. Panteleeva and E. V. Cherepanova (Leningr. Tekhnol. Inst. im. Lensoveta, Leningrad, U.S.S.R.).
Khim. Sel. Khoz. 9 (8), 615-19 (1971) (Russ).
CA 76, 2802.
A differential photometric method was developed to increase the precision of the standard photometric method for determining P_2O_5 as Mo blue by obtaining a more stable coloring of solutions, and in order to increase the range of the determined concentrations (>20% P_2O_5). The differential method differs from the direct photometric method by the fact that measurements are performed compared with a reference solution. This method permits rapid determination (60 min/one determination) of high concentrations of P_2O_5 (20-60%), and it is not less accurate (0.2-0.5%) than the standard gravimetric analysis. Impurities such as CaO, Fe_2O_3, Al_2O_3, SiO_2, SiF_6^{2-}, and F^- in amounts exceeding by 25-, 15-, 15-, 4-, 22-, and 15-times, respectively, the wt content of P_2O_5 in the analyzed sample do not interfere with P_2O_5 determination.

102
Precision Determinations of High Level Phosphorus Pentoxide Contents.
J. I. Longest and C. J. Martin (Central Phosphates, Inc., Plant City, Fla.).
Automat. Anal. Chem. Technicon Symp., 3rd, 1, 261-4 (1967) (Pub.,1968); Mediad Inc.: White Plains, N. Y.
An automatic method using the vanadomolybdate colorimetric procedure for determination of P_2O_5 is discussed. Samples are digested in either aqua regia, hydrochloric, or neutral ammonium citrate solution; there are no interferences but ammonium citrate provides a faster response on peak read outs. To enhance accuracy and precision of high concentrations of P_2O_5, a baseline standard containing 0.352 mg P_2O_5/ml was provided for the wash receptacle of the sampler programmed to operate at 20 samples/hour with a 1:1 wash to sample ratio. HCl reagent (910 ml H_2O, 90 ml concentrated HCl, and 0.05 ml Levor IV) and air were mixed with the sample stream, ammonium vanadate, and ammonium molybdate. The combined stream enters a time delay coil in a constant temperature bath and a controlled rate of air and liquid is removed before the stream enters the flow cell of the colorimeter equipped with 475 millimicron filters. The results of four readings show deviations less than ± 0.05% P_2O_5 equivalent for concentrations of 46-54% P_2O_5 content of material analyzed.

103
Spectrofluorimetric Determination of Orthophosphate as Rhodamine B Molybdophosphate.
G. F. Kirkbright, R. Narayanaswamy, and T. S. West (Chem. Dep., Imp. Coll., London, Engl.).
Anal. Chem. 43 (11), 1434-8 (1971).
Between 0.04 and 0.6 μg of P is determined as orthophosphate by formation of the ion-association complex of molybdophosphate with the basic dyestuff Rhodamine B. After extraction of excess dye reagent into $CHCl_3$, the Rhodamine B molybdophosphate is extracted into $CHCl_3$.BuOH (4:1 vol/vol) and the intensity of the fluorescence in this solvent measured at 575 nm with excitation at 350 nm. Optimal conditions for the determination were established, and the effects of 100-fold excesses of each of 37 foreign ions were examined. The determination is highly selective, large amounts of silicate do not interfere, and As(III) and V(V) are tolerable at 25- and 50-fold wt excesses, respectively. The structure of the ion-association complex was examined.

104

A Rapid Indirect Titrimetric Determination of Microgram Amounts of Orthophosphate.

G. F. Kirkbright, A. M. Smith, and T. S. West (Imperial College, London, Engl.).

Analyst (London) 94 (1117), 321-3 (April 1969).

Microgram amounts (10 to 50 micrograms) of P as orthophosphate have been determined in a sample volume of 1 to 4 ml, by addition of excess of thorium nitrate solution and micro titration of the excess of thorium with standard EDTA solution. Filtration of the solution before titration is not required. The presence of large excesses of chloride, bromide, iodide, nitrate, sulfate, perchlorate, and silicate can be tolerated, but fluoride, borate and arsenate interfere. Microgram amounts of orthophosphate have been determined in synthetic sample solutions containing other anions. Any one result is accurate to within ± 1 microgram of P.

105

Study of the Separation, by Means of Citrates, of Calcium Orthophosphates Contained in Fertilizers.

Y. Bardin (National Inst. Agron. Res., Alsace Center, Colmar, France).

Ann. Agron. 21 (1), 95-108 (1970).

The analysis of calcium orthophosphates in fertilizers with the help of ammonium citrate solutions shows that the results depend partially on the characteristics of the solution used. This study, while underlining that this solubilization has value only in the case of calcium orthophosphates, allows to explain the causes of these differences. It tries to determine the parameters of the solution providing the best separation of dicalcium phosphate from the apatitic form and shows that it is of interest to use a solution having a high pH close to 10.6 which is the case with Joulie citrate.

106

Determination of Orthophosphate in the Presence of Nitrate Ions.

E. J. Duff and J. L. Stuart (Turner Dent. Sch., Univ. Manchester, Manchester, England).

Analyst (London) 96 (1148), 802-6 (1971).

Orthophosphate in the presence of nitrate ions is determined spectrophotometrically as the molybdenum blue complex at 820 nm after reduction of the nitrate ions to NH_3 by Al and aqueous NaOH and removal of NH_3 by heating. The phosphate is converted to the molybdophosphate complex which is reduced to molybdenum blue. Beer's law is obeyed for $\leqslant$0.10 mg P/50 ml. The method is sensitive to $\geqslant$ 0.0004 mg P/ml. Orthophosphate ($10^{-4}M$) can be determined in the presence of $\sim 10^{-1}M$ nitrate. $Al_2(SO_4)_3$ solution was added to eliminate the fluoride interference.

107

Infrared Spectroscopic Study of Orthophosphoric Acid Triamide and the Products of Its Thermal Decomposition.

M. Ya. Koroleva and V. G. Dubinin.

Zh. Prikl. Spektrosk. 5 (3), 344-8 (1966) (Russ).

J. Appl. Spectrosc. 5 (3), 256-9 (Sept. 1966).

A spectroscopic study was made of the products of the thermal decomposition of orthophosphoric acid triamide. The thermal treatment of the $OP(NH_2)_3$ was carried out in dry air at temperatures of 50-800°. Polycondensation takes place slowly up to 100°, and at 130-400° appreciable P-NH-P polycondensation takes place. The action of heat on $OP(NH_2)_3$ leads to almost complete disappearance of the NH_2 group. At 400-800° the spectra show that poly-condensation proceeds further. In some cases the structure of the polymer can be represented as a three-dimensional network in which each N atom is joined to three P atoms. Thermal treatment of $OP(NH_2)_3$ gives polymetric products with different degrees of polymerization and different structures.

108

Microdetermination of Orthophosphate Using the Ring Oven Technique.

S. L. Sachdev and P. W. West (Louisiana State Univ., Baton Rouge).

Atmos. Environ. 2 (4), 331-7 (1968).

A rapid and highly selective method for the microdetermination of PO_4^{3-} by using *o*-dianisidine molybdate reagent and the ring oven technique is presented. As little as 0.1 μg of PO_4^{3-} can be determined with reasonable accuracy. Very little interference is involved. Only Zr^{4+}, Al^{3+}, and Th^{4+} interfere when present in 100-fold excess. The method is of special interest for air pollution studies.

109

The Determination of Phosphorus in Phosphoric Acid and Sodium Tripolyphosphate.

S. F. Holder (Works Lab., Albright and Wilson Ltd., Oldbury, Engl.).

Proc. Fert. Soc., No. 104, 69-79 (1968).

Recent developments in the quinoline molybdate method for the determination of phosphates are given. Examples are given of results obtained in collaborative work on phosphoric acid and sodium tripolyphosphate by the single-solution reagent method.

110

Composition Analysis of "Strong Phosphoric Acids" in a pH Titration Method.

Daido Ishii, Masashi Goto, and Kazuyoshi Hayashida (Nagoya Univ., Nagoya, Japan).

Bunseki Kagaku 19 (6), 838-40 (1970) (Japan).

CA 73, 105210.

The components of "strong phosphoric acid," ortho-, pyro-, tripoly-, and tetrapolyphosphoric acids, were determined by using an auto-titrator. A 1-g sample was diluted to 100 ml with H_2O, a 5-ml aliquot was diluted to $\sim$50 ml with H_2O and was titrated with 0.1 *N* NaOH. The titer (in mole number) to the first inflection and that to the second one are *A* and *B*, respectively. Then $CaCl_2$ solution is added, and the titration is continued to the third inflection. This titer is *C*. To a separate aliquot adjusted to pH 3.8-3.9, $Zn(OAc)_2$ solution is added to precipitate $P_2O_7^{4-}$. After dissolving the precipitate the solution is titrated with 0.1 *N* NaOH. The titer is *D*. The mole numbers of ortho-, pyro-, tripoly-, and tetrapolyphosphoric acid, x_1, x_2, x_3, and x_4, respectively, satisfy the following simultaneous equations: $x_1 = C, x_2 = D, x_1 + 2x_2 + 3x_3 + 4x_4 = A$, and $x_1 + 2x_2 + 2x_3 + 2x_4 = B$.

111

Effects of Washing Technique in the Determination of Citrate-Insoluble and Available P_2O_5 in Triple Superphosphate.

W. J. Harwell (Farmland Ind., Inc., Bartow, Fla.) and E. B. Hewitt (USS Agri-Chem., Inc., Bartow, Fla.).

J. Assoc. Offic. Anal. Chem. 52 (5), 946-9 (Sept. 1969).

The results of the citrate-insoluble and available P determinations are influenced by the technique used in the initial step, the removal of the water-soluble fraction. An "active" washing technique in removing all of the water-soluble fraction will give lower values for citrate-insoluble P and higher values for available P.

112

Infrared Spectra of Fused Defluorinated Phosphates.

E. V. Poletaev, S. I. Kalmykov, and Yu. A. Kushnikov.

Trudy Inst. khim. Nauk, Akad. Nauk kazakh. SSR 25, 42-7 (1969) (Russ).

Anal. Abstr. 21, 619.

These spectra are used to determine the content of P soluble in citric acid. Measurements are made in the region of the PO_4^{3-} deformational vibrations at 560 and 600 cm^{-1} and at 580 cm^{-1}, with the sample (2 mg) pressed into a KBr tablet (700 mg). The error is within 5%, and an analysis takes ≃1 hr.

113

Determination of Phosphate and Arsenate Ions by Precipitation Titration.

Laszlo Szekeres (Allatorvostud. Egyet., Kemiai Tanszek, Budapest).

Magy. Kem. Lapja 22 (6), 326-7 (1967) (Hung).

CA 68, 9122.

Solutions containing 50-100 mg PO_4^{3-} or 50-150 mg AsO_4^{3-} are buffered to pH 10 and titrated with 0.1 *M* $MgSO_4$ in the presence of phthalein violet. Ca, Mg, Ni, Zn, and Cu are masked by EDTA; Fe^{3+} is reduced by ascorbic acid and then masked by KCN. The method can be used to determine PO_4^{3-} in superphosphates and AsO_4^{3-} in herbicides.

114

Amperometric Determination of Triphosphate Ion.

G. O. Omarkulova, O. A. Songina, and N. A. Freze (Kaz. Khim. Tekhnol. Inst., Alma-Ata, USSR).

Zavod. Lab. 36 (1), 20-1 (1970) (Russ).

CA 72, 117429.

Sodium tripolyphosphate until recently, was determined indirectly either by titration of H^+ evolved by addition of excess Zn^{++} at pH 3.8 or by precipitation by $BaCl_2$ at pH 5. Interference by $P_2O_7^{4-}$ is encountered with the latter method. Presently $P_3O_{10}^{5-}$ is determined directly either by chromatography or gravimetrically by precipitation with $Co(en)_3Cl_3$. The amperometric procedure is a variant of this gravimetric method. The titration was carried out with a dropping Hg electrode at -0.8 V vs SCE. The solubility of the precipitate was decreased by adding EtOH to 30-50 vol %. One g of $Na_5P_3O_{10}$ was dissolved in H_2O and diluted to 100 ml. A 10-ml aliquot plus sufficient HCl (~0.5 ml) to give pH 3.6 and 10 ml of a buffer solution made up of 105 ml HOAc, 25-30 ml of EtOH, and 5-6 small pellets of gelatin were placed in the polarographic cell. Oxygen was purged by bubbling through CO_2 for 3-5 min and the solution was titrated with $Co(en)_3Cl_3$ with agitation and continued CO_2 purging. The precipitate formed slowly and a constant current reading indicating the equivalence point was not achieved until 4-5 min after the first appearance of the precipitate. Statistical comparison of the gravimetric and amperometric methods at the 95% confidence level gave variances of 0.28% and 0.30%, respectively. Thus, while the accuracy of both procedures was experimently the same, the amperometric method is preferred because a determination takes only 20-30 min.

115

Complexometric Analysis of Technical Triphosphates.

Erich Heinerth (Anal. Lab., Henkel und Cie., G.m.b.H., Duesseldorf, Ger.).

Chim. Phys. Appl. Prat. Ag. Surface, C. R. Congr. Int. Deterg., 5th, 1, 261-6 (Sept. 9-13, 1968) (Pub. 1969) (Ger). Ediciones Unidas, S.A.: Barcelona, Spain.

CA 74, 27793.

Diphosphate and triphosphate were determined indirectly in samples of known total H_3PO_4 content by precipitation with excess $Zn(OAc)_2$ in OAc^- buffer (pH 4.7-4.9) as $Zn_2P_2O_7 \cdot 5H_2O$ and $Zn_2NaP_3O_{10} \cdot 9H_2O$, respectively, and by subsequent EDTA titration of the free Zn. The relative error and relative standard deviation were ± 1% and ± 0.5%, respectively. Trimetaphosphate, < 10% SO_4^{2-}, and < 1% monophosphate did not interfere.

116

Spectrophotometric Determination of Pyrophosphate with Trans-dichlorobis(ethylenediamine)cobalt(III).

C. L. Sharma (Roorkee Univ., Roorkee, India).

Indian J. Chem. 9 (3), 279 (1971).

CA 75, 14664.

Pyrophosphate in aqueous medium gives a violet color (stable for 24 hr) with *trans*-$[Co(en)_2Cl_2]^+$ having maximum absorbance at 510 nm. Based on this reaction a spectrophotometric method is proposed for the estimation of 40-950 ppm pyrophosphate. The mean sensitivity is 20 $\mu g/cm^2$/0.005 absorbance unit. A number of foreign ions including ortho- and metaphosphates do not interfere even if present in excess, while traces of Cu^{2+}, VO_2^{2+}, MoO_4^{2-}, Ce^{4+}, Th^{4+}, and Mg^{2+} interfere in the estimation of pyrophosphate.

117

Gravimetric Determination of Pyrophosphate Using *Cis*-Dichlorobis(Ethylenediamine)Cobalt(III) Chloride.

C. L. Sharma (Dep. Chem., Univ. Roorkee, Roorkee, India).

Fresenius' Z. Anal. Chem. 257 (2), 133 (1971).

CA 76, 67697.

$P_2O_7^{4-}$ (20-80 mg) was quantitatively precipitated as golden yellow $Na[Co(en)_2P_2O_7]$ by addition of *cis*-$[Co(en)_2Cl_2]Cl$ in a 20% excess at pH 10-12 adjusted with NaOH. The precipitate was washed with H_2O and dried at 110-20°. Ag, Cu, V(V), Mg, As(III), Bi, Ce(IV), and Th interfered and must be removed before the determination.

118

Determination of Water-Soluble Phosphorus Pentoxide in Fertilizer Solutions Containing Short-Chain Linear Polyphosphates. I. Preliminary Study.

D. A. Palgrave, T. J. Paton, and R. Elson (J. W. Chafter Ltd., Doncaster, Engl.).

J. Sci. Food Agr. 21 (6), 273-5 (1970).

A study of the official vanadium phosphomolybdate spectrophotometric method, to determine H_2O-soluble P_2O_5 in fertilizers, has shown that incomplete recovery may occur if a substantial proportion of the P_2O_5 is present as short-chain linear polyanions. Minor modifications of the method are needed, including the use of a greater volume of acidulant and a more precise definition of the term "incipient ebullition."

119

Spectrophotometric Method for Determining Phosphorus in Condensed Phosphates.

S. I. Kalmykov, K. I. Malakhova, and N. P. Shevchenko (Inst. Khim. Nauk, Alma-Ata, U.S.S.R.).

Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 21 (3), 1-4 (1971) (Russ).

CA 75, 83851.

The spectrophotometric determination of P as the yellow complex with vanadate and molybdate in acid medium was adapted for condensed phosphates. Samples to be analyzed were converted to orthophosphates by boiling with HCl. This procedure gave better results than those involving treatment with HNO_3 or with mixtures of HNO_3 and HCl or $HClO_4$, which caused lower results by the formation of nitrite and

reduction of the Mo–V–P complex.

120
Potentiometric Titration of Hypophosphite and Phosphite with Vanadate.
T. Matsuo, J. Shida, and K. Kudo (Yamagata Univ., Yonezawa, Japan).
Bunseki Kagaku 18 (4), 488-91 (1969) (Japan).
CA 71, 56373.
Hypophosphite is oxidized by vanadate to phosphate through phosphite as an intermediate in the presence of Ag^+, but phosphite is not oxidized to phosphate in the absence of Ag^+. To determine 15–30 mg hypophosphite, add an excess of 0.1*N* vanadate containing 0.2–3.5*N* H_2SO_4 and boil for 2–3 minutes. Titrate the remaining vanadate with 0.1*N* Mohr's salt. To another aliquot, add 2 ml 5% Ag_2SO_4 solution containing H_2SO_4 and a definite excess of 0.1*N* vanadate. Titrate the solution with 0.1*N* Mohr's salt to obtain the total hypophosphite + phosphite.

121
Rapid Oxidimetric Determination of Hypophosphite with Dichromate.
V. R. S. Rao (Indian Inst. Technol., Madras, India).
Fresenius' Z. Anal. Chem. 246 (6), 384 (1969).
CA 71, 108845.
Add 30 ml H_2SO_4 to 10 ml sample solution containing 0.2–0.3 millimole $H_2PO_2^-$ to give >7.5*M* acidity. Add 20 ml 0.1*N* $Cr_2O_7^{2-}$ to the sample solution, mix well, dilute gradually with H_2O to 150 ml, cool, and titrate with 0.1*N* ferrous ammonium sulfate against *N* phenylanthranilic acid indicator. Correct the titrant volume for the blank value. The method also oxidizes HPO_3^{2-} to PO_4^{3-}. Consequently, mixtures containing HPO_3^{2-} and $H_2PO_2^-$ can be analyzed by combining the $Cr_2O_7^{2-}$ method with the method of M. N. Sastri and C. Kalidas (1957), involving the use of $FeCl_3$ which oxidizes only $H_2PO_2^-$ to HPO^{2-}

122
Nomogram for the Separate Determination of Concentrations of Mono- and Diammonium Phosphates in Aqueous Solutions.
A. N. Sarbaev and Z A. Polyakova.
Khim. Prom. (Moscow) 47 (7), 520-2 (1971) (Russ).
CA 75, 104769.
The nomogram is based on determination of NH_3 and P_2O_5 concentration and measurement of pH in 5-30% solutions of orthophosphates containing varying amounts of $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$.

123
Measurement of Phosphorus in Waste Water.
S. G. Jankovic, D. T. Mitchell, and J. C. Buzzell.
Water Sewage Works 114 (12), 471-4 (Dec. 1967).
A simple and rapid method for measuring the P content of domestic waste water is presented. A method proposed by J. Murphy and J. Riley (*Anal. Chem. Acta 27*, 31-6, 1962) is recommended. It is outlined with respect to treatment of the three principal types of P compounds usually present: ortho, poly, and organic. Ascorbic acid was found to be superior to $SnCl_2$ as a reducing agent. Changes in pH from 1.2-10.5 or the presence of small amounts of $K_2S_2O_8$ or Na_2SO_3 did not seriously affect the results.

124
Determination of Phosphate in Water with Tungsten-185.
Richard B. Hahn and Thomas M. Schmitt (Wayne State Univ., Detroit, Mich.).
Anal. Chem. 41 (2), 359 (Feb. 1969).
The 185-tungstomolybdophosphoric acid complex is extracted into an organic solvent; the extracted W activity is then counted and related to the original phosphate concentration.

125
Determination of Inorganic Phosphorus in Water Samples.
V. A. Stenger and D. N. Armentrout (to Dow Chemical Co.).
U.S. 3,607,070, Sept. 21, 1971, Appl. Feb. 4, 1970; 5 pp.
The title determination consists of adding a very small amount of an alkali metal salt to the sample, atomizing the solution with air, and injecting the atomized droplets into a flame ionization detector. An interaction between the alkali metal and the P produces an enhanced ionization of the flame that is proportional to the P concentration. Apparatus is described.

SEE ALSO the following numbered abstracts in other sections: 321-31, 334-39, 407-8, 416, 442.

CONDENSED PHOSPHATES

126
Microcrystalline Cellulose Thin-Layer Chromatography of Phosphates.
Nobuharu Takai, Takaya Iida, and Takeo Yamabe (Univ. Tokyo, Tokyo, Japan).
Seisan-Kenkyu 19 (3), 87-8 (1967) (Japan).
CA 69, 24166.
Various phosphate ions, monomer, and polymer. were separated. The absorbent was a 0.2-mm-thick layer of microcrystalline cellulose. The plate was first developed in a basic solvent, PrOH-H_2O-28% NH_3OH (3:1:1), then turned 90° and was developed in an acidic solvent. The acidic solvent was a mixture of dioxane, Cl_3CCO_2H, HOAc, NH_4OH, iso-PrOH, and H_2O. The result was comparable to paper chromatography.

127
Separation of Phosphates by Thin-Layer Chromatography and Thin-Layer Electrophoresis. II. Qualitative Separation of Polycondensed Phosphates by Thin-Layer Electrophoretic Analysis.
E. F. Wagner (Waeschereiforsch. Krefeld e.v., Krefeld, Ger.).
Seifen-Oele-Fette-Wachse 94 (2), 27-30 (1968) (Ger).
CA 69, 48909.
Mono-, di-, and triphosphates are separated by thin-layer electrophoresis on cellulose at pH 2 and a total potential of 400 v. Polyphosphates are separated by thin-layer chromatography at right angles to the prior electrophoresis.

128
The Reactions of Calcium Trimetaphosphate in Paper Chromatography Concerning Ammonium-Calcium-Trimetaphosphate.
Von W. Fedlmann and I. Grunze.
Z. Anorg. Allgem. Chem. 360 (5-6), 225-30 (Aug. 1968).
During paper chromatography using NH_4^+-containing solvents calcium trimetaphosphate solution forms crystalline, non-moving ammonium-calcium trimetaphosphate. The latter can also be obtained from aqueous solution as a sparingly soluble salt. Its composition does not exactly correspond to the formula $NH_4CaP_3O_9 \cdot aq$ for it contains a small excess of Ca and a small deficit of ammonium.

129

Note on Removal of Cation Interference in Paper Chromatography of Concentrated Wet-Process Phosphoric Acid.

T. C. Woodis (Tennessee Valley Authority, Muscle Shoals, Ala.)

J. Assoc. Official Analytical Chemists 52 (1), 30 (Jan. 1969).

Revisions in procedures (*Anal. Chem. 36,* 1682-3, 1964) are described which make paper chromatographic methods applicable to those concentrated wet-process phosphoric acids that contain insoluble Fe- and Al-tripolyphosphates. These revisions should be useful in the fertilizer industry.

130

Highly Sensitive Color Reactions for Localization of Small Amounts of Phosphoric Acid on Paper Chromatograms.

Fritz Jungnickel (Friedrich-Schiller-Univ., Jena, Ger.).

J. Chromatog. 31 (2), 617-18 (1967) (Ger).

CA 68, 101450.

A method for detection of 0.02 μg amounts of P is described. Spray the chromatograms with a freshly prepared solution consisting of 5 ml 25% HCl, 5 ml 1% ammonium molybdate, and 90 ml Me_2CO. Heat at 85° for 3-6 min. Then, dip the chromatogram briefly in a solution which has been filtered after standing 3 hr and which was prepared by mixing a solution containing 2 g of crystal violet, aniline green, or iodine green in 350 ml of H_2O, and a solution containing 4 g of ammonium molybdate, and 50 ml of 10*N* HCl/100 ml aqueous solution. Lay the chromatogram on dry filter paper. The crystal violet separation appears as a blue spot on a yellow background; with aniline green, green against an orange background; with iodine green, turquoise against a colorless-yellow background.

131

Separation of Lower Oxo Acids of Phosphorus by Paper Chromatography.

Shigeru Ohashi, Terumasa Nakamura, and Shinobu Katabuchi (Kyushu Univ., Fukuoka, Japan).

J. Chromatogr. 43 (2), 291-2 (1969).

Twelve oxo acids of P with oxidation numbers lower than five were studied using paper chromatography. R_f values of the oxo acids of P are given for the anions developed with an acidic solvent (325 ml acetone, 25 g trichloroacetic acid, 1.75 ml aqueous ammonia (28%), and 150 ml H_2O) and with a basic solvent (190 ml ethyl alcohol, 150 ml isobutyl alcohol, 2.7 ml aqueous ammonia (28%), and 225.3 ml H_2O). The paper sheet was sprayed with an acidic molybdate solution and was exposed to uv light until the blue spots appeared.

132

Relation Between Paper Chromatographic R_f-Values and Two Phase-Distribution Ratios of Phosphate Ions.

Shigeru Ohashi, Yoshiaki Hirai, and Hirohiko Waki (Kyushy Univ., Hakozaki, Fukuoka, Japan).

Bull. Chem. Soc. Japan 40 (10), 2307-12 (1967).

An easy and useful method reflecting the behaviors of phosphate ions in paper chromatography was proposed. Under some assumption, the correlations between R_f in the paper chromatography and the distribution ratio D_s or D_f in the solvent extraction or in the filter paper batch equilibrium were investigated. When the water-miscible solvents are used, D_f-values may reflect R_f-values considerably well. If the water-immiscible solvents are used, rather D_s-values reflect R_f-values well. Although the partition only has so far been considered in these types of paper chromatography, the results showed that the adsorption phenomena cannot entirely be ignored in some solvent systems like a basic benzyl alcohol system.

133

Paper Chromatography of Condensed Phosphates.

C. Liteanu and Ana Ungureanu (Univ. "Babes-Bolyai," Cluj, Rom.).

Stud. Cercet. Chim. 19 (4), 365-75 (1971) (Rom).

CA 75, 94221

A review is given on the paper chromatography separation and determination of phosphates such as Na_2HPO_4, $Na_4P_2O_7$, $Na_6P_3O_{10}$, and $Na_4P_4O_{12}$. (67 ref)

134

Separation of Condensed Phosphates by Spiral Paper Chromatography.

M. N. Nabiev *et al* (Inst. Khim., Tashkent, U.S.S.R.).

Uzb. Khim. Zh. 15 (3), 18-20 (1971) (Russ).

CA 75, 115439.

The separation of phosphates by spiral chromatography (in which the paper is twisted into a spiral) is possible with small amounts of solvents at constant temperature. The R_f (R_x) values for PO_4^{3-}, $P_2O_7^{4-}$, $P_3O_{10}^{5-}$, $P_3O_9^{3-}$, and $P_4O_{12}^{4-}$ are 0.7(1), 0.4(0.56), 0.2(0.3), 0.14(0.2), and 0.1(0.13), respectively.

135

Determination of Phosphates in Sodium Tripolyphosphate by Column Chromatography.

A. Pion and E. Delrue (Lab. Contr. UCB S.A., Oudenburg, Belg.).

Automat. Anal. Chem., Technicon Symp., 3rd 1967 (2), 247-50 (Pub. 1968) (Fr.), Mediad, Inc.. White Plains, N.Y.

CA 71, 45524.

Tripolyphosphate and the three common impurities, namely pyrophosphate, trimetaphosphate, and orthophosphate, were separated on an AGl-X8 anionic resin column and eluted with KCl solution. The separated phosphates were hydrolyzed with hot HNO_3 to orthophosphate and determined colorimetrically as the vanadomolybdate. The authors modified the method of Koloff and were able to determine the pyro-, tripoly-, and trimetaphosphates in two hours by using an Auto Analyzer.

136

Chromatography of Phosphorus Anions.

G. Nickless and C. J. Peacock (Univ. Bristol, Bristol, Engl.).

J. Chromatogr. 40 (1), 192-3 (1969).

The ion-exchange chromatographic retention times of $PO_2(NH_2)_2^-$, $POS(NH_2)_2^-$, $PO_3NH_2^{--}$, $PO_2SNH_2^{--}$, and $PO_nS_{4-n}^{3-}$ (n = 0-4) were correlated with structure. Chromatography was carried out on a Dowex 1 X 10 anion-exchange resin column by continuous elution with an approximate linearly increasing concentration of KCl in H_2O, buffered at pH 11.4 with NH_3. To a very good approximation, the retention times were proportional to the eluent flow rate and to the gradient. Also, when the gradient was not started from zero KCl concentration, retention time decreased by a time approximately equivalent to the time required to reach the initial concentration if the elution had started from zero concentration. The additive effects of structural features on retention times and the use of the retention time-structure correlation in predicting structures of unknown compounds are demonstrated.

137

Rapid Determination of Polyphosphates by an Improved

Chromatographic Method Using Ion-Exchange Resin.

C. Benz and L. M. Paixao (Colgate-Palmolive Co., Piscataway, N.J.).

Chim. Anal. 50 (5), 247-50 (1968) (Fr).

Anal. Abstr. 17 (4), Abstr. No. 2067 (Oct. 1969).

The automated ion-exchange procedure of Lundgren and Loeb (*Anal. Abstr., 1961, 8*, 4125) has been modified, to reduce the time for an analysis, by use of a smaller sample, a shorter column, and a slightly changed system of gradient elution (with aqueous KCl). The illustrated apparatus includes a 4- or 5-cm column of Dowex 1-X8 resin (Cl^- form, 100 to 200 mesh); chromatograms are obtained in ≈20 minutes for mixtures of ortho-, pyro-, and tri-phosphates, or in ≈27 minutes when trimetaphosphate is also present. From 12 to 15 samples can be analyzed in 7.5 hours; accuracy and reproducibility are high.

138

Ion-Exchange Chromatographic Analysis of Condensed Phosphates in Lake Water and Wastewater.

G. W. Heinke (Univ. Toronto, Ontario, Canada) and H. Behmann (McMaster Univ., Hamilton, Ontario, Canada).

Advances in Automated Analysis-Industrial Analysis, Technicon Int. Congr. 2, 115-20 (1969) Pub. 1970 Mediad Corp., White Plains, N. Y.

Ion-exchange chromatography coupled with AutoAnalyzer equipment can be used successfully for the differential analysis of a mixture of condensed phosphates at low levels of concentration in lake and wastewater. A correction factor must be applied to the areas under the elution curve at lake water levels of concentration (0.5 mg PO_4/l.). Further work is required to identify and eliminate interferences with certain surface waters.

139

Elution Peak Positions of Linear Phosphates in Gradient Elution Chromatography with an Anion-Exchange Resin.

Shigeru Ohashi *et al.* (Kyushu Univ., Fukuoka, Japan).

J. Chromatogr. 50 (2), 349-53 (1970).

Experimental observed peak elution vol for linear phosphates with degree of polymerization = 1–9 on a Dowex 1-X4 (Cl^- form) anion-exchange column agreed within 9.3% with those predicted theoretically by the method of S. Ohashi and K. Koguchi (1967). The gradient elution was carried out with KCl solutions buffered at pH 9.3 with NH_3 and NH_4Cl. An elution curve obtained from a mixture of KH_2PO_4, tetra-Na diphosphate, and glassy Na polyphosphate (average degree of polymerization = 10) is given.

140

Ion-Exchange Chromatographic Analysis on the Chain Length of Polyphosphate Products.

Niro Matsuura, Tsin-ko Lin, and Yoshimitsu Kobayashi (Univ. Tokyo, Komaba, Meguro-ku, Tokyo, Japan).

Bull. Chem. Soc. Jap. 43 (9), 2850-8 (1970).

The ion-exchange chromatographic technique was used in order to find the average chain number of a polyphosphate product. For the assignment of the *n*th polymer in the obtained chromatogram, the dependence of the distribution coefficient, K_d, on the eluent concentration was examined by the use of both 20-cm and 60-cm resin columns. A lower series of polyphosphate was included in a relatively large amount in order that the average chain number based on the chromatographic analysis could be duly appreciated only for the case of basic polymers with lower molecular-wt. For a product "Graham Salt" with a number of phosphate links, the higher series of polyphosphate could not be desorbed entirely from the resin column; the accurate estimation of the average number was, then, improbable. The viscosity method is also not advisable to use the computation of a mean polymerization number in the polyphosphate with a low molecular wt. An attempt was made to improve the data on the average chain number by the viscosity measurements together with the chromatographic analysis of the polymer consitituent.

141

Separation of Cyclic Phosphates by Ion-Exchange Chromatography.

Shigeru Ohashi, Genichiro Kura, and Mutsukazu Kamo (Kyushu Univ., Fukuoka, Japan).

Mem. Fac. Sci., Kyushu Univ., Ser. C. 7 (1), 43-9 (1970).

CA 73, 105125.

A mixture of cyclic phosphates in Graham's salt was concentrated as an oily substance by fractional precipitation with Me_2CO, and separated on a column of Amberlite IRA-400 anion-exchange resin. The phosphates were eluted successively with 0.31 and 0.50 *M* KCl buffered at pH 5.2. Each phosphate in the effluent was identified by paper chromatography. Cyclic phosphates were eluted in the order: hexameta- (plus higher metaphosphates), pentameta-, tetrameta-, and trimetaphosphate. Pentameta-, tetrameta-, and trimetaphosphate in mixtures were completely separated from each other.

142

Thin Layer Chromatography of Condensed Phosphates.

Takeo Yamabe, Takaya Iida, and Nobuharu Takai (Univ. Tokyo, Tokyo, Japan).

Bull. Chem. Soc. Japan 41 (8), 1959-60 (1968).

Thin layer plates were prepared from silica gel or cellulose powder suspended in 0.05% aqueous Na polyacrylate or 1% cellulose acetate in $HCONMe_2$. Na salts of ortho-, pyro-, tripoly-, trimeta-, and tetrametaphosphates were spotted (1 microliter, 0.2% aqueous solution) on the plates and developed in a closed chamber at room temperature. The solvent was developed ≤10 cm from the spotting point, the plates were dried in air, the phosphates were hydrolyzed with 1:1 aqueous HNO_3, and colored, with $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and $SnCl_2$. When acidic developing solvents were used, the order of *Rf* values was ortho- > poly- > metaphosphate, and when basic solvents were used, the order of *Rf* values was meta > ortho- > polyphosphate.

143

Analysis of Oxyphosphorus Acids by Means of Thin-Layer Chromatography.

W. J. van Ooij and J. P. W. Houtman (Reactor Inst. Delft, Neth.).

Fresenius Z. Anal. Chem. 244 (1), 38-43 (1969).

Various thin-layer chromatography techniques were compared for the separation of P containing acids of various types (monoacids, ortho-, and metapolyacids) on cellulose layers. Improvements with respect to known techniques could be obtained by gradient elution and by using wedgetipped layers for one- and two-dimensional techniques. When applied to various commercial metaphosphoric acids or their phosphates at least twelve, but sometimes more than twenty different species could be distinguished.

144

Anion-Exchange Thin-Layer Chromatography of Condensed Phosphates.

Takaya Iida and Takeo Yamabe (Inst. Ind. Sci., Univ., Tokyo, Japan).

J. Chromatogr. 56 (2), 373-8 (1971).

The Na salts of ortho-, pyro-, and poly-phosphates were subjected to the title method on precoated PEI-cellulose F layers with aqueous NaCl and aqueous NH_4Cl of various concentration as the mobile phases. The apparent valencies of P in the phosphates, calculated from R_M values and the Cl^- concentration in the mobile phases, were lower in the systems containing NH_4Cl than in those containing NaCl and were not rectilinearly related to R_M values.

145

Rapid, Thin-Layer Chromatographic Determination of Phosphates in Metal Cleaners.

Cs. Lovasz and J. Kappler (Firma Daimler-Benz A.-G., Stuttgart, Ger.).

Metalloberflaeche 25 (3), 73-4 (1971) (Ger).

CA 75, 14663.

Condensed phosphates were determined by thin-layer chromatography on commercial cellulose plates with the solvent system: 60 ml MeOH, 30 ml dioxane; 30 ml 7:1 iso-PrOH–H_2O, 8 ml 2:8 HOAc–H_2O, and 40 ml of a solution of 125 g CCl_3CO_2H and 32 ml 25% NH_4OH/l. H_2O. The time needed for a 10 cm run is 100 min. The spots are revealed by a first spraying with a molybdate solution (40 kg Na molybdate·$2H_2O$ and 50 g NH_4NO_3/l. H_2O; diluted this solution is added to 100 ml H_2SO_4) then, after drying, with a reducing solution (300 g Na pyrosulfite, 10 g Na_2SO_3, and 2 g Metol dissolved in 1 liter H_2O and filtered). Monophosphates give strong dark blue spots, diphosphates give sky blue, and triphosphates light blue spots. Higher phosphates show only weak blue colors and are often difficult to see. The best quantity range is for Na_3PO_4 0.25-2.5 μg, for $Na_4P_2O_7$ 0.5-10 μg, for $Na_5P_3O_{10}$ 1-10 μg. The thin-layer chromatogram is quantitatively evaluated by comparison with standard solutions.

146

Separation of Phosphates by Thin-Layer Chromatography and Thin-Layer Electrophoresis. III. Qualitative Separation and Determination of Polycondensed Phosphates.

E. F. Wagner (Waeschereiforsch, Krefeld, e. V., Krefeld, Ger.).

Seifen-Oele-Fette-Wachse 94 (14), 443-8 (1968) (Ger).

CA 69, 73743.

Thin-layer chromatographic analysis of mixtures of phosphates on cellulose is both qualitatively and quantitatively equivalent to paper chromatographic analysis. Plates were developed in a variety of solvent mixtures containing either MeOH or dioxane in admixture with iso-PrOH, CCl_3CO_2H, and NH_3 sometimes with small percentages of HOAc or H_2O. The extent of hydrolysis of the higher polyphosphates during the analysis depended on the composition of the solvent. After visualization with a spray of NH_3 molybdate solution, the bands were removed and treated to decompose the support material, either by boiling with H_2SO_4, H_2O , and a catalyst or, more efficiently, by direct heating in a Pt crucible. Residual phosphate was recomplexed with NH_4 molybdate and determined spectrophotometrically. The procedure was applied to phosphate melts and commercial detergents. (17 ref)

147

Gel Chromatographic Behavior of the Oxo Acids of Phosphorus.

Yoichiro Ueno, Norimasa Yoza, and Shigeru Ohashi (Kyushu Univ., Fukuoka, Japan).

J. Chromatogr. 52 (3), 469-80 (Nov. 1970).

A number of oxo anions of P which contain one to four P atoms in the molecule were eluted with KCl solutions on Sephadex columns. The K_d values of the oxo anions of P were measured as functions of the concentration and pH of the eluents, sample concentration and gel porosity. K_d values obtained by both the column and batch method were compared to each other. The conclusions are as follows: (1) When pure water was used as an eluent, extremely low K_d values were observed because of the electrostatic repulsion between the sample anions and the negatively charged gel matrix. (2) The K_d values increased with increasing concentration of KCl. This may be due to the variation in the degree of hydration of sample anions. (3) At sample concentrations lower than 10^{-2} g atom P/l. the elution curves were symmetrical, while unsymmetrical elution curves were obtained at the higher sample concentrations. (4) The K_d values did not depend on the pH values of the eluent. (5) The most satisfactory separation of ortho-, di- and triphosphate anions was carried out on a Sephadex G-25 column. (6) The effective sizes of the oxo anions of P in aqueous solution were estimated from the gel chromatographic data.

148

Gel Chromatographic Behavior of Linear Phosphates.

Yoichiro Ueno, Norimasa Yoza, and Shigeru Ohashi (Kyushu Univ., Fukuoka, Japan).

J. Chromatogr. 52 (3), 481-5 (Nov. 1970).

Linear phosphates with degrees of polymerization of 1-13 were chromatographed on a Sephadex G-25 column with a 0.1 *M* KCl solution and the following results were obtained. (1) The K_{av} values of the linear phosphates did not depend on pH of the eluents. (2) A linear relationship was observed between the K_{av} values and the logarithms of the degrees of polymerization. (3) Average degrees of polymerization of polyphosphate fractions determined by pH titration agreed approximately with those calculated from the gel chromatographic data.

149

Determination of the Degree of Polymerization of Sparingly Water-Soluble Potassium Polyphosphates by Potentiometric Titration.

G. G. Aleksandrova and L. V. Kubasova.

Zh. Neorg. Khim. 16 (2), 471-3 (Feb. 1971) (Russ).

Russ J. Inorg. Chem. 16 (2), 248-50 (Feb. 1971).

A method is proposed for determining the average degree of polymerization of sparingly soluble modification of $(KPO_3)_n$. Specimens of potassium polyphosphates of the type $(KPO_3)_n$ were obtained by dehydrating KH_2PO_4 at 1000° with subsequent cooling of the melt in different ways. The average P_n of specimens ranged from 193 to 316. The solvents were 0.1-0.4 *N* solutions of NaBr, NaCl, and $NaNO_3$. With increase in the concentration of the solvent the values of the average degree of polymerization decreased. The best solvent tested was 0.1 *N* $NaNO_3$. The potentiometric titration was done with an LPU-01 pH meter and glass electrodes. Equations are given for calculating results.

150

Determination of The Degree of Polymerization of Ammonium Polyphosphates by Potentiometric Titration.

L. V. Kubasova and T. D. Pozharskaya.

Russ J. Inorg. Chem. 15 (1), 23-4 (1970).

The degree of polymerization of the dehydration products of $NH_4H_2PO_4$ under pressure of NH_3 was determined. The dehydrated phosphates were prepared by the thermal

dehydration of $NH_4H_2PO_4$ in a stream of gaseous NH_3 with a constant pressure drop of two atmospheres and a temperature range of 300-400°C. The ammonium polyphosphates were titrated with a 0.1 *N* solution of tetramethylammonium hydroxide using an LPU-01 pH meter and glass electrodes. The average number of P atoms in the chain increased from 12 to 56 with an increase in temperature from 300 to 400°C. Calculation of the degree of polymerization of dehydrated phosphates from potentiometric titration data is possible only for unbranched chain structures; ultraphosphates are unstable in solution and are rapidly hydrolyzed.

151

Chromatographic Behavior and Structural Units of Condensed Phosphates. II. Influences of Developing Solvents.

Takaya Iida and Takeo Yamabe (Univ. Tokyo, Japan).
J. Chromatogr. 54 (3), 413-21 (1971).

Ortho-, pyro-, tri-, trimeta-, tetrameta-, and hexametaphosphates were subjected to chromatography on cellulose layers (Avicel). The acidic solvents were mixtures of aqueous NH_3 with excess of acetic and trichloroacetic acids, H_2O and isopropyl alcohol. The basic solvents were mixtures of aqueous NH_3, H_2O, isopropyl alcohol, and isobutyl alcohol. The plates were developed at 5° by allowing the solvent to travel 10 cm from the origin. Spots were detected by acid hydrolysis [aqueous HNO_3 (1:1)] to orthophosphate, followed by spraying with solution of $(NH_4)_6Mo_7O_{24}$ and $SnCl_2$. The R_F values were used to determine the relationship between R_M and structural features. The main factors affecting the R_F values were the H_2O content and the apparent pH of the solvent mixture.

152

Identification of Certain Oxysalts of Phosphorus.

L. G. Harris, J. D. Lee, and D. T. Burns (Loughborough Univ. Technol., Loughborough, Engl.).
Loughborough Univ. Technol., Dep. Chem., Sum. Final Year Stud. Proj. Theses, No. 10, 27-31 (1969).
CA 73, 52054.

A qualitative analysis scheme is given for P oxysalts in which the salts are first classified into the following groups by reaction with $AgNO_3$: formation of yellow or white precipitate by orthophosphate, pyrophosphate, tripolyphosphate, and high-molecular-wt phosphates; formation of black or brown precipitate by phosphite, hypophosphite, and hypophosphate; no precipitate formed by trimetaphosphate and tetrametaphosphate. Subsequent identification tests involve reactions with $Co(NH_3)_6Cl_3$, $HgCl_2$, $Zn(OAc)_2$, $FeSO_4$, $KMnO_4$, and $CuSO_4$. Additional confirmatory tests are included.

153

Determination of Orthophosphate in the Presence of Condensed Phosphates by a Kinetic Method.

E. E. Kriss, V. K. Rudenko, and G. T. Kurbatova (L. V. Pisarzhevskii Inst. Phys. Chem., Kiev. U.S.S.R.).
Zh. Anal. Khim 26 (5), 1000-2 (1971) (Russ).
CA 75, 58379.

A kinetic method is suggested for orthophosphate determination in the presence of condensed phosphates based on a color reaction of molybdenum blue, its rate of formation increasing in the presence of orthophosphate The method allows the determination of PO_4^{3-} in the presence of 20-30-fold amounts of pyro- and tripolyphosphates The minimum PO_4^{3-} amount detected is 1 x 10^{-2} μg/ml. Sodium molybdate (2.4 ml 0.125 *M*), ascorbic acid (2 ml 0.5 *M*), H_2SO_4 (2.8 ml 0.5 *M*), and the sample are mixed, and the color change recorded photometrically for 15-17 min. Orthophosphate content was determined by comparison with a calibration curve.

154

Simplified Method for Determining the Average Degree of Polymerization of Insoluble Polymetaphosphates.

Mei-Fang Lu (Natl. Taiwan Norm. Univ., Taipei, Taiwan).
Hua Hsueh, (1-2), 5-8 (1970) (Ch).
CA 75, 58274.

Instead of HCl hydrolysis, the polymetaphosphate is dissolved in aqueous NaCl or LiCl and titrated with 0.01 *N* and 0.005 *N* NaOH. The average degree of polymerization is calculated from $2000W/MC_1V_1$, where W is the wt of the sample, M is the wt of the structural unit of the polymetaphosphate, C_1 is the normality of the alkali solution and V_1 is the titer in ml. The results obtained by this method agree with those obtained by the conventional method.

155

Determination of Pyrophosphate Ion in the Presence of Ortho- and Tripolyphosphate Ions.

O. A. Songina, V. M. Bliznyuk, and G. O. Omarkulova (Kazakh. Khim.-Tekhnol. Inst., Alma-Ata, U.S.S.R.).
Zavod. Lab. 37 (3), 271-3 (1971) (Russ).
CA 74, 134637.

A method is described for determining pyrophosphates by amperometric titration in the presence of ortho- and tripolyphosphate ions based on the insolubility of Cd pyrophosphate. The sample solution was brought to pH = 4 with acetate buffer and EtOH and some agar-agar were added, and the solution was deoxygenated by passing in CO_2 gas. The sample was then titrated with standard 0.1 *M* $Cd(NO_3)_2$ solution by using a dropping Hg electrode at the potential of 1.1-1.2 V vs. S.C.E. The current was measured with a mirror galvanometer (sensitivity 0.003 A). The relative standard deviation when determining mg amounts of pyrophosphate ions was less than 4% and the time required for an analysis was 20-30 min. The composition of the Cd pyrophosphate precipitate was $Na_2CdP_2O_7$.

156

Phosphorus Nuclear Magnetic Resonance in Polyphosphates and Determination of Their Hydrolysis Rate Constants.

Makoto Kawabe, Osamu Ohashi, and Ichiro Yamaguchi (Sophia Univ., Tokyo, Japan).
Bull. Chem. Soc. Jap. 43 (12), 3705-10 (Dec. 1970).

The P nuclear magnetic resonance spectra of several condensed phosphates (polyphosphates) were measured in aqueous solutions. The NMR spectra generally consist of three peaks which correspond to the P atoms at the end and middle of the molecular chain and in H_3PO_4 which is the final product of the hydrolysis. The chemical shift and, for some phosphates, spin-spin coupling constants were obtained. Both depend on pH of the solution. The chemical shifts for the end and middle P atoms depend also on the chain length of the molecule. The hydrolysis process of the phosphates can be traced by the observation of the time dependence of spectral line intensities. From this observation the rate constant of the hydrolysis is obtained for several phosphates. The values are comparable with those obtained by other methods.

157

Chromatographic Method for Determining Phosphorofluoridic Acid and Its Salts During the Acid Reprocessing of Apatite Phosphorites.

N. G. Rokova, V. V. Shiryak, and S. I. Van'ko.

Khim. Prom. (Moscow) 46 (5), 362-4 (1970) (Russ).
CA 73, 62396.

The proposed paper chromatography method for determining H_2PO_3F in acid-treated phosphorites in the presence of ortho-, pyro-, and polyphosphates is based on the use of the solvent *I* (75 ml iso-PrOH, 25 ml H_2O, 5 g of trichloroacetic acid, and 0.3 ml 25% NH_3 solution) and the chromatogram development by the method of H. Grunze and E. Thilo (1955). Treat a sample of the phosphorite with a calculated amount of acid at 80°, mix for three min and keep for one hr at 100-5°. Dissolve 2.5 g of the acid-treated phosphorite in H_2O with the addition of 45% K_2CO_3 solution to pH 7 and make up to 100 ml. Place drops of the test solution on strips of chromatographic paper and keep in solution *I* overnight. After drying in air and for 10 min in an oven at 75°, spray the chromatograms with a solution containing 1 g $(NH_4)_2MoO_4$, 85 ml H_2O, 10 ml of 0.1*N* HCl, and 5 ml of 60% $HClO_4$ solution. Dry the chromatograms at 75-85°. Reduce the chromatograms by ultraviolet irradiation. Cut out the spots and wash out the phosphates at 100° with a solution containing 10 ml H_2O, 2 ml 8*N* NH_4OH, and 5 ml 8*N* H_2SO_4. Filter the washing, reduce to blue ammonium molybdophosphate, measure the absorbance at 540 nm, and compared with standards. The relative error of the determination increases with increasing PO_3F^{--}/PO_4^{3-} ratio and varies between 0.6 and 44.1%.

158

Study of Polyphosphates: Separation, Identification and Determination. I. Sodium Mono-, Pyro- and Tri-Phosphates.

R. Deswaef (CEBEDEAU, Liege, Belgium).
Trib. CEBEDEAU 21, 312-17 (1968) (Fr).
Anal. Abstr. 17, 3407.

For qualitative separation of Na_3PO_4, $Na_4P_2O_7$ and $Na_5P_3O_{10}$, 20 microliters of sample solution is applied 2.5 cm from the lower edge of a paper cylinder and the cylinder is placed in a beaker containing 65 ml of acetone, 10 ml of H_2O and 25 ml of a solution containing 100 g of trichloroacetic acid and 7 ml of concentrated aqueous NH_3/500 ml. After development for 20 minutes, the paper is dried at 80° for 45 minutes, then sprayed with a molybdate solution [200 ml of 5% aqueous $(NH_4)_6Mo_7O_{24}4H_2O$ mixed with 10 ml of concentrated HCl and 50 ml of 72% $HClO_4$ and diluted to 1 liter]. After further heating for 2 to 3 minutes, the paper is sprayed with $SnCl_2$ solution (to 100 ml of 0.2*N*-HCl is added 5 drops of concentrated HCl saturated with $SnCl_2$). The R_F values were 0.83 for Na_3PO_4, 0.63 for $Na_4P_2O_7$ and 0.46 for $Na_5P_3O_{10}$. For quantitative separation, the sample is adsorbed on Amberlite IRA 400 anion-exchange resin (Cl-form) and KCl solution, increasing in concentration from 0.1*M* to 1 *M* and buffered at pH 5, and is passed upwards through the column at 6 ml/minute. Monophosphate is completely separated, and there is negligible overlap between the pyro- and tri-phosphates.

POTASSIUM

159

Analysis of Potassium Salts.

Jesus Mir.
Afinidad 26 (267), 349-54 (1969) (Span).
CA 73, 31169.

Direct and indirect gravimetric methods are reviewed. Precipitation as $KBPh_4$, flame photometry, radiological measurements, and fluorescence are discussed. (14 ref).

160

Response Characteristics of the Orion Potassium Ion Selective Electrode.

Sudarshan Lal and G. D. Christian (Univ. Kentucky, Lexington).
Anal. Lett. 3 (1), 11-15 (1970).

The Orion K ion selective electrode (92-19) was evaluated in terms of Nernstian response, selectivity, anion, and pH effects. The response is slightly less than Nernstian and a linear calibration curve is obtained over the concentration range 10^{-4} to 10^{-1} *M* K. The calculated selectivity ratio for K over Na depends on the relative concentrations of Na and K. Slight anion effects are noted with the most significant occurring with iodide, hydroxide, chromate, and oxalate. Tetraphenyl borate ion causes a large negative potential shift and this effect appears to render the electrode only moderately useful for titrations with this reagent.

161

Solid Potassium Ion Selective Electrode.

I. H. Krull, C. A. Mask, and R. E. Cosgrove (Beckman Instrum., Inc., Fullerton, Calif.).
Anal. Lett. 3 (2), 43-51 (1970).

A solid membrane K selective electrode has been developed. The following parameters of the K^+ electrode were investigated: Nernstian response to K^+ activity, response time to step changes in K^+ activity, the effect of pH on K response, and the electrode response to other cations.

162

Microdetermination of Potassium in Inorganic and Organic Substances Using Monovalent Cation Selective Electrode.

Naoshige Akimoto and Keiichiro Hozumi (Kyoto Univ., Kyoto, Japan).
Bunseki Kagaku 20 (9), 1186-92 (1971) (Japan).
CA 75, 147478.

The microdetermination of K by direct potentiometric measurement with a monovalent cation-selective electrode was studied. By using a sample volume of 50-100 ml containing 10^{-3}-10^{-4} *M* K^+, the electrode potential reached a steady state within several min and gave reproducible results. Good linear calibration curves were obtained by varying α in the equation, pK reading = -log $[K^+]$ + α; the empirical values for α ranged (0.08-0.1) x 10^{-4}. The flask combustion method was used for the preparation of analytical samples from organic compounds such as K H tartrate, K propionate, and K gluconate; the standard deviation was 0.2%. Potassium acid phthalate was recommended for calibration since its recovery was 100% in the combined method of the flask combustion and selective electrode potentiometric measurement.

163

Simple K^+-sensitive Microelectrode with a Minimal Working Surface.

L. N. Vorob'ev and Yu A. Khitrov (Dep. Biophys., Moscow State Univ., Moscow, U.S.S.R.).
Fiziol. Rast. 18 (5), 1054-9 (1971) (Russ).
CA 76, 10011.

A new type of K^+-sensitive microelectrode which has the smallest sensitive surface possible for a microelectrode was fabricated by precipitating at the microelectrode tip a K salt having cation exchanger properties. This microelectrode has the same sensitivity and selectivity as similar glass K^+-microelectrodes but its time characteristics are better and its manufacture is easier.

164

Determination of Potassium by an Automatic Ultraviolet Absorptiometric Method.

J. M. Skinner and A. C. Docherty (Imp. Chem. Ind. Ltd., Billingham, England).

Talanta 14 (12), 1393-40 (1967).

CA 68, 35584.

An automatic uv absorptiometric method was developed for the determination of K. The method involves precipitation of K by addition of a known excess of $NaBPh_4$, removal of the $KBPh_4$ precipitate by filtration, and measurement of the excess of $NaBPh_4$ in the filtrate by means of its absorbance at 254 mμ. Most of the apparatus, including a continuous filter, is standard AutoAnalyzer equipment but a Uvicord uv absorptiometer replaces the conventional colorimeter. Build-up of precipitate in the system is eliminated by immersing the mixing coils in an ultrasonic bath which is actuated intermittently by a simple timing mechanism. The method is especially suitable for K analytically in production plant where flame photometer results are sometimes affected by fertilizer dust in the air surrounding the burner. (15 ref)

165

Indirect Spectrophotometric and Atomic Absorption Spectrometric Methods for the Determination of Potassium.

E. A. Khreish and D. F. Boltz (Wayne State Univ., Detroit, Mich.).

Mikrochimica Acta, No. 6, 1174-80 (1970).

Indirect spectrophotometric and atomic absorption spectrometric methods for the determination of traces of K are proposed which are based on the precipitation of K tetraphenylborate and the determination of excess reagent in the supernate. The tetraphenylborate forms the tetraphenylborato-bis-(2, 9-dimethyl-1, 10-phenanthroline)-copper (I)-complex which is extracted with ethyl acetate. Either the absorbance of colored extract is measured spectrophotometrically at 456 nm, or the Cu in the extract in measured by atomic absorption spectrometry using the 324.7 resonance line.

166

Interferences Encountered in Determining Potassium in Fertilizers by Atomic Absorption Spectrophotometry.

W. L. Hoover and J. C. Reagor (Texas A & M Univ., College Station).

J. Ass. Offic. Anal. Chem. 51 (1), 211-16 (1968).

In the development of an atomic absorption method for the analysis of K, several interfering materials were found that influenced the absorption of 7664.9 Å radiation by K. The same interfering materials had very little effect on absorption at 4044.1 Å. However, high content caused varying amounts of interference at 4044.1 Å, depending on the presence of other ions. Various grades of fertilizer were analyzed by the proposed atomic absorption procedure at 4044.1 Å. Atomic absorption analyses, even though there was a low bias, compared favorably with other procedures used by commercial laboratories. The proposed atomic absorption method has merit because of its speed and simplicity.

167

Automatic Methods for the Determination of Potash.

A. C. Docherty (Agr. Div., Imp. Chem. Ind., Ltd., Billingham, Engl).

Proc., Fert. Soc., No. 104, 45-67 (1968).

Core samples from potash explorations were analyzed by x-ray fluorescence for total K, Cl, Si, Fe, Al, Ca, Mg, and S. A Technicon AutoAnalyzer flame photometer measured the H_2O-soluble Na and K, and a computer calculated the concentrations of K, Na, and Cl for a large number of samples. A standard Technicon AutoAnalyzer with a continuous filter, an ultrasonic bath, and a special filtrate mixing chamber were used to determine K with $(BPh_4)^-$. A uv absorptiometer at 253.7 millimicrons measured the excess $NaBPh_4$ in solution after filtration. Glass electrodes selectively responsive to K are discussed.

168

Collaborative Study of the Automated Method for Potassium Oxide in Fertilizers.

L. G. Hambleton (Purdue Univ., Lafayette, Ind.).

J. Ass. Offic. Anal. Chem. 54 (3), 646-50 (1971).

The automated method for K_2O in fertilizers was studied. The results from the automated method were compared to those obtained by the official STPB method, 2.090, for 10 typical fertilizer samples and a KNO_3 primary standard. Nine complete sets of data are evaluated by the technique of closely matched pairs. The data show no difference between the different models of flame photometers. The means and standard deviations from the automated method compare favorably to those received with the official method. The automated method for K_2O in fertilizers was adopted as an official first action.

169

Collaborative Study on an Automated Method for K_2O in Fertilizers.

L. G. Hambleton (Purdue Univ., Lafayette, Ind.).

J. Ass. Offic. Anal. Chem. 53 (3), 456-60 (1970).

An automated method for K_2O in fertilizers utilizes basic Technicon equipment and the Technicon range expander. The range of 35-55 ppm was expanded to read 20 to 80% *T* respectively. Nine laboratories studied the automated method and the official STPB method 2.085 for 10 fertilizer samples and a KNO_3 standard. The study lacked participation from laboratories having AutoAnalyzer equipment. The method is recommended for further study.

170

Automatic Methods for the Determination of Potash.

A. C. Docherty (Imperial Chem. Ind. Ltd., Billingham, Teesside).

Fertiliser Soc. Symp. on Fertilizer Analytical Methods, No. 104, 45-61 (held London, England, Oct. 24, 1968).

Methods are described for the automatic determination of K by three techniques. Na and K were simultaneously determined by a 2-channel flame photometer in prospect samples. The sodium tetraphenylborate procedure was automated for routine analysis of fertilizer samples. A brief description of the use of specific ion electrodes is also given.

171

Determination of Potassium Chloride in Mineral Fertilizers by Photoelectric Titration.

A. A. Zagorovskaya, V. V. Fruzorova, and V. F. Aleksandrovich (Inst. Obshch. Neorg. Khim., Minsk, U.S.S.R.).

Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk 1, 61-3 (1971) (Russ).

CA 75, 19208.

Photoelectric titration method for the determination of KCl in mineral fertilizers by employing Na-tetraphenylborate was described. The reagent solution for the titration was prepared by dissolving 15 g of Na-tetraphenylborate in 500 ml of H_2O, filtering the solution, adding 10 ml of 0.2 *N* NaOH, and finally

adjusting the total vol to 1 liter. The preparation of the sample consisted of weighing 4 g of the material, dissolving it in H_2O and filtering it into 500 ml flask, diluting it to 100 ml and adjusting with 0.1 *N* NaOH to a slightly alkaline reaction with phenolphthalein indicator (pink color). The titration of the sample was carried out by employing of an electrophotometric titrator. The end point of the titration was established by observing the movement of the microampermeter needle during the titration procedure, until it stops and would not respond to the additional drops of the reagent. The described method produced reliable results showing a relative error in the range of 1.1%.

172

Determination of Potassium in Fertilizers by Titrimetric Sodium Tetraphenylborate (Kalignost) and Flame-Photometric Methods.

Frigyes Thamm (Res. Inst. Soil Sci. Agr. Chem., Hung. Acad. Sci., Budapest, Hungary).

Agrokem. Talajtan 20 (1-2), 187-93 (1971) (Hung).

CA 76, 58125.

The official methods of analysis of the AOAC procedure for K determination was modified as follows: Sterogenol (0.5% solution of cetylpyridinium bromide) and a mixture of bromophenol blue: methylorange as indicator were used for back titration. The flame photometric determination was done from the same fertilizer with a 1% solution prepared for titrimetric determination after a 100-fold dilution. The error for the titrimetric method was 0.5% and that for the photometric one 0.7%. For practical purposes the flame photometric method, as less time-consuming, can be used.

173

Volumetric Determination of Potassium by Heterometric Titration.

A.H.I. Ben-Bassat and Anath Azrad (Hebrew Univ. Jerusalem, Jerusalem, Israel).

Isr. J. Chem. 9 (5), 557-62 (1971).

Heterometric procedures for the volumetric determination of K are proposed. The use of direct and reverse titrations, precipitate-forming ligands as titrants, and the addition of solvents, such as EtOH, make possible the determination of a large number of cations and anions as their insoluble compounds. Two procedures are described: one uses direct heterometric titrations for the formation of the $KBPh_4$ precipitate for 40-60 ppm K^+; the second uses indirect titrations for the formation of $K_2Na[Co(NO_2)_6]$ in HOAc-EtOH, for samples containing 4-10 mg K^+. The end point of the heterometric titration is obtained by photometric measurement of the absorbance of suspensions.

174

Rapid Titrimetric Determination of Potassium.

Andras Halasz and Erno Pungor (Anal.-Kem. Transz., Veszpremi Vegyip. Egy., Veszprem, Hung.).

Magy. Kem. Foly. 76 (12), 640-3 (1970) (Hung).

CA 74, 82777.

Potassium is precipitated by excess $NaBPh_4$. The precipitate is removed by filtration. The excess $NaBPh_4$ in an aliquot of filtrate is back-titrated by alkylbenzyldimethylammonium chloride with a bromophenol blue-Titan yellow indicator mixture. The analysis time was 10-20 min.

175

Potassium Determination by the Volumetric Tetraphenylborate Method with Electric End Point Indicator (Dead-Stop Method).

H. J. Schmidt (Chem. Fabrik Kalk G.m.b.H., Cologne-Kalk, Ger.).

Landwirt. Forsch., Sonderh. 23 (11), 166-70 (1969) (Ger).

CA 72, 110297.

To 1250 mg fertilizer add 5 ml 6*N* HCl, H_2O, heat and bring to 250 ml. Pipet 20 ml into a 100 ml flask, add 2 ml 2*N* NaOH, warm, and add 2 ml of Na tetraphenylborate. Cool, allow precipitate to form, and filter. Titrate with 0.02*M* $TlNO_3$. If chelaters are present, sample must be ashed. This procedure takes ~30 min. Error is ±0.5%.

176

Indirect Voltametric Determination of Potassium and Cesium and Direct Amperometric Determination of Potassium with Tetraphenylborate Using Silicone Rubber Based Graphite Electrodes.

E. Siska and E. Pungor (Cty. Inst. Food Control Chem. Anal., Szekesfehervar, Hung.).

Fresenius' Z. Anal. Chem. 257 (1), 7-11 (1971) (Eng).

CA 76, 30380.

BPh_4^- was electrochemical oxidized to BPh_2^+ and biphenyl on a silicone rubber based graphite electrode. For 0.2m *M* $NaBPh_4$, the half-peak potential and the peak current i_p, both independent of the pH between 2.2 and 8, were 0.44 V and 2.79 μA, respectively, and their relative standard deviations were 2.73 and 1.22%, respectively (10 runs). The temperature coefficient of i_p was 2.4%/degree. A linear relation was obtained between the concentration and i_p in the range of 0.2-3 mmole $NaBPh_4$/l. Potassium (1-10 mg) and Cs (3-30 mg) were determined indirectly at pH 5 by precipitation with 0.05 *N* $NaBPh_4$, dissolution in Me_2CO and voltammetric determination of BPh_4^- after dilution with pH 5 acetate buffer. The solubility product of $KBPh_4$ and $CsBPh_4$ was calculated to be 2.53×10^{-8} and 2.6×10^{-9}, respectively. A more precise determination of K was performed by amperometric titration of 10 ml 0.01 *N* KCl with 0.1 *N* $NaBPh_4$ at +0.75 V. The relative standard deviation was 0.85% (10 runs).

177

Determination of Potassium in Salts and Potassium Fertilizers.

A. A. Zagorovskaya and V. F. Aleksandrovich (Inst. Obshch. Neorg. Khim., Minsk, USSR).

Vestsi Akad. Navuk Belarus. SSR, Ser. Khim. Navuk, No. 1, 108-11 (1969) (Russ).

CA 71, 29594.

A rapid titrimetric method is given for the determination of K as percent KCl in mixtures of KCl-NaCl and as percent K_2O in industrial samples of fertilizers containing K. Semimicropotentiometric titrations were carried out on the respective samples with an LP-5 pH meter and a glass-calomel electrode system with a 10-ml microburet. The dried 0.1–0.2 g sample is dissolved in 0.5 ml H_2O, and heated to boiling Excess Et_4NOH, prepared according to Kreshkov, and 20 ml EtOAc are added. The mixture is stirred for one minute, and is titrated with standardized methanolic $HClO_4$ from -400 v to +600 v. The equivalence point occurs between +200 v and +300 v. The time required for a single analysis is 20 minutes. Results obtained by this method agreed with those obtained by flame photometry for mixtures of KCl-NaCl containing 10-30% KCl by wt. Mixtures containing 10-30% KCl by wt showed an error of ±2.00%. Satisfactory agreement was found for a series of titrimetric, gravimetric, and flame photometric values of K as percent K_2O in fertilizers containing 40-43% K_2O by wt.

178

Potentiometric Determination of Tetraphenylborate Ions With Silver Nitrate. Determination of Silver, Potassium, and Thallium (*I*).

E. Siska and E. Pungor (Cty. Inst. Food Control Chem. Anal., Szekesfehervar, Hung.).

Fresenius' Z. Anal. Chem. 257 (1), 12-18 (1971) (Eng).

CA 76, 30381.

The potentiometric titration of $NaBPh_4$ with 0.1 *N* and 0.01 *N* $AgNO_3$ at pH 5 was investigated with Ag and silicone rubber based halide-selective membrane electrodes as indicator electrodes and a calomel reference electrode. The standard deviation was 0.38-0.49% for 0.2 mmole $NaBPh_4$ (10 runs). After applying a polarization current, the use of the electrode couples Ag-Calomel, Ag-Ag, Ag-Pt, Pt-Ag, and graphite-Ag was studied. Addition of an organic solvent, for example Me_2CO, DMF, dioxane, or MeCN, caused a decrease in the potential change at the end point in each case. Potassium (4-20 mg) was determined indirectly by addition of excess $NaBPh_4$ and back titration with 0.05*N* $AgNO_3$ with a Ag or a halide-selective membrane electrode. Silver, K, and Tl(I) were titrated with 0.1 *N* $NaBPh_4$ with an anodically polarized graphite electrode and a calomel reference electrode. The relative standard deviation for 7.8 mg K and 20.3 mg Tl was 1.96 and 1.07%, respectively (10 runs).

179

Potentiometric Determination of Potassium in the Presence of Sodium.

Rudolf Geyer and Peter Stein (Tech. Hochsch. f. Chem. 'Carl Schorlemmer', Leuna-Merseburg, Germany).

Acta Chim. Hung., 67 (1), 1-3 (1971) (Ger).

Anal. Abstr. 22, 33.

The sample solution, of pH 2 to 8, is titrated with 0.2*M*-Na tetraphenylborate, the indicator-electrode being a wax-impregnated spectrographic-carbon rod or a dry-cell carbon rod. The limit of determination of K is 5m*M*. For 40 mg of K in a 10m*M* solution that is also 0.1*M* in Na the error is ≃1%.

180

Determination of Potassium Using Dipicrylamine by a Differential-Photometric Method.

H. Kuus, K. Ranne, and E. Lond.

Uch. Zap. Tartu. Univ., No. 235, 121-7 (1969) (Russ).

CA 74, 150758.

The feasibility of differential-photometric determination of K is shown, which is based on its precipitation in the form of dipicrylaminate, dissolution of the precipitate in Me_2CO, and photometric determination of dipicrylamine color with a spectrophotometer at 436 mμ or with a FEK-56 with no. 5 light filter (with maximum transmission at 490 mμ). Mathematical processing of the calibration graphs plotted for various concentration ranges showed that the optimum range for determination with SF-4 and FEK-56 is 1.0-15.0 and 2-5 mg K_2O in 5 ml solution, respectively. Variation coefficient is ~1%.

181

Low-Temperature Flame Photometry. Determination of Potassium.

P. Stanchev and J. Simova.

God. Nauchnoizsled. Proekt. Inst. Rudodobiv Obogat., Obogat. 6 (6), 74-81 (1968) (Bulg).

CA 72, 50634.

Potassium is determined by low-temperature (that is, with a gasoline flame) photometry of the 769.9 nanometer resonance line. The line intensity (*I*) was not affected by alkali metals, Pb, Zn, Ni, Cu, Mn, and Co; large excesses of Mg, Ca, Al, Fe, and Cd reduce *I* while Ba causes an increase. Inorganic acids (HCl, H_2SO_4, HNO_3, $HClO_4$, H_3PO_4), glycerol, and ethylene glycol reduce *I*, while AcOH, $EtCO_2H$, HCO_2H, MeOH, EtOH, iso-PrOH, *tert*-BuOH, $C_5H_{11}OH$, *sec*-BuOH, and BuOH increase it. Potassium silicate rocks, Fe and Mn ores, and other natural materials were analyzed.

182

Review and Recommended Changes in the Flame Photometric Method for Determination of Potassium in Fertilizers.

L. G. Hambleton (Purdue Univ., W. Lafayette, Ind.).

J. Ass. Offic. Anal. Chem. 51 (4), 857-8 (July 1968).

Ammonium oxalate is historically the oldest extractant for available K_2O in fertilizer. Lower results have been obtained by the flame photometric method 2.077 than with the other official methods, possibly because of the extractant, $(NH_4)_2CO_3$. It is recommended that the preparation of solution 2.079 (a) be changed to indicate ammonium oxalate as the extractant in place of $(NH_4)_2CO_3$.

183

Comparative Evaluation of Tetraphenylborate Methods for Determination of Potassium.

V. P. Zhivopistsev, E. A. Selezneva, and T. B. Cherepanova (U.S.S.R.).

Uch. Zap., Perm. Gos. Univ., No. 207, 172-83 (1970) (Russ).

CA 75, 83803.

The argentometric method by precipitating K with $NaBPh_4$, filtering, and dissolving the precipitate in Me_2CO, adding a given amount of $AgNO_3$ to form AgBPh, and titrating the excess $AgNO_3$ with NH_4SCN involves the time-consuming disadvantage of precipitation and filtration which can also give rise to inaccuracies. The potentiometric titration of K salts (fertilizers) with $NaBPh_4$ with Pt/Cu or Pt/Ag electrodes is not a satisfactorily reproducible K determination when high levels of impurities are present. The latter is then best carried out by introducing an acetate buffer (pH 5.2), NaCl, and SO_4^{-2} to the sample solution containing 5-25 mg K. Bis(4-dimethylamino-phenyl)antipyrinylcarbinol ("tetramethyl") is used as the indicator since it forms slightly soluble compounds with BPh_4^- with a change in color from violet to grey-blue. For sharpness of color change, $CHCl_3$ is added The dye decomposes on long standing or heating. When using low concentration KCl samples it is necessary to add a certain measured quantity of KCl to make it up to the required minimum content for $KBPh_4$ formation and separation.

184

Sodium Tetraphenylboron; Its Analytical Applications. II.

K. Ueno, M. Saito, and K. Tamaoku.

Bunseki Kagaku 18 (1), 81-95 (1969) (Japan).

CA 70, 73724.

A review is given on the determination of K, including experimental procedures and precautions. (84 references)

185

Electrometric Method of Potassium Determination in Fertilizers.

H. J. Ostmann (Anal. Lab., Farbwerke Hoechst A.-G., Frankfurt/M., Ger.).

Landwirt. Forsch. 23 (2), 162-71 (1970) (Ger).

CA 73, 108759.

Potassium was determined in fertilizers by the electrometric titration method of H.-J. Schmidt (1957), involving addition of excess $NaBPh_4$ and titration with $TlNO_3$ of the excess after digestion. The end point was detected by the change in the

polarization resistance of an amalgamated Ag double electrode. A correction curve was obtained by analyzing synthetic standards. The absolute standard deviation was 0.08% for 14-22% K_2O in fertilizers. The samples were dissolved in dilute HCl, and the interfering NH_4^+ was removed by evolution as NH_3.

186

Radiometric Determination of Potassium.

Jaroslav Ullrych (Fyz. Chem. Hutnike Fak., Vys. Sk. Banska, Ostrava, Czech.).

Sb. Ved. Pr. Vys. Sk. Banske Ostrave, Rada Hutn. 14 (5), 47-55 (1968) (Czech).

CA 74, 134579.

The radiometric method for K is applicable to any solid material sampled from a stream of approximately known composition. Compared with the gravimetric $KClO_4$ method, the time for the determination with an error of ± 1% is 4 times faster, hence the method is adapted for rapid routine production testing. The determination is based on the radioactivity of the ^{40}K constituent of natural K, with a half-life of 1.3 x 10^9 yr, decaying into isotopes of Ar and Ca and producing 34% β + 66% γ radiation at maximum energies of 1.4 and 1.5 mV, respectively. It is preferred to measure the β, since in deeper than saturation layers (0.35 g/cm^2 for KCl, KI, KNO_3) the radiation dose/min is linear with K concentration and is unaffected by sample size. With γ radiation the dose/min increases even after the saturation layer has been penetrated. The accuracy is strongly affected by the sample composition due to self absorption. The humidity and grain size $\leq$3 mm do not affect the dose/min. A low voltage GM detector tube was used. The GM tube was mounted coaxially in a Plexiglass sample holding tube fitted with a screw cap of the same material. The sample was poured without compacting into the annular space. The depth of the sample surrounding the GM tube was 6 mm. The counting was done within a Pb block shield with 4 cm thick walls. A type CSAV 1957 counter was used. The method was applied to two fertilizers. One contains a second emitter, Ce, at a concentration ~ 0.3% K which value must be subtracted from the final result. The accuracy was checked on a lab prepared sample with 18.33% K. After subtracting the correction the average of 10 determinations was 18.36% K. Another homogenized sample gave 15.33% K for an average of 11 determinations compared to 15.31% average of 5 gravimetric ($KClO_4$) determinations. In the second sample which has no other β emitter and which was lab mixed to 11.57% K, the average of 3 radiometric determinations was 11.47% K.

SEE ALSO the following numbered abstracts in other sections: 357, 414.

FLUORINE

187

Determination of Fluorine.

H. Deelstra (Univ. Officielle Bujumbura, Bujumbura, Burundi).

Ind. Chim. Belge 34 (3), 177-82 (1969) (Neth).

CA 70, 120714.

Several analytical methods for the determination of F are reviewed with special emphasis on F sensitive electrodes, principles, applications, and interferences. (41 references)

188

Spectrophotometric Determination of Fluorine in Fossils and Phosphatic Materials.

Fernando Burriel-Marti, A. Cabrera-Martin, and J. M. Marinas (Dep. Quim. Anal., C.S.I.C., Madrid, Spain).

Inform. Quim. Anal. 24 (6), 200-4, 220 (1970) (Span).

CA 75, 83878.

In fossils containing ~2.5% F and ~25% P_2O_5, with 100 F/P_2O_5 ratios of 1-9, the F was distilled from a H_2SO_4 solution and determined spectrophotometrically by using Alizarin Fluorine Blue.

189

Determination of Fluoride by Atomic Absorption Spectrometry.

A. M. Bond and T. A. O'Donnell (Univ. Melbourne, Victoria, Australia).

Anal. Chem. 40 (3), 560-3 (Mar. 1968).

Fluoride ion depresses the absorption of Mg in the air-coal gas flame, the change in absorbance of the Mg resonance line at 2852 Å being proportional to the fluoride concentration over the range 0.2-20.0 μg/ml (10^{-5}-$10^{-3}M$). In the absence of interfering ions, principally sulfate and phosphate, the effect can be used to determine fluoride ion in this concentration range. An alternative, though somewhat less sensitive, technique is based on the enhancement of Zr absorption by fluoride ion in the nitrous oxide-acetylene flame; this allows the determination, with a high degree of freedom from interference, of fluoride ion over the range 5-200 μg/ml (2.5 x 10^{-4}-$10^{-2}M$). In the presence of phosphate, which interferes with the Zr method, a similar enhancement of Ti absorption can be used for fluoride determinations in the range 40-400 μg/ml (2 x 10^{-3}-2 x $10^{-2}M$). These atomic absorption methods for fluoride determinations were found to be considerably more rapid than more classical methods and in many cases can be used directly without prior separation of fluoride. Their application was demonstrated in the analysis of a wide range of inorganic fluorides.

190

Determination of Fluoride in Calcium Phosphates with a Fluoride-Selective Electrode.

E. J. Duff and J. L. Stuart (Univ. Manchester, Manchester, Engl.).

Anal. Chim. Acta 52 (1), 155-7 (1970).

Fluorine is determined in synthetic $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$, and $Ca_5F(PO_4)_3$ by using a F^- selective electrode. Dissolve 100 mg of a synthetic Ca phosphate in 10 ml of *M* HCl, add 5 ml of H_2O, 20 ml of *M* Na citrate, and measure the pF value. To determine F^- dissolve 0.2 g of finely powdered sample in 10 ml of HCl, and dilute to 100 ml with H_2O. To a 10 ml aliquot, add 5 ml of H_2O, 20 ml of *M* Na citrate, and measure the pF. For calibrations using 5 ml of 0.2*M* HCl + 5 ml 0.2*M* Na citrate + 1 ml H_2O, and 5 ml *M* HCl + 5 ml *M* Na citrate + 1 ml H_2O, the log F^- concentration versus mV curves are linear for 0.8–1000 and 0.4–1000 μg F^- respectively. Calcium, 5000-fold excess, does not interfere.

191

Determination of Fluorine in Fertilizers and Plants with the Fluoride Ion Activity Electrode.

Fumio Yamazoe (Natl. Inst. Agr. Sci., Tokyo, Japan).

Nippon Dojo-Hiryogaku Zasshi 42 (1), 44 (1971) (Japan).

CA 75, 87476.

Fluorine was distilled from the sample, fertilizer or plant, as fluorosilicic acid, which was measured with the electrode. The amount of F was determined from a calibration curve for silicofluoride (0.01-1.000 ppm F). Cyanamide, phosphoric acid, silicic acid, or carbonic acid interfered positively, and Ca, Mg, Fe, Al, Cr, or Ti negatively.

192

Determining Fluoride in Rocks with a Specific Ion Electrode.

B. L. Ingram and Irving May (U.S. Geol. Surv., Washington, D.C.).

U.S. Geol. Surv., Prof. Pap., No. 750-B, 180-4 (1971).

Fluorine was determined in 1% KNO_3 solution after distillation (Grimaldi, 1955). Direct potentiometric measurement and null-point (titration) methods were equally accurate (standard deviation 0.00009 ppm). A method for direct determination of F in phosphate rock without distillation is given. Interference from Al is controlled with citrate.

193

Direct Determination of Fluoride in Phosphoric Acid and Calcium Sulfate Using a Specific Ion Electrode.

W. C. Hanson and D. J. Lloyd (Levington Res. Sta., Fisons Ltd., Ipswich/Suffolk, England).

Chem. Ind. (London), No. 1, 41-2 (1972).

Fluoride in phosphoric acid solution and gypsum obtained by the reaction of phosphate rock (apatite) with H_2SO_4 was determined by using the F^- activity electrode. Fluoride contents of 0.1-1.1 and 0.02-1.1% determined in phosphoric acid (30 or 50% P_2O_5) and in gypsum by the electrode method agreed within 0.006-0.02 and 0.002-0.05% F^-, respectively, with those determined by using a Willard-Winter distillation and a colorimetric method.

194

A Rapid Method for the Determination of Fluoride in Rocks and Soils, Using an Ion-Selective Electrode.

W. H. Ficklin.

U. S. Geol. Surv. Prof. Pap., No. 700-C, 186-8 (1970).

A rapid method for the direct determination of fluoride in rocks and soils is presented. No prior separation of fluoride by distillation is required. Results are listed for 19 rock samples from the Cripple Creek mining district of Colorado, eight U.S. Geological Survey standard rock samples, and five soil samples from New Mexico. The results of the proposed method agree to within about 20% of the values obtained by other methods and are reproducible to within about 15%. The minimum fluoride content detected is 40 ppm.

195

Direct Determination of Fluorine in Phosphates by the Fluoride Electrode.

Jan Tusl (Vyzk. Ustav Vyz. Zvirat, Pohorelice, Czech.).

Chem. Listy 64 (3), 322-4 (1970) (Czech).

CA 72, 139379.

Fluorine was determined by the special F^- electrode Orion Model 99-09, the potential of which was measured by the OP-205 pH meter at 25 ± 1°. The potential is measured after three min and the F^- content is read from a calibration curve (potential vs concentration). Before the analysis of phosphates the calibration curves for various buffers adjusted to pH ~5.5 were measured. Results obtained with the F^- electrode agree with those found by other methods.

196

Trace Fluoride Determination with Specific Ion Electrode.

E. W. Baumann (E. I. duPont de Nemours & Co., Aiken, S. C.).

Anal. Chim. Acta 42 (1), 127-31 (July 1968).

A method is described for determining 10^{-5} to $10^{-4}M$ fluoride in a variety of solutions potentiometrically with a fluoride-specific electrode by a standard addition method. The relationship between potential and fluoride concentration follows the Nernst equation, and the unknown concentration can be calculated. Experimental data are given for several solutions, including H_3PO_4. Metal ions (for example, Al^{3+}, UO_2^{2+}, Fe^{3+}, and Th^{4+}) that interfere by forming complexes with fluoride can be precomplexed with H_3PO_4. The relative error is estimated at 10% and the relative standard deviation is less than 5% in the range 10^{-5} to $10^{-4}M$ fluoride.

197

Activity Measurements with a Fluoride-Selective Membrane Electrode.

K. Srinivasan and G. A. Rechnitz (New York State Univ., Buffalo).

Anal. Chem. 40 (3), 509-12 (Mar. 1968).

The nature of the fluoride species present in acidic solutions has been elucidated by means of the fluoride-selective membrane electrode. Results obtained by direct measurement of free fluoride ion concentration can be fully explained in terms of the species F^-, HF, and HF_2^- and do not require postulation of polynuclear complexes. The electrode is shown to respond to F^- activity in highly acidic media.

198

Determination of Fluoride in Bone with the Fluoride Electrode.

Leon Singer and W. D. Armstrong (Univ. Minnesota, Minneapolis).

Anal. Chem. 40 (3), 613-14 (Mar. 1968).

A simple and direct method for the determination of F in bone involves the use of the Orion Model 94-09 fluoride ion electrode and a conventional KCl electrode, with a Corning Model 21 research pH meter, provided with an expanded scale, for measurement of the F-ion activity of the solutions. Four to 6 mg of bone ash was weighed in a small glass boat, transferred to a 50 ml polyethylene beaker, and dissolved in 1 ml of 0.250*M* HCl. The excess HCl was nearly neutralized with 0.125*M* NaOH and the pH was adjusted to 4.7 with 0.050*M* Na acetate solution. The total volume was made up to 5 ml with distilled H_2O. The electrodes were inserted and the solution was stirred until a constant millivoltage reading was obtained. This required 5-10 min. The millivoltage readings with standard solutions were plotted on the rectangular axis against their fluoride concentrations on the log axis of semilog paper. The curves so obtained were straight lines, and were used to translate the millivoltage readings of the unknowns to fluoride concentration. The method is rapid and accurate. The average of the mean results, 0.231% F, compared favorably with the reference method.

199

Rapid Distillation Separation of Microgram Quantities of Fluoride.

Hisashi Kubota (Oak Ridge Natl. Lab., Oak Ridge, Tenn.).

Microchem. J. 12 (4), 525-33 (1967).

CA 68, 101482.

The Willard-Winter distillation, in which F^- is steam-distilled as fluorosilicic acid, is modified for the rapid distillation of γ-amounts of F^- from solutions containing cations that form stable F^- complexes and large amounts of volatile mineral acids. F^- is determined subsequently by the spectrophoto-

metric method of Yamamura *et al* (1962), except that $La(NO_3)_3$ is substituted for $Ce(NO_3)_4$. F^- from the 5-ml sample solutions is liberated with 1:1 H_2SO_4 (50 ml) and the distillate volume is limited to 20 ml. The distillate is neutralized to the phenolphthalein end point, then the alizarin (*I*) is added and the absorbance is measured at 617 mμ after 1 hr. A calibration curve is presented for 0-25 γ F^-. The apparatus and procedure can be scaled down to give relative standard deviations for six replicate determinations of 14, 10, and 4% for 1, 2.5, and 5 γ F^-, respectively. The stability of the *I* chromophore to the effects of ^{60}Co radiation indicates that the analysis can be used in hot cells in which radiation intensity can attain ~10^2 rads/hr.

200

Determination of Fluoride in Phosphate Shale and Phosphoric Acid.

F. W. Czech and T. P. Hrycyshyn (FMC Corp., Carteret, N. J.).

Automat. Anal. Chem. Technicon Symp., 3rd, 1, 273-8 (1967) (Pub. 1968); Mediad Inc.: White Plains, N. Y.

Steam distillation by the Technicon AutoAnalyzer system separates the fluoride from interfering substances. The F is determined colorimetrically by the decolorization of a Zr and Na 2-(*p*-sulfophenylazo)-1,8-dihydroxynaphthalene-3,6 disulfonate (SPADNS) lake. The method is recommended for liquids containing 0.1-20 ppm F. Two SPADNS reagent solutions containing different dye concentrations are necessary for the complete F range. The standard deviation of the method is 0.07 ppm F calculated from 23 determinations on samples containing 8.0 and 10.0 ppm F.

201

Complexometric Microdetermination of Fluorine in the Presence of Calcium and Phosphate.

R. P. Singh and T. S. B. Narasaraju (Banaras Hindu Univ., Varanasi, India).

Fresenius' Z. Anal. Chem. 247 (1), 52-3 (1969).

CA 71, 131312.

A method is described for the rapid and accurate microdetermination of F in the presence of Ca and phosphate. F^- in the presence of synthetic hydroxyapatite, $3Ca_3(PO_4)_2 \cdot Ca(OH)_2$, was precipitated with standard $Ce(NO_3)_3$ solution such that Ce^{3+} remained in excess after complete precipitation of CeF_3. The excess Ce^{3+} was titrated with standard EDTA so that an excess of EDTA remained after complexing with unreacted Ce^{3+}, the excess being back-titrated against standard $MgSO_4$ solution. Thus, solutions theoretically containing 95.00 or 570.00 micrograms F were analyzed to contain 94.60 or 571.00 micrograms F, respectively, with an error of 0.42 or 0.18%, respectively.

202

The Use of Pyrohydrolysis for Determining Fluorine in Slags of the Production of Phosphorus.

M. M. Vinnik and Z. A. Sazonova (Ya. V. Samoilov Scientific-Res. Inst. Fert. Insectofungicides, Moscow, U.S.S.R.).

Zh. Anal. Khim. 26 (12), 2446-50 (Dec. 1971) (Russ).

A pyrohydrolytic method with an alkalimetric finish is described for determining F in slags of the production of elemental P. The accuracy of the method is 1% relative. One analysis takes 50-60 min. Optimum conditions for the quantitative extraction of F were found. The rate constants of F isolation from slags at 1000, 950, 900, 835° were determined. Under similar conditions the rate constants of pyrohydrolysis in the presence of WO_3 for slags from the tap-hole, granulated and crystallized practically coincide. The activation energy of the process of isolating F from slags is 27 ± 2 kcal/mole.

203

Manual Procedures for the Estimation of Atmospheric Fluorides.

G. H. Farrah (Aluminum Co. of America, New Kensington, Pa.).

J. Air Pollut. Contr. Ass. 17 (11), 738-41 (1967).

A review of the manual methods for determination of air-borne fluorides, including the discrimination of gaseous and particulate forms. Comparative sampling data for published methods indicate advantages of some newer techniques in sampling, separation, and quantitation. (18 ref)

204

A Source Sampling Technique for Particulate and Gaseous Fluorides.

J. A. Dorsey and D. A. Kemnitz (Natl. Center Air Pollut. Contr., Cincinnati, Ohio).

J. Air Pollut. Contr. Ass. 18 (1), 12-14 (Jan. 1968).

In industrial operations such as production of P fertilizers, sampling of effluents that contain fluorides is often hampered by the reactivity of HF. Although techniques have been developed for sampling ambient air, they are not applicable to stack effluents which contain high concentrations of fluoride, H_2O, and particulates. A sampling system for the separation and collection of gaseous and particulate fluorides was devised and tested. A heated glass probe serves as a reactor for converting HF to SiF_4 before the particulate is filtered. The equipment has performed satisfactorily in field sampling.

205

The Use of Triethanolamine in a Buffer for the Determination of Fluoride in Calcium and Transition Metal Orthophosphates, Using a Fluoride-Selective Electrode.

E. J. Duff and J. L. Stuart (Univ. Manchester, Manchester, England).

Talanta 19 (1), 76-80 (Jan. 1972).

A method is described for the determination of fluoride in inorganic orthophosphates. Interference by complex-forming metal ions is avoided by the use of a citric acid-triethanolamine buffer, pH <7 5.

206

Microdetermination of Fluoride in the Presence of Phosphate by Potentiometric Titration.

Walter Selig (Lawrence Radiation Laboratory, Univ. Calif., Livermore).

Mikrochim. Acta., No. 2, 229-34 (1970).

A method for the microdetermination of fluoride in the presence of phosphate is described. Up to a 10-fold excess of P (as phosphate) can be tolerated. Phosphate is adsorbed on Zn oxide which is added in excess and need not be removed prior to titration of fluoride. Fluoride is determined potentiometrically with 0.02 *M* lanthanum (III) at pH 5-7. A fluoride ion specific electrode is used with an expanded-scale pH meter to monitor the emf.

207

Spectral Method for Determining Fluorine in Phosphorites and Apatites.

V. I. Zabiyako and A. M. Tkach.

Zh. Prikl. Spektrosk. 10 (2), 311-12 (1969) (Russ).

CA 70, 111355.

Spectrographic determination of F in phosphorite and apatite ores gave good results when compared with chemical analysis.

The error after 40 analyses of one sample was 4.5%. Samples were mixed with graphite powder (containing 40% NaCl) in 1:9 ratio, placed in a 2-mm diameter, 5-mm deep channel of a C electrode, and were examined at the CaF line, 5296.8 angstroms. The gap between electrodes was 1.5 mm and the slit-width 0.02 mm. Standards containing 2.1-3.1% F were prepared and gave a straight line calibration graph in ΔS vs log C coordinates.

208

Measurement of pH in Acid Fluoride Solutions and Evidence for the Existence of $(HF)_2$.

L. J. Warren (Roy. Sch. Mines, Imp. Coll. Sci. Technol., London, Engl.).

Anal. Chim. Acta 53 (1), 199-202 (1971).

The quinhydrone electrode is suitable for pH measurements under acid fluoride conditions where the glass electrode gives erroneous readings. The results in concentrated HF solutions can be accounted for if the dimer $(HF)_2$ is assumed to be present: $H^+ + F^- = HF$ (K_1); $HF + F^- = HF_2^-$ (K_2); $2HF = (HF)_2$ (K_d). At ionic strengths of 0.050 to 0.062, K_d remained constant at 2.7 ± 0.3 which strongly supported the existence of the dimer. The results were not consistent with the assumption of tetramer, hexamer, or HF_3^{2-} type species.

209

An Evaluation of Some Methods for the Determination of Fluoride in Potable Waters and Other Aqueous Solutions.

N. T. Crosby (Laboratory of the Government Chemist, Cornwall House, London, Engl.).

Analyst 93, 643-52 (Oct. 1968).

Five spectrophotometric procedures for the determination of fluoride were evaluated with respect to reproducibility, sensitivity, range, stability of colored products and of reagents, specificity, and effect of temperature. The $Th(NO_3)_4$ titration is briefly discussed, and the use of the Orion fluoride-ion electrode for pF measurement was investigated. The electrode was found to be less susceptible than the colorimetric methods to interference from other ions, and to give theoretical recoveries. (24 references)

210

Instrumental Techniques for the Titration of Fluoride in the Presence of Cryolite and Aluminum Fluoride.

Paolo Rinaldo and Paolo Montesi (Montecatini Edison S.p.A., Porto Marghera, Italy).

Chim Ind. (Milan) 53 (1), 26-34 (1971) (Ital).

CA 75, 71039.

Fluorine was determined after distillation as fluorosilicic acid, by titration with $Th(NO_3)_4$. Since visual observation of the end point with Alizarin Red S as indicator (alone or in mixtures with methyl blue or methylthymol blue) is difficult, a F^- selective electrode was used. Results were compared with those obtained by visual titration, spectrophotometric titration, and high frequency titration with $La(OAc)_3$. When using the F^- selective electrode, H_2SO_4 present in the distillate produced small interferences. The use of selective electrode gave better precision.

211

Reaction of Thorium Chloranilate with Fluoride.

C. D. West, R. L. Birke, and D. N. Hume (Massachusetts Inst. of Technology, Cambridge).

Anal. Chem. 40 (3), 556-60 (Mar. 1968).

The reaction between thorium chloranilate and fluoride ions in aqueous pH 4.7 buffer under analytical conditions yields one chloranilate anion in solution for each two fluoride ions, and thorium difluorochloranilate as a solid phase. In 1:1 methyl Cellosolve-water medium, the same reaction takes place but the colored thorium difluorochloranilate is soluble, enhancing the sensitivity. Larger amounts of fluoride lead to the formation of insoluble thorium fluoride. From the standpoint of practical analytical application, the results confirm those of previous workers that the method is convenient, sensitive, and reliable. It should be noted, however, that at very low fluoride concentrations where the uv peak must be used, there is danger of nonlinearity, which is particularly striking in the purely aqueous solvent. The reagent blank in higher methyl Cellosolve concentrations also become quite large in the uv and may become a source of error with samples low in fluoride.

212

A Study of the Optimal Conditions for Potentiometric Titration of Fluoride with Lanthanum and Thorium in Unbuffered Media.

T. Eriksson and G. Johansson (Univ. Umea, Umea, Sweden).

Anal. Chim. Acta 52 (3), 465-73 (Dec. 1970).

This study was undertaken to obtain more complete information about the equilibria present during a potentiometric fluoride titration. Such information may be extracted from kinetic measurements, from simultaneous accurate measurements of pH and pF, and by a computer-fit of the results to a calculated curve.

213

An Improved End-Point for the Determination of Fluoride with Thorium Nitrate.

Walter Selig (Lawrence Radiation Lab., Univ. California, Livermore).

Analyst 93 (1103), 118-20 (Feb. 1968).

The end-point for the titrimetric determination of fluoride with $Th(NO_3)_4$ was improved by the use of methylthymol blue indicator. Up to 10 mg of fluoride can be determined in a solution buffered with glycine-perchlorate at pH 3.35.

214

A Modified Method for Estimation of Fluorine in Fluorite Samples.

N. R. Sen Gupta (Geol. Surv. India, Calcutta).

Indian Mineral 19 (3), 266-8 (1965).

A sample of about 0.1 g of fluorite is fused with 1 g Na_2CO_3 and 0.2 g ZnO for 30 minutes. The fused mass is dissolved in H_2O and filtered. The filtrate is distilled with H_2SO_4–H_3PO_4 mixture (40 ml H_2SO_4 + 5 ml H_3PO_4 diluted to 100 ml with H_2O). The distillate is collected and made up to volume. An aliquot corresponding to a 5 mg sample for more than 25% F or a 10 mg sample for less than 25% F is titrated with $Th(NO_3)_4$ solution using a mixture of alizarine red S (0.1%) and methylene blue (0.05%) as indicator. The results are good.

215

Accurate and Rapid Method of Analysis for Fluorine in Phosphate Rocks.

L. Evans, R. D. Hoyle, and B. J. Macaskill (New Zealand Fert. Manufacturers' Res. Ass., Otara, N.Z.).

N. Z. J. Sci. 13 (1), 143-8 (1970).

Samples were prepared for use in the determination of F in phosphate rocks by the following methods: Willard-Winter distillation; cation-exchange resin dissolution according to Schafer (1963); NaOH fusion; and dissolution in 2-3 *M* $HClO_4$. Fluorine was determined in the sample solution colorimetrically or by measurement with the F^- electrode at

pH 7.0 (Na citrate buffer). The latter method is more accurate and rapid. The ion-exchange method of sample preparation gave consistently low results.

216

Determination of Fluorine in Geological Materials.

R. Pouget (Serv. Mineral., Commis. Energ. At., Paris, Fr.).

Chim. Anal. (Paris) 53 (7), 479-83 (1971) (Fr).

CA 75, 83912.

Fluorine in rocks was determined by measurements with a F^--specific electrode in pH 6.5 NH_4OAc solution after attacking the rock with NH_4Cl and HCl or after Na_2CO_3-fusion at 1000° followed by distillation of SiF_4 from acid solution. Fluorine was separated from interferences by collection with $(NH_4)_2CO_3$. The sensitivity was 0.005% F^-, and the absolute standard deviations for determining 0.100 and 1.00% F^- were 0.01 and 0.05% F^-, respectively. The NH_4Cl-HCl attack is especially suitable for phosphate rocks of the apatite type.

217

Nuclear Magnetic Resonance Investigation of Fluoride Ions in Hydroxyapatite.

W. Van der Lugt, D. I. M. Knottnerus, and W. G. Perdok (Univ. Groningen, Groningen, Netherlands).

Acta Crystallogr. B27 (Part 8), 1509-16 (1971).

The position of fluoride minorities in hydroxyapatite $[Ca_5OH(PO_4)_3]$ was studied by NMR methods. There is experimental evidence for the existence of OH-F-vacancy and OH-F-HO configurations parallel to the *c* axis. The internuclear distances permit the formation of weak OH...F hydrogen bonds.

218

The Determination of Fluorine in Rocks and Minerals by a Pyrohydrolytic Method.

R. L. Clements, G. A. Sergeant, and P. J. Webb (Dep. Trade and Ind., Lond, Engl.).

Analyst (London) 96 (1138), 51-4 (Jan. 1971).

A rapid pyrohydrolytic method, with simple apparatus, is described for the determination of F in rocks and minerals. The sample is heated with a three-component flux in a stream of moist air, and the liberated HF is absorbed into an alkaline solution. The recovered F is determined either colorimetrically or by means of a fluoride-specific electrode. The method is suitable for determining F at concentrations down to about 50 ppm.

219

Determination of Small Amounts of Fluoride in Solution.

Society for Analytical Chemistry, Fluorine Sub-Committee of the Analytical Methods Committee (Savile Row, London, England).

Analyst (London) 96 (1142), 384-92 (1971).

To determine F^- in aqueous solution to 20 ml of test solution (pH 4-5) containing <40 μg of F^- add 5.0 ml of 0.1*M*-succinate buffer of pH 4.6, 10 ml of 2m*M*-$La(NO_3)_3$-0.2m*M*-alizarin fluorine blue (1:1) and 10 ml of acetone, with mixing after each addition. Dilute the solution to 50 ml, and after 30 min measure the extinction at 625 nm. Tolerance levels are given for interfering ions.

220

A Simple Diffusion Method for the Determination of Fluoride.

J. L. Stuart (Univ. Manchester, Manchester, Engl.).

Analyst (London) 95 (1137), 1032-8 (Dec. 1970).

A method is described for the determination of sub-microgram amounts in inorganic fluoride. Diffusion on to a thin layer of solid alkali is used to separate fluoride from any contaminants. The diffused fluoride may be determined with an ion-selective fluoride electrode or by spectrophotometric methods. Phosphate and sulfate do not interfere. The interferences of halides, carbonate, nitrate, and acetate is discussed. Organic material was found not to interfere with the recovery of fluoride except in determinations involving human serum. High-temperature ashing of organic samples was found to lead to loss of fluoride. When used with the ion-selective electrode the method is applicable over the range 0.05 to 200 μg of fluoride.

SEE ALSO the following numbered abstracts in other sections: 392, 424, 515.

SECONDARY ELEMENTS

221

Analytical and Biochemical Measurements with a New, Solid-Membrane Calcium-Selective Electrode.

G. A. Rechnitz and T. M. Hseu (State Univ. of New York, Buffalo).

Anal. Chem. 41 (1), 111-15 (Jan. 1969).

Evaluation of an immobilized matrix type Ca-ion selective membrane electrode showed several advantages over an earlier liquid membrane electrode. In particular, the electrode was shown to have a reduced selectivity for the H ion, resulting in a useful extension of the electrode's pH range into the acidic region. Selectivity for Ca over common interfering univalent and divalent cations was satisfactory for most practical measurements. The new electrode was successfully used for direct potentiometry, potentiometric titrations, and study of three Ca complexes of biological significance.

222

A Calcium-Sensitive Electrode Based on a Liquid Ion Exchanger in a Poly(Vinyl Chloride) Matrix.

G. J. Moody, R. B. Oke, and J.D.R. Thomas (Univ. Wales Inst. Sci. Technology, Cardiff, Wales).

Analyst 95 (1136), 910-18 (Nov. 1970).

A long life, rapid response, Ca-sensitive electrode that nearly follows Nernstian behavior between O and 48 was made by incorporating a liquid ion exchanger into a poly(vinyl chloride) matrix. Selectivities were obtained by several methods for Zn^{2+}, Mg^{2+}, Ba^{2+}, Na^+, K^+, and H^+. The determination of Ca in tap water with the PVC electrode and by a standard EDTA method is discussed.

223

Naphthenic Acid Extraction of Calcium for Determination by Atomic Absorption Spectrophotometry.

L. Szego and J. M. Calvert (Australian Atomic Energy Commission, Lucas Heights, New South Wales).

Anal. Chim. Acta 42 (1), 1-6 (July 1968).

Investigation of the title procedure showed it to be suitable for the determination of Ca and Mg in the presence of silicate, for Ca in the presence of large amounts of other salts, and for very low level Ca determinations. It is not as accurate as direct atomic absorption spectrophotometric analysis in the absence of interfering ions.

224

Interference by Phosphate in the Determination of Calcium by Atomic Absorption Spectroscopy.

J. Spitz (C.E.N. Grenoble, Grenoble, Fr.).

Spectrochim. Acta, Part B 24 (7), 399-403 (1969) (Fr).

The interference of P on the flame spectrometric determination of Ca is due to the formation of an apatite, chloroapatite or hydroxyapatite, which decompose later to Ca pyrophosphate. This mechanism was indicated by electron microdiffraction examination of the solid particles obtained after removal of the solvent.

225

Some Interferences in the Atomic Absorption Spectrophotometry of Calcium.

C. Rocchiccioli and A. Townshend (Univ. Birmingham, England).

Anal. Chim. Acta 41 (2), 93-8 (1968).

A previous paper (D. J. Halls and A. Townshend, *This J. 36*, 278) gave a detailed study of chemical interferences in the atomic absorption spectrophotometry of Mg and gave information on the mechanism of atom production in the flame and the nature of the interference effects. The present paper extends the investigation to Ca under similar conditions. The results obtained, in conjunction with those obtained earlier for Mg permit an improved explanation of alkaline earth interactions in flames. (6 fig, 17 ref)

226

A Method for Decreasing the Atomic-Absorption Sensitivity of Calcium by Using the Germanium 422.657 nm Line.

K. C. Thompson (Southern Analytical Ltd., Camberley, Surrey, England).

Analyst (London) 95 (1137), 1043-4 (Dec. 1970).

A method for decreasing the atomic-absorption sensitivity of Ca by using the overlap of the Ge 422.657 nm non-resonance line profile with the Ca 422.673 nm resonance line profile is described. Almost linear calibration graphs were obtained with concentrations of up to 1500 $\mu g\ ml^{-1}$ in the air-acetylene flame (sensitivity 8.3 $\mu g\ ml^{-1}$), and up to 1000 $\mu g\ ml^{-1}$ in the nitrous oxide-acetylene flame (sensitivity 6.0 $\mu g\ ml^{-1}$).

227

Enhancement of Calcium Absorption in the Nitrous Oxide-Acetylene Flame by Sodium and Potassium.

J. A. Murdoch and F. W. Heaton (Univ. Lancaster, Lancaster, England).

Clin. Chim. Acta 28 (3), 505-6 (1970).

There was no interference by phosphate or sulfate in the Ca determination by atomic absorption when a N_2O-C_2H_2 flame was used, especially with a N_2O flow rate of six l./min and a C_2H_2 flow of three l./min. Potassium and Na greatly enhanced Ca absorption, with Mg having a much smaller effect. Potassium or Na at 10-15 m*M* gave the same enhancement; at higher concentrations there was no more enhancement. Potassium, <10 m*M* caused greater enhancement than did Na.

229

Determinations of Traces of Calcium in Phosphoric Acid and its Salts by Atomic-Absorption Spectrometry.

M. Yanagisawa, M. Suzuki, and T. Takeuchi (Dep. of Synthetic Chem., Nagoya Univ. Chikusa-ku, Nagoya, Japan).

Talanta. 14, 933-6 (1967).

At. Absorption Flame Emission Spectrosc. 3, 578.

To remove interfering substances, samples containing traces of Ca are extracted as the $C_6H_6O_3$ complex into an organic solvent, prior to analysis with atomic-absorption spectrometry (AAS). Phosphoric acid samples are prepared by adding 6 *M* HCl and Na tartrate, neutralizing with 6 *M* NaOH, diluting, adding NaCl, then adding 2:3:5 butyl cellosolve: 8-$C_6H_6O_3$: buffer. After shaking with 3-methyl-l-butanol the organic phase is aspirated into a Hitachi photoelectric spectrophotometer EPU-2A with atomic-absorption attachment RA-1, air-acetylene flame, and hollow cathode lamp sources. Operating conditions are given. Phosphate samples are dissolved in 1 *M* HCl and Na-tartrate, diluted, then treated as above (if the pH is < 13, solutions are adjusted with NaOH). 3-methyl-l-butanol is the best solvent for extracting Ca hydroxyquinolate. Eighty-nine % Ca is extracted in one pass and the amount extracted is constant with a pH >12.5 and more than 100 mg of added C_9H_7NO. Calibration curves are almost linear, attributed to absorption by C_9H_7NO. The effect of diverse ions on extraction is examined; Ca absorption is affected by large concentrations of Al, Ti, Cr and Mo; the last two interferences are controlled by altering the air-fuel ratio. Copper lowers the Ca reading, and CN is used to keep Cu in solution. Calcium absorption is affected by the air-fuel ratio. Effect of altering the acetylene pressure is shown graphically; beam height does not affect maximum absorption. Results are tabulated for analysis of phosphoric acid and phosphates. Coefficient of variation is 3.7%. Good recovery of added Ca is obtained.

230

Flame-Photometric Determination of Calcium in Phosphate-Containing Solutions.

M. L. Buchtela and K. Buchtela (Analyt. Inst., Univ. Wien, Austria).

Mikrochim. Acta, No. 5, 992-6 (1968) (Ger).

Anal. Abstr. 18, 140.

Anions that interfere with the flame-photometric determination of Ca are removed by electro-dialysis at 30 V in an electrolyte of 0.1*M*-lactic acid and 0.02*M*-HCl. For 10 ml of test solution containing 50 ppm of Ca, transfer of Ca to the cathode compartment of the cell is complete in 30 min.

231

Phosphate Interference on Calcium in Flame Spectrometry.

K. C. Singhal, V. K. Srinivasa, and B. K. Banerjee (Fert. Corp. India Ltd., Sindri, India).

Technology 6 (2-3), 146-8 (1969).

The mechanism of interference on Ca by orthophosphate and pyrophosphate has been studied. Calcium orthophosphate and pyrophosphate solutions were aspirated and collected over hot

glass slide with the flame off and the unevaporated portion of Ca-orthophosphate system was collected over the flame. X-ray diffraction pattern reveals that the initial products in cases of orthophosphate and pyrophosphate are $CaHPO_4$ and $[CaCl_2 \cdot Ca(H_2PO_4)_2 \cdot 2H_2O]$, respectively. In the unevaporated portion of orthophosphate only Ca pyrophosphate is detected. A reaction mechanism of interference has been suggested.

232

Compleximetric Determination of Calcium in Impure Calcium Carbonate and Limestone.

J. O. Page (Texas A & M Univ., College Station).

Anal. Chim. Acta 42 (2), 233-8 (Aug. 1968).

The compound [ethylene bis (oxyethylene nitrillo)]-tetraacetate, "EGTA," was investigated as a titrant because it chelates Ca ion selectively in the presence of Mg. Titrations were made with 0.01*M* disodium EGTA at pH 12 in the presence of at least 0.6 mg Mg and a maximum of 500 μg of Fe(III) using a pH 12.5 buffer and Calcon indicator. The results were compared with those obtained by titrating at pH 10 the $Ca(ClO_4)_2$ solutions derived from Ca oxalate, and with those of a modification of a method described earlier (L. L. Lewis and L. M. Melnick. *Anal. Chem. 32*, 38, 1960). The results for Mg obtained by difference were in fair agreement. Mg can be titrated compleximetrically as $Mg(ClO_4)_2$ but the reagent blank must be determined.

233

Complexometric Determination of Calcium in Phosphoric Acid.

Horst Bornmann (Dir. Forsch. Entwickl., VEB Chem. Coswog, Coswig/Anh., Ger.).

Z. Chem. 10 (1), 36 (1970) (Ger).

CA 72, 74397.

The method of R. Pribil (1961) was modified to permit Ca^{2+} determinations in H_3PO_4. Calcium in the acid solution complexed with excess EDTA, the solution was adjusted to, and buffered at, pH 10, $MgNa_2L$ (H_4L = EDTA) was added, and excess EDTA was titrated with $CaCl_2$ against Eriochrome Black T indicator. The relative errors were <2.5% for 2-3.5 mg Ca^{2+} in the presence of 397 mg PO_4^{3-}.

234

Comparison of Various Indicators for the Chelatometric Determination of Calcium in the Presence of Magnesium.

Jiri Ditz, Jiri Neumann, and Vaclav Suk (Farschungsinst. Anorg. Chem., Usti nad Labem, Czech.).

Fresenius' Z. Anal. Chem. 251 (5), 298-9 (1970) (Ger).

CA 73, 116004.

The relative error in the titration of 25 ml 0.01 *M* Ca^{2+} in the presence of Mg^{2+} (molar ratio 1:1) with EDTA by using 9 indicators was: murexide −0.80, fluorexon −2.28, thymolphthalexon −0.06, glyoxal bis(*o*-hydroxyanil) −0.84, calcone +0.12 calcone carboxylic acid −0.04, calcone-*o*-anisidide −0.12, calcone-*p*-anisidide +0.08, and calcone-*m*-nitroanilide−0.04(%). Calcone and its derivatives were recommended.

235

Evaluation of 2-Hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic Acid and Hydroxynaphthol Blue as Metallochromic Indicators in the EDTA Titration of Calcium.

Atuko Itoh and Keihei Ueno (Kyushu Univ., Fukuoka, Japan).

Analyst (London) 95 (1131), 583-9 (June 1970).

The acid dissociation constants and the chelate stability constants for Ca were determined spectrophotometrically on purified samples of 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid (Patton and Reeder's dye) (HSN) and hydroxynaphthol blue, both of which were used as indicators in EDTA titrations of Ca. By comparison of experimental and theoretical curves of the indicator color change at the end-point, these two dyes are suitable indicators for the titration of Ca at pH 12-13, with a slightly more satisfactory end-point indication given by hydroxynaphthol blue.

236

Microdetermination of Calcium in Biological Material by Automatic Fluorometric Titration.

A. B. Borle and F. N. Briggs (Univ. Pittsburgh School of Medicine, Pa.).

Anal. Chem. 40 (2), 339-44 (Feb. 1968).

A method is described for the determination of very small amounts of Ca in biological material by automatic fluorometric titration of a Ca-calcein complex with EDTA. The method does not require the separation of Ca. It is very rapid, the titration of 25 nmoles Ca (1 μg) requiring only 2 min. The titration is done in a Turner fluorometer and recorded on a milliampere recorder. Delivery of μl. of the EDTA titrant is made by a modified lambda pump and mixed by a specially designed microstirrer placed in the fluorometer. The method is extremely sensitive and can detect 1 nmole (0.04 μg) Ca with a coefficient of variance of less than 2%. It is highly specific and free of interference since Mg, phosphate, and ATP do not interfere up to molar ratios of 200, 20,000, and 40,000, respectively.

237

Gravimetric Determination of Calcium in the Presence of Phosphate Ions.

A. M. Dymov and T. I. Romantseva (Mosk. Inst. Stali Splavov, Moscow, USSR).

Zavod. Lab. 35 (4), 428-9 (1969) (Russ).

CA 71, 45439.

The optimum conditions for precipitating CaC_2O_4 in the presence of large amounts of PO_4^{3-}, Mn^{++}, Fe^{3+}, Al^{3+}, and Mg^{3+} are at pH 7-8 in the presence of ≥ 1.5 g ferron at 80-90°. At this pH, the other metals are complexed. A 0.5-g sample (slag, silicate rock, etc.) is moistened with 2-3 ml H_2O and dissolved in 20 ml HCl, then 3-5 ml HNO_3 is added, and the mixture is filtered. The solution is diluted to 250 ml, a 100-ml aliquot is heated to boiling, 50 ml 3% ferron is added, NH_3 is added slowly to a slight odor, and the pH is adjusted to 8, 80 ml 5% $(NH_4)_2C_2O_4$ is added, the mixture is heated at 80-90° for two hours, filtered, and the precipitate is ignited to constant wt at 900-1000°. The Ca content can be determined gravimetrically with a relative error of 0.2-1.0% in the presence of >20% P_2O_5.

238

Use of Calcium for the Removal of Interfering Effect of Phosphate-Ion in Atomic Absorption Determination of Magnesium.

N. P. Ivanov and G. V. Kozyreva.

Tr., Vses. Nauch.-Issled. Inst. Khim. Reaktivov Osobo Chist. Khim. Veshchestv, No. 31, 164-7 (1969) (Russ).

CA 74, 150719.

The presence of phosphate ions decreased the atomic absorption of Mg somewhat. The effect of phosphate ions can be eliminated by adding Ca which fixes the phosphate ion into the difficultly volatile and stable compound $Ca_3(PO_4)_2$. A spectrophotometer based on ZMR-3 monochromator, tube with hollow Cu cathode containing Mg in the form of impurity, and C_3H_8-air flame 15 mm diameter were used.

239

Atomic-Fluorescence Spectroscopy of Magnesium with a High-Intensity Hollow-Cathode Lamp as Line Source.

T. S. West and X. K. Williams (Imperial College, London, England).

Anal. Chim. Acta 42 (1), 29-37 (July 1968).

Atomic fluorescence of Mg is possible in air-propane or air-acetylene flames at 285.21 nanometers, using a high-intensity hollow-cathode Mg lamp for excitation. The technique permits determination of Mg in the range 0.01-5.00 ppm, namely, with more than 10 times the sensitivity of the atomic absorption method even for this most sensitive element. The detection limit in either flame is 1 nanogram/ml (signal: noise ratio 1:0.75). In a N_2O-acetylene flame, atomic fluorescence may be carried out with linear signal/concentration dependence up to 100 ppm without interference even from metals such as Al and Ti at a 1000-fold excess ratio to Mg. A brief comparison is made with atomic absorption using the same source and equipment.

240

Spectrophotometric End-Point Detection for Determination of Magnesium in the Presence of Calcium and Phosphate by Titration with CDTA.

D. E. Jordan and D. E. Monn.

Anal. Chim. Acta 39 (3), 401-4 (Nov. 1967).

A significant improvement has been made in a method previously presented for the accurate determination of Mg in phosphate rock and H_3PO_4 down to 0.03% MgO in the presence of 0-70% P_2O_5 by titration with CDTA. (Jordan and Monn, *Anal. Chim. Acta 37*, 42-8, 1967). Spectrophotometric detection utilizes a constant wavelength for each titration and eliminates variation of color sensitivity associated with the human eye which results in easier and more consistent end-points especially for very low concentrations. Calcium is determined by fluorescence.

241

Magnesium Spinel Interferences in Air-Acetylene vs. Nitrous Oxide-Acetylene Flames in Atomic Absorption Spectrometry.

W. W. Harrison and W. H. Wadlin (Univ. Virginia, Charlottesville).

Anal. Chem. 41 (2), 374 (Feb. 1969).

In this study, Mg was chosen as the analyte, and Al as the major interferent along with Ti and Zr. Proper selection of flame parameters minimizes the effect of interferences.

242

Nephelometric Measurements by Use of a Spectrofluorometer. I. Determination of Sulfate and Determination of Calcium.

L. Gonen and E. Cogan (IMI-Inst. Res. Dev., Haifa, Israel).

Isr. J. Chem. 9 (1), 25-33 (1971).

Quantitative nephelometric measurements using a spectrofluorometer are presented. The measurements are performed with the aid of a monochromatic filter, which is transparent for the line 546 nm and by adjusting the monochromator for the same wavelength. The method was applied to the determination of micro amounts of: (*1*) SO_4^{2-} as $BaSO_4$ in colorless or colored aqueous solutions, in H_3PO_4, in the presence of large amounts of Fe and in ores, it is also suitable for determination of total inorganic S after oxidation to SO_4^{2-}, and in organics after combustion; (*2*) Ca as Ca naphthalhydroxamate in aqueous and H_3PO_4 solutions; and (*3*) Ca in the presence of large amounts of Mg. The proposed technique has proved useful for quantitative nephelometric determinations in colored solutions. The high sensitivity also permits the use of micro samples.

243

Atomic Absorption Spectrophotometric and Ethylenediaminetetraacetate-Titration Methods for Calcium and Magnesium Determinations.

James Lee and Charles M. Campbell (Univ. Hawaii, Honolulu).

J. Dairy Sci. 52 (1), 121-4 (Jan. 1969).

Ethylenediaminetetraacetate-titration and atomic absorption spectrophotometric methods were compared for determining Ca and Mg in solutions of known concentration and in subtropical forages. Concentrations of Ca and Mg in known solutions ranged from 0.68-13.59 ppm and 0.06-1.18 ppm, respectively. At this low level of concentration, the EDTA-titration method was not reliable for determining Mg. Concentrations determined by atomic absorption varied less from known concentrations than were found with EDTA-titration method at concentrations used in the test solutions. The subtropical forage samples analyzed contained from 0.17-0.52% Ca and 0.11-0.31% Mg, respectively, on an oven-dried wt basis. Slightly, but not significantly, higher results for Ca and Mg were obtained by EDTA-titration than for those obtained by atomic absorption. Results obtained by the atomic absorption method agreed with known values of Ca and Mg, and the rapid and accurate analyses made possible by this method were important factors in its favor over the EDTA-titration for routine analyses.

244

Atomic Absorption by the Double Aspiration Method. I. Interference of Phosphoric and Sulfuric Acid in Atomic Absorption Spectroscopy for Calcium and Magnesium.

Mitsutomo Tsuhako and Eiichi Sekido (Fac. Sci., Kobe Univ., Kobe, Japan).

Bunseki Kagaku 19 (4), 525-30 (1970) (Japan).

CA 73, 51961.

The influence of H_3PO_4 and H_2SO_4 on the atomic absorption of Ca and Mg was studied by use of a glass atomization chamber equipped with two atomizers. The intensity of atomic absorption of Ca and Mg was increased considerably when Ca or Mg solution was supplied from one atomizer and H_3PO_4 or H_2SO_4 solution from the other. The enhancing effect observed by this double aspiration method could not be ascribed to physical factors, such as viscosity and surface tension of the solution, C_2H_2 pressure and characteristics of the aspiration chamber, but to some chemical reactions occurring in the flame. The depressing effect of H_3PO_4 or H_2SO_4 on the ordinary atomic absorption of Ca or Mg was considered to be caused by the formation of phosphate or sulfate in solution which would then give refractory substances in the C_2H_2 flame. (For Part II, See *FA 3*, 1774)

245

Successive Chelatometric Titration of Calcium and Magnesium Using Hydroxy Naphthol Blue (HNB) Indicator.

Atsuko Ito and Keihei Ueno (Kyushu Univ., Fukuoka, Japan).

Bunseki Kagaku 19 (3), 393-7 (1970). (Japan).

CA 73, 10365.

Calcium in a mixture with Mg^{2+} is titrated with EDTA (di-Na salt) by using HNB indicator at pH 13, and then pH is reduced to 10 to titrate Mg^{2+} with the same reagent. A mixture of 2-4 mg Ca^{2+} with 1.2-0.24 mg Mg^{2+} (mole ratio 1:1-10:1) can be successively titrated with 0.01 *M* EDTA. Fe^{3+} and Al^{3+} are masked with triethanolamine or KCN. A large amount of NaCl (200-fold molar) excess does not interfere. The method can be used to analyze natural waters, sea water, or river water.

246

Determination of Calcium and Magnesium in Rocks, Soils, and Water by Voltammetric End Point Indication with EGTA and EDTA.

Guenter Thielicke.

Notizbl. Hess. Landesamtes Bodenforsch. Wiesbaden 96, 281-9 (1968) (Ger).

CA 72, 28069.

Ca and Mg in rock, soil, and water were determined by complexometric titration at pH 10.5 with voltammetric indication, with an amalgamated Ag electrode as indicator and a graphite electrode as counter electrode. Ca was determined with EGTA at a constant current of 1 microampere, Mg with EDTA di-Na salt at 20 microamperes.

247

EDTA Titration of Calcium and Magnesium with a Calcium-Selective Electrode.

T. P. Hadjioannou and D. S. Papastathopoulos (Univ. Athens, Athens, Greece).

Talanta 17 (5), 399-406 (1970).

Direct semi-automatic and automatic derivative potentiometric EDTA procedures for the determination of Ca and (or) Mg with a Ca selective electrode are described. Calcium is titrated in the presence of Mg at pH 12.0 and the total Ca and Mg is determined at pH 9.7. Calcium in the range 1-8 mg and Mg in the range 0.7-5 mg are determined semi-automatically with average errors of ~ 0.2 and 0.3%, respectively, and automatically with average errors of 0.4 and 0.7%. Titration times vary from a few sec to a few min.

248

Separation of Calcium and Magnesium from Heavy Metals by Ion Exchange Chromatography.

Jadwiga Chwastowska and Swietlana Szymczak (Inst. Badan Jad., Warsaw, Poland).

Chem. Anal. (Warsaw) 14 (5), 1161-8 (1969) (Pol).

CA 72, 117331.

The sample (0.25-0.5 g) containing ≤ 0.03 g of Ca and Mg, and also Fe, Al, Zn, Cu, and Mn was dissolved in HCl and treated with 50-150 ml 0.1*M* EDTA; the vol of the solution should be 100-400 ml and pH 3.6. A part of the solution (25 ml) was passed through a column of cation exchanger Dowex 50WX8 and washed with 25 ml EDTA pH 3.6. Iron, Al, Zn, Cu, and Mn passed into the effluent as EDTA complexes whereas Ca and Mg were retained. The column was washed with 25 ml EDTA and 5 ml H_2O; calcium and Mg were eluted with 25 ml 4*N* HCl and determined in the eluate complexometrically, colorimetrically, or by flame photometry. The method was used for determining Ca and Mg in various Fe ores.

249

High-Precision Measurement of Calcium in Calcium Phosphate Plant Materials, and a Micro-Method for Both Calcium and Magnesium in Brine.

R. L. McCullough, J. K. MacKay (Hooker Chemical Corp., Niagara Falls, N. Y.), and G. R. Padmanabhan (Hoffmann LaRoche, Inc., Nutley, N. J.).

Automat. Anal. Chem. Technicon Symp., 3rd, 1, 233-8 (1967) (Pub. 1968); Mediao Inc.: White Plains, N. J.

A method for the accurate assay of the Ca content of Ca phosphate products in the range 19-26% and 29-36% Ca using a Technicon AutoAnalyzer was devised. Preliminary sample preparation is necessary to remove F (both Fe and Al were also removed) and to complex most of the Ca with EDTA. Calmagite (1-[1-hydroxy-4-methyl 1-2-phenylazo]-2-naphthol-4-sulfonic acid) is used as indicator in an automated colorimetric method for Ca. The method was modified by incorporating Mg-EDTA in the flow system to measure both Ca and Mg in aqueous brine systems. Interference by Al, Fe, and Hg in the modified method for brine analysis is avoided by the use of masking agents, such as K cyanide-triethanolamine mixtures.

250

Complexometric Determination of Calcium and Magnesium.

L. Ferencova (VUIS, Bratislava, Czech.).

Stavivo 47 (5), 156 (1969) (Slo).

CA 71, 108733.

Several indicators recommended for the complexometric determination of Ca in the presence of Mg were tested. The best one is a mixture of fluorexon with phenolphthalexon, which in strongly alkaline media gives a very clearly visible equivalence point (change from green to pink-orange). The method is suitable for the determination of Ca in limestones, silicates, and dolomites containing high percentages of Mg.

251

Complexometric Method for Determining Calcium and Magnesium in Rocks with the Removal of Interfering Cations by Sodium Diethyldithiocarbamate.

R. S. Yasina.

Metody Khim. Anal. Sostav Miner., pp. 33-6 (1971) (Russ). Edited by I. D. Borneman-Starynkevich "Nauka": Moscow, U.S.S.R.

CA 75, 115488.

Ten ml of the filtrate after removal of silicic acid was diluted with H_2O to 50 ml and neutralized with 1:1 aqueous NH_3. Then, solid Na diethyldithiocarbamate was added and the suspension stirred for 5 min. After 15 min, the precipitate containing Al, Fe, Ti, Mn, Ni, Co, Zn, Cu, and Pd was filtered off and the filtrate used to determine Ca and Mg by the Complexon III method.

252

Indirect Determination of Sulfur Dioxide by Atomic Absorption Spectrometry after Precipitation of Lead Sulfate.

S. A. Rose and D. F. Boltz (Wayne State Univ., Detroit, Mich.).

Anal. Chim. Acta 44 (1), 239-41 (1969).

SO_2, 0.25-25 mg (10-1000 ppm), is determined by measuring the atomic absorbance of Pb at 283.3 millimicrons after separating the $PbSO_4$ (equivalent SO_2) precipitated with excess $Pb(ClO_4)_2$. Place 25 ml of sample solution or an aliquot in a flask, add three drops of 3% aqueous H_2O_2 solution, mix, and add 30 ml of 9.86 x $10^{-4}M$ $Pb(ClO_4)_2$ (dilute ~0.01*M* $Pb(ClO_4)_2$ with H_2O). Add 25 ml of absolute EtOH, dilute to 100 ml with H_2O, and allow to stand for five minutes. Centrifuge the mixture in a tube for 15 minutes. Aspirate the decantate solution in a reducing C_2H_2-air flame (18 psi air/6 psi C_2H_2). Prepare a calibration curve of Pb absorbance vs ppm SO_2. Beer's law is obeyed for 2-20 ppm SO_2. A Ne-filled multi-element hollow cathode tube was operated at 14 milliamperes. Cl^-, NO_2^-, NO_3^-, ClO_4^-, Na^+, K^+, NH_4^+, Cu^{++}, and Mg^{++}, 500 ppm each, OAc^- 250, di-Na salt of EDTA 20, and Ba^{++} and Al^{3+}, 10 ppm each, do not interfere; Fe^{3+} and PO_4^{3-} do. The relative standard deviation of eight recoveries of 5 ppm of SO_2 is ±3.6%.

253

Indirect Sulfate Determination in the Presence of Phosphate by Atomic Absorption Spectrometry.

B. Magyar and F. Sanchez Santos (Eidg. Tech. Hochsch., Zurich, Switz.).

Helv. Chim. Acta 52 (3), 820-7 (1969) (Ger).
CA 70, 111418.

When Ba^{++} and SO_4^{--} are mixed, the final equilibrium in the formation of $BaSO_4$ is reached very slowly; the ionic product (Ba^{++}) (SO_4^{--}), however, becomes constant after 0.5 hours, especially when the suspension is seeded with a specially prepared $BaSO_4$. The apparent solubility product, somewhat larger than the theoretically expected value, varies with the presence of other solutes than Ba^{++} and SO_4^{--}, and with the equilibrium time, but is independent of the Ba^{++}:SO_4^{--} ratio, allowing the indirect determination of SO_4^{--} by adding Ba^{++} and determining its excess by atomic absorption spectrometry.

254

Indirect Sulfate Determination by Atomic-Absorption Spectrometry.

Amina Kadow, Elham Rabban, and I. Rubeska (Chem. Lab., Inst. Appl. Res. Nat. Resour., Baghdad, Iraq).
Inst. Appl. Res. Natur. Resour., Abu-Ghraib, Iraq, Tech. Rep., No. 1, 8 pp. (1970) (Eng).
CA 76, 30353.

Sulfate in soils was determined indirectly by precipitation with Ba^{2+} and determination of excess Ba^{2+} in solution by atomic absorption spectroscopy with a C_2H_2 flame by using the 5536-Å Ba line. La^{3+} (0.02 *M*) was used to suppress the effects of Al^{3+} or phosphate. The occlusion of foreign ions, in particular La^{3+}, by the precipitate affects the determination. A Ca-SO_4^{2-} ratio of 2:1 has no effect on the determination. For samples containing 6.26 and 304.7 meq SO_4^{2-}/l., 6.34 ± 0.43 and 308 ± 10.8 meq SO_4^{2-}/l. were recovered with a relative standard deviation of 3.6%.

255

Rapid Volumetric Determination of Sulfate Ion in Phosphoric Acid with the Indicator Nitchromazo.

N. N. Basargin and N. A. Nikitina (V. I. Vernadsky Inst. Geochem. Anal. Chem., Acad. Sci., U.S.S.R.).
Zav. Lab. 32 (5), 517-19 (1966) (Russ).
Anal. Abstr. 14 (9), 5809 (Sept. 1967).

The title method is for use on wet-process H_3PO_4 for fertilizer manufacture. The sample (2-4 g) is diluted to 250 ml and a 5-10 ml aliquot is diluted to 20 ml. A pH of 1.7-2.0 is required; if that of the diluted aliquot is less than 1.7 a smaller aliquot is taken, and if greater than 2.0 an addition of 0.1*N* HCl is made. The solution is treated with 1-2 drops of an aqueous 0.2% nitchromazo solution (*Anal. Abstr. 13*, 4801, 1966) and an equal vol of ethanol or acetone, and the SO_4^{2-} is titrated with 0.02*N* $BaCl_2$ to a color change from violet to blue.

256

Estimation of Sulfate Ion in Wet-Process Phosphoric Acid Slurry.

K. A. Sherwin (to Fisons Fertilizers Ltd.).
Brit. 1,173,152, Appl. July 1, 1966.
Anal. Abstr. 19, 776.

The slurry is fed at constant rate into a mixing chamber, into which is pumped a liquid reagent, for example aqueous $BaCl_2$, that reacts with SO_4^{2-} to form a precipitate. The mixture is fed to a photo-electric detector for determining the turbidity, or other physical characteristic of the solution. Fluctuations in the turbidity are automatically controlled by varying the rate of supply of the reagent, which gives a measure of the SO_4^{2-} content of the slurry.

257

Improved Titration Medium for Sulfate-Ion Indicators.

E. E. Archer, D. C. White, and R. Mackison (BP Chem. Int. Ltd., Epsom/Surrey, England).
Analyst (London) 96 (1149), 879-80 (1971).

For the direct titration of SO_4^{2-} with $Ba(ClO_4)_2$, for example, in the determination of S by flask or furnace-tube combustion, carboxyarsenazo as indicator gave sharper end points with more rapid equilibration than did either Sulfonazo III or Dimethylsulfonazo III. The sharpness of the end point observed with carboxyarsenazo was improved by carrying out the titration in a 2:1 Me_2CO-H_2O solution buffered to pH ~5.8 with pyridine and $HClO_4$. Small amounts of Na and Cl^- interfere slightly. Large amounts of cations were removed by ion exchange prior to titration.

258

Differential Turbidimetric Method for Determining Sulfate Ions in Phosphoric Acid Solutions.

E. P. Panteleeva and I. N. Krupina (Leningrad Technol. Inst., Leningrad, U.S.S.R.).
Zh. Anal. Khim. 25 (10), 1989-94 (1970) (Russ).
CA 74, 49365.

A rapid and accurate differential turbidimetric method is suggested for the determination of 0.01–40.0% SO_4^{2-} in phosphate fertilizers, extraction acids, and other phosphate solutions. Stable $BaSO_4$ suspensions in strongly acid media (pH < 1) were obtained by using glycerol as a stabilizer and by adding a large excess of H_3PO_4. The absorbance of the suspensions was measured by a differential method with respect to a neutral light filter with an absorbance close to that of the suspension with 0.384 mg SO_4^{2-} in 50 ml; 10-fold amounts of Ca(II), Mg(II), SiO_3^{2-}, and SiF_6^{2-} and 40-fold Fe(III) and Al(III) do not interfere. In the determination of 0.6–1.2 mg SO_4^{2-}, the error was ± 4%.

259

Determination of Sulfate in Presence of Phosphate Arsenate and Other Ions. Part II.

L. Szekeres (Vet. Univ., Budapest, Hungary).
Microchem. J. 13 (3), 349-56 (1968).

Sulfate ions are titrated with barium chloride in presence of ammonium chloride, ammonia, eriochrome black-T, and magnesium EDTA complex. Alkaline earth interference is avoided with EDTA, and Fe and Al masked with DCyTA. After sequestration of cations, phosphate and arsenate may be titrated with magnesium chloride. Finally, sulfate titration is carried out in the same solution with barium chloride.

260

Short-Circuit Amperometric Titration of Sulfate Ion.

S. Murakami and H. Hayakawa (Kobe Univ., Kobe, Japan).
Kobe Daigaku Kyoikugakubu Kenkyu Shuroku, No. 40, 11-15 (1968) (Japan).
CA 70, 84045.

Sulfate is determined by short-circuit amperometric titration with Ba^{++} at pH 5.3–7.3 with a relative error of 0.6% by using a S.C.E. as a reference electrode and chromate as indicator. To the solution add 10 ml 0.01*M* K_2CrO_4 and 0.5 ml phosphate buffer, dilute to 50 ml with H_2O and titrate with 0.01*M* $BaCl_2$. Add 16 ml Me_2CO when >95 mg Cl^- is present. Interference from Br^- is avoided by treating with Ag^+ and then with Cl^-. I^-, AcO^-, and large amounts of CO_3^{--} interfere. K or Cr alum and sea water have been analyzed.

261

Potentiometric Titrations of Sulfate Using an Ion-Selective Lead Electrode.

J. W. Ross and M. S. Frant (Orion Res., Inc., Cambridge,

Mass.).
Anal. Chem. 41 (7), 967-9 (June 1969).
Potentiometric titrations of SO_4^{--} with $Pb(ClO_4)_2$ was carried out using a Pb-selective indicating electrode and a 50% dioxane media. Cu^{++}, Hg^{++}, Ag, and PO_4^{3-}, as well as 100-fold excess of Cl^- and NO_3^-, interfere with the determination. HCO_3^- interferences can be eliminated by adjusting the pH to 4. The relative standard deviation is ± 0.2 and ±1.0% at $> 5 \times 10^{-4}M$ and at $10^{-5}M$ SO_4^{--}, respectively.

262
The Nephelometric Determination of Small Amounts of Sulfate Ion.
J. M. Martin and W. I. Stephen (Univ. Birmingham, England).
Anal. Chim. Acta 39 (2), 175-80 (Oct. 1967).
The title method is suitable for SO_4 ion determination in concentrations from 2.5 to 25.0 ppm in test vol of 10 ml. The SO_4 is precipitated with a solution of 4-amino-4-chlorodiphenyl hydrochloride and the resulting suspension of amine sulfate is stabilized with gum ghatti. Phosphate ions interfere and are removed beforehand as NH_4MgPO_4. Fluoride ion up to 25.0 ppm has no effect on the determination.

263
Sulfur Dioxide Determination Based on the Pararosaniline Method at Temperatures Below 0°.
Johannes Huhn, Julius Wagner, and Reinhart Fahnert (VEB Farbenfabrik, Wolfen, Ger.).
Chem. Tech. (Berlin) 19 (9), 564 (1967) (Ger).
CA 68, 45983.
To the Na tetrachloromercurate(II) solution used in the West and Gaeke pararosaniline method is added glycerol to make a 50% solution. The aspirator bottles are filled with a 40% aqueous solution of diglycol. With these changes the determination can be carried out at temperatures well below 0°.

264
Absorptiometric Determination of Sulfide Ion.
S. A. Rahim and T. S. West (Imperial Coll. Science and Technology, London, Engl.).
Talanta 17 (9), 851-6 (Sept. 1970).
An absorptiometric method is described for sulfide ion, based on the green color which is formed when sulfide ions are treated in ammoniacal solution with Fe (III) and an excess of nitrilotriacetic acid. The recommended procedure can be applied from 1200 down to 8 ppm of sulfide and is interfered with seriously only by selenite from among 17 other anions examined. The color system is stabilized by an excess of sulfite. Suggestions are made about the nature of the color body and its mechanism of production.

265
An Indirect Chelometric Method for Sulfate.
T. C. Woodis, F. J. Johnson, and J. M. Cummings (Tennessee Valley Authority, Muscle Shoals, Ala.).
J. Ass. Offic. Anal. Chem. 53 (5), 928-30 (Oct. 1970).
Sulfate is determined rapidly and reliably by precipitation with a measured excess of $Pb(NO_3)_2$ solution (0.025*N*) and titration of the excess Pb with 0.025*N* EDTA solution. Interfering ions, including phosphate, are removed with ion exchange resins.

266
Detection of Sulfur on the Nanogram Scale. I. Organic and Inorganic Sulfur Compounds.
P. Luis, C. N. Carducci, and A. Sa (Univ. Buenos Aires, Buenos Aires, Argentina).
Mikrochim. Acta, No. 6, 1229-32 (1968).
A very sensitive nanogram method for the detection of S in organic and inorganic substances is described. The ultramicro method for S in organic and inorganic substances of C. N. Carducci, *et al* (1967) was improved by heating the sample with H_3PO_4, HCl, or $HClO_4$ and Mg in a capillary combustion chamber under reduced pressure. The SO_2 produced is absorbed in a sodium tetrachloromercuriate solution and reduced to H_2S with $HCl-H_3PO_2-KI$ mixture. The H_2S is then detected by a specific reagent prepared by mixing 0.5 ml dioxane, 1 drop of polysorbate 80, and 1.5 ml of 0.01% $Pb(NO_3)_2$ with 0.5 ml of 32 mg 4-(2-pyridylazo)-resorcinol in 25 ml 0.01*M* NaOH and then adding 0.5 ml of buffer solution (5.5 g H_3BO_4 + 5.5 g $NaBO_3$ in 100 ml). The sensitivity ranges 3-5 ng of S. (See *FA 2*, 1252 for Part II).

267
Detection of Sulfur on the Nanogram Scale. II. Anions Containing Sulfur.
P. Luis, C. N. Carducci, and A. Sa (Univ. Buenos Aires, Buenos Aires, Argentina).
Mikrochim. Acta, No. 6, 1233-6 (1968).
Sensitive ultramicro procedures for the common anions of S are described. The procedures are used for the detection of S^{--}, SO_3^{--}, $S_2O_3^{--}$ as H_2S either directly or after reduction. SO_4^{--} is detected with the $BaCl_2$ test at the tip of a capillary pipette. A precipitate can be obtained even at a 1:(2 X 10^4) dilution. S^{--} is determined directly and SO_3^{--} and $S_2O_3^{--}$ after reduction, as H_2S by using 4-(2-pyridylazo)-resorcinol-Pb^{--} reagent. Sensitivities range from 1.5 ng S^{--} to 15 ng $S_2O_3^{--}$ in the presence of S^{--} and SO_3^{--}. The use of HCO_3^- as a release agent for S^{--} prevents its oxidation in an acid medium. An acid solution of *I* is used to prevent interference by SO_3^{--} when determining $S_2O_3^{--}$. Excess SeO_4^{--} and SeO_3^{--} interfere by oxidizing SO_2 to SO_4^{--} upon acidification. (See *FA 2*, 1251 for Part I).

268
Total Sulfur.
Charles Thompson and C. S. Allbright (Bur. of Mines, Bartlesville, Okla.).
Anal. Chem. Sulfur Its Compounds 1, pp. 89-144 (1970). Edited by J. H. Karchmer, Wiley-Intersci.: New York, N. Y.
A systematic selection was made for the best analytical method for the determination of total S in a broad spectrum of products. A review of analytical methods for total S is given. (231 ref)

269
Determination of Sulfate by Automatic Colorimetric Analysis.
M. E. Gales, W. H. Kaylor, and J. E. Longbottom (U.S. Dep. Interior, Federal Water Pollut. Contr. Adm., Cincinnati, Ohio).
Analyst 93 (1103), 97-100 (Feb. 1968).
An automatic colorimetric method for determining SO_4^{2-} in river water in the range 5-400 mg/l. is described. The method is based on the precipitation of $BaSO_4$ by $BaC_6Cl_2O_4$ and the release of the highly colored acid chloranilate ion. The color intensity is proportional to the amount of SO_4^{2-} present. A manifold was developed to adapt this method to use in the Technicon AutoAnalyzer. The method will handle 15 samples/hr with accuracy and precision equal to, or better than, the standard turbidimetric method.

270

Determination of Sulfur in Nonmetallic Materials.
R. F. Statham (Samuel Fox and Co. Ltd., Engl.).
BISRA (Brit. Iron Steel Res. Ass.) Open Rep., MG/D/412/70, 17 pp. (1970).
CA 75, 70973.

A combustion method for the determination of S by using N as carrier gas was critically examined and, from the information obtained, the method has been modified so that it can be used for the determination of the S content of a wide variety of oxide type materials The time taken for a determination varies, with the type of sample, from 5 to 30 min. The sample together with a mixture of SiO_2, Cu_2O, WO_3, and Fe oxide is heated at 1200°. The SO_2 formed is absorbed in dilute HCl containing starch and KI and the solution is titrated with standard KIO_3 solution. Although the recovery of S is not stoichiometric, a constant yield of ~95% is obtained. On a routine basis, a correction factor of 1.05 can be applied or, alternatively, samples of similar material, of known S content, can be used as standards and the factor calculated. As the titration is an oxidation-reduction reaction, there is no interference from any F present in the sample.

SEE ALSO the following numbered abstracts in other sections: 275, 361, 362-65, 367-68, 370-73, 417-18, 442, 455, 477.

MICRONUTRIENTS

271
Micronutrients in Nitrogenous, Phosphatic, and Mixed Fertilizers.
K. T. Joseph, M. Parameswaran, and S. D. Soman (Bhabha At. Res. Center, Bombay, India).
Curr. Sci. 39 (7), 145-7 (1970).
CA 73, 24327.

Methods of analysis were compared. Phosphatic and mixed fertilizers were digested with concentrated HCl or with $HF-HNO_3$ and the extracts analyzed by atomic absorption spectrophotometry. The HCl method gave generally higher results for K, Mg, and Fe. The results agreed well for Cu, Mn, and Rb. For Zn the two methods differed widely but not consistently. The trace elements were low in both the phosphatic and the mixed fertilizers, as well as in $(NH_4)_2SO_4$ and urea fertilizers.

272
The Determination of Trace Elements in Fertilizers.
J. M. Skinner (ICI Ltd., Billingham, Teesside, Engl.).
Proc. Soc. Anal. Chem. 6 (8), 131-154 (1969).
At. Absorption Flame Emission Spectrosc. Abstr. 1, 803.

Atomic absorption spectroscopy is a useful technique for analysis of fertilizers. Samples are easy to prepare, standard solutions can be prepared from pure solutions, interferences are few and results accurate over a wide concentration range. However, use of a different hollow cathode lamp for each element makes the technique undersirable for general use and the solid-source mass spectrometer has been investigated.

273
Ion-Exchange Determination of Trace Elements in Phosphorus Fertilizers.
I. K. Tsitovich and N. G. Gaidukova (Kubansk. Sel'skokhoz. Inst., Kraznodar).
Zh. Prikl. Khim. 40 (8), 1708-12 (1967) (Russ).
CA 68, 12034.

The method was suggested for the determination of the following trace elements in phosphate fertilizers: Cu (0.16-0.30 g/100 g P_2O_5), Zn (0.6-0.8), Mn (0.8), Mo (0.1-0.2), and Co (0.10-0.15). For the separation, a column of KU-1 cation-exchanger in the NH_4^+ form, washed with Petermann citrate reagent, was used. Fifty-ml portions of aqueous and aqueous-citrate extracts from a fertilizer were mixed and allowed to flow through the column. Only Cu and Zn were sorbed. Manganese, Co, Mo, and Fe were washed from the column with 120-5 ml of Petermann reagent and determined photometrically (Mo as thiocyanate, Co as β-nitroso-α-naphtholate, and Mn as MnO_4^-). After washing the column with H_2O, Cu or Zn were eluted with 40 or 50 ml, respectively, of 2*N* HCl and determined photometrically as dithizonates.

274
Determination of Trace Elements in Mineral Fertilizers by Atomic Absorption.
K. Teicher (Bayer. Hauptversuchsanst. Landwirt., Tech. Hochsch. Muenchen-Weihenstephan, Munich, Ger.).
Landwirt. Forch., Sonderh. 23 (11), 177-81 (1969) (Ger).
CA 72, 89285.

The trace elements Mg, Mn, Cu, Zn in mineral fertilizers were determined quantitatively by colorimetry, gravimetric methods, and atomic absorption spectroscopy. The latter method was less time-consuming and more accurate than the others. The diluted HCl extracts of ground fertilizer samples could be sprayed directly into the flame. This method was not sufficient for the detection of B and Co.

275
Application of X-Ray Fluorescence Spectrometry in the Determination of Metal Trace Elements in Chemical Fertilizers.
V. Bruno and Giuseppe Ristori (Univ. Firenze, Florence, Italy).
Agrochimica 13 (6), 502-5 (1969) (Ital).
CA 72, 2567.

Metal trace elements (Mn, Cu, Zn, Co) were determined in chemical fertilizers by x-ray fluorescence spectrometry. Results were in agreement with those obtained by chemical analysis. The proposed method was simple, easy, and particularly suitable for industrial controls.

276
Determination of Secondary and Minor Plant Nutrients in Fertilizers by Atomic Absorption Spectrophotometry. IV.
C. H. McBride (Armour Agr. Chem. Co., Decatur, Ga.).
J. Ass. Offic. Anal. Chem. 51 (4), 847-51 (July 1968).

The results of three previous collaborative studies of the title subject (*J. Ass. Offic. Anal. Chem. 48*, 406-12; *48*, 1100-03; *50*, 401-7) are reviewed and recalculated. On this basis, the atomic absorption spectrophotometric method is recommended for adoption as official, final action for Ca, Cu, Fe, Mg, Mn, and Zn.

277
Quantitative Analysis of Copper and Zinc in Fertilizers by Atomic Absorption Spectrophotometry. II. Quantitative Analysis of Copper.
T. Toyoda.
Hiken Kaiho 21 (5), 1-7 (1968) (Japan).

CA 70, 114180.
Coexistence of inorganic and organic compounds in fertilizer did not have an effect on the determination of Cu by the title method. Results from the analysis agreed well with the results from polarographic analysis.

278
Micronutrient Analysis of Fertilizers with Special Reference to Frits.
H. E. Hammar and N. R. Page (Clemson Univ., Clemson, S.C.).
At. Absorption Newslett. 6 (2), 33-4 (1967).
Fertilizer samples containing added micronutrients were analyzed for B, Mn, Cu, Zn, and Fe to determine the cause of a large number of deficiencies in the micronutrient content of regulatory fertilizer samples. The micronutrients were added in the form of frits and soluble salts. The sample (1 g) was digested in 10 ml of concentrated HCl at a slow boil until nearly dry. Then 20 ml of 0.5*N* HCl was added, the mixture was boiled for several minutes, and filtered. The filtrate and washings were diluted to 100 ml with H_2O and analyzed. Boron was determined by electrometric titration; Mn, Cu, Zn, and Fe were determined by atomic absorption spectrophotometry. The results demonstrated that quality control procedures rather than analytical methods were responsible for deficiencies.

279
Determination of Small Quantities of Boron by Atomic Absorption Spectroscopy.
R. Harris (Monsanto Res. Corp. Mound Lab., Miamisburg, Ohio).
At. Absorption Newslett. 8 (2), 42-3 (1969).
B (enriched in ^{10}B) in potassium chloride was determined in concentrations of less than 1%. The standard additions technique was used since it affords a more reliable procedure for solutions containing 25 micrograms/ml or less. The presence of fluoride in the samples and the high isotopic content of ^{10}B had little effect on the final B value.

280
Atomic Absorption Spectrophotometric Determination of Water-Soluble Boron in Fertilizers.
J. R. Melton, W. L. Hoover, and P. A. Howard (Texas A & M Univ., College Station, Tex.).
J. Assoc. Offic. Anal. Chem. 52 (5), 950-3 (Sept. 1969).
Water-soluble B is extracted into a mixture of 2-ethyl-1,3-hexanediol and methyl isobutyl ketone for determination by atomic absorption spectrophotometry. The extraction procedure brings the fertilizer sample, water, and extraction solvent in contact simultaneously. The organic layer which contains the extracted B is aspirated into the flame. There are no significant interferences from elements commonly found in fertilizers. The proposed method is fast and accurate for determining water-soluble B in fertilizers.

281
Determination of Boron in Fertilizers by Atomic Absorption Spectrophotometry.
S. J. Weger, L. R. Hossner, and L. W. Ferrara (International Minerals and Chemical Corp., Libertyville, Illinois).
J. Agr. Food Chem. 17 (6), 1276-8 (Nov.-Dec. 1969).
A procedure for the determination of small amounts of B in fertilizers and related compounds by atomic absorption spectrophotometry is described. The B is complexed and extracted from aqueous acid solution with 2-ethyl-1,3-hexanediol in chloroform. This separation decreases the amount of interferences common to atomic absorption and increases the sensitivity of the B determination. The detection limit is 1 ppm B with a good signal-to-noise ratio. The working concentration range in solution is 0–100 ppm B with a sensitivity of 1.5 ppm per 1% absorption at 2497.7 Å. Interfering ions were considered and their effects were found to be negligible.

282
Spectrophotometric Determination of Water-Soluble Boron in Complex Fertilizers Using Azomethine H Following a Separation by Extraction with 2-Ethyl-1,3-Hexanediol.
Andreas Hofer, Eva Brosche, and Rudolf Heidinger (Hauptlab., Oesterr. Stickstoffwerke A.-G., Linz, Austria).
Fresenius' Z. Anal. Chem. 253 (2), 117-19 (1971) (Ger).
CA 74, 86827.
Boron was separated from a 0.1*N* HCl extract from fertilizer by extraction with 20% 2-ethyl-1,3-hexanediol in iso-BuCOMe, reextracted with 0.5*N* NaOH, and determined photometrically with Azomethine H (the condensation product of 1-amino-8-naphthol-3,6-disulfonic acid and salicylaldehyde) at pH 5.2 and 415 nm. Thus, .001–.006% B were determined in complex fertilizers.

283
Modified Spectrophotometric Method for the Determination of Traces of Boron Using Quinalizarin in a Sulfuric Acid-Acetic Acid Medium.
H.K.L. Gupta and D. F. Boltz (Wayne State Univ., Detroit, Mich.).
Mikrochim Acta 4, 577-81 (1971).
Boron was determined by the title method at 577 nm with a sensitivity of 0.00037 $\mu g/cm^2$ as compared to 0.003 $\mu g/cm^2$ when only a H_2SO_4 solution was used. Beer's law was followed for 0.5-7 μg B/25 ml, and the relative standard deviation was 1.35% for determining 0.16 ppm B/25 ml. Fluorine, Ge, NO_3^-, Se, and Ti interfered. The tolerance to 34 additional ions is given.

284
Quantitative Determination of Boric Acid in the Presence of Interfering Impurities by Means of an Extraction Method.
E. Svarcs *et al.* (Inst. Inorg. Chem., Riga, U.S.S.R.).
Latv. PSR Zinat. Akad. Vestis, Kim. Ser., No. 6, 685-8 (1971) (Russ).
CA 76, 80581.
To determine 0.03-0.1*M* H_3BO_3, 0.8 g NaCl is added to 3-4 ml of the sample, the pH is adjusted to 1-2 with HCl or NaOH, and the solution is diluted with H_2O to 5 ml. The solution is extracted with 5 ml of a 1:1 mixture of $CHCl_3$ with higher diols (4-methyl-2-pentene-1,4-diol, 3-methyl-4-pentene-1,3-diol, 3-methylpentane-1,3,5-triol, 3-methyl-2-hydroxymethylbutane-1,3-diol, and 4-methylpentane-1,3,4-triol, which are the byproducts of the isoprene synthesis) for 5 min; the extraction is repeated three times; 10-20 ml H_2O is added to the extracts and the solution is titrated with 0.05*N* NaOH, after addition of mannitol or glycerol, potentiometrically or by using α-naphtholphthalein as indicator. PO_4^{3-}, Fe^{3+}, Bi^{3+}, Sb^{3+}, Sn^{2+}, Th^{4+}, MnO_4^-, As^{3+}, Al^{3+}, and La^{3+} do not interfere. Silica and F^- interfere.

285
Determination of Boron in the Presence of Phosphates, Fluorides, and Heavy Metals.
E. Svarcs, A. Dzene, and A. Ievins (Inst. Neorg. Khim., Riga, USSR).
Latv. PSR Zinat. Akad. Vestis, Kim. Ser., No. 6, 749

(1968) (Russ).
CA 70, 63827.

Add 1 g NaCl, $NaNO_3$, or $Mg(NO_3)_2$ to 10 ml neutral or weakly acid B solution in H_2O and extract three times with 10 ml 1:4 $CHCl_3$-3-methylbutane-1,3-diol. Add 50 ml H_2O to the combined organic extracts and titrate HBO_3 with 0.1*N* NaOH with naphtholphthalein as indicator, by using mannitol or glycerol. This determination of B is not affected by the presence of Ag, Pb, Cu, Cd, As^{3+}, Zn, Ni, Co, Fe, Mn^{++}, Al, Hg, Sn^{++}, F^-, and PO_4^{3-}. Only organic α-polyhydroxy compounds forming nonextractable B complexes and also Sb(III) and SiO_2 interfere. The maximum error is 0.3%; it increases to 1% only in the presence of Ag, Mn^{++}, Al, Hg^{++}, or F^-.

286

Determination of Boron in Fertilizers, Soils, Plants, and Mineral Waters with Nile Blue A.

E. Gagliardi and E. Wolf (Univ. Graz, Australia).
Mikrochim. Acta, No. 1, 140-7 (1968) (Ger).
CA 68, 68072.

A photometric method which employs Nile Blue A is described for determination of 0.01-130.00 μg B in fertilizer, soil, plant, and mineral water samples. Samples were prepared as follows: for analysis of fertilizers, heat 100 mg for 10 min with 1 ml concentrated H_2SO_4 while slowly blowing N through the mixture. Cool, dilute with water, and filter. Dilute to 100 ml. For determination of B available for plant absorption in soil, reflux 2.5 g soil with 20 ml of H_2O for 5 min, cool and centrifuge. For determination of total B content in soil, treat as the fertilizer samples. For determination of B in plants, prepare the sample by the MacDougell and Briggs method. No preparation of water sample is required. For determination of 20-130 μg B, to 10 ml of sample solution add 10 ml of 2% HF solution. After 20 min, dilute with a small amount of water, add 10 ml of $Fe_2(SO_4)_3$ solution containing 100 mg % Fe and 5 ml of 0.1% aqueous Nile Blue solution. Shake vigorously with 20 ml of PhCl for 30 sec. Dilute a 5-ml aliquot of the organic layer to 50 ml with MeOH. Measure absorbance of Nile Blue fluoroborate at 647 nuclear magnetons in a 1-cm cuvette *vs* a similarly prepared blank. For determination of 0.01-20.00 μg B follow the same procedure with the following changes: use only 1 ml of the Nile Blue solution. Extract with 2-5 ml portions of *o*-dichlorobenzene. Separate the organic layer and dilute the combined extracts to 50 ml with MeOH. Results include (material analyzed, B content, relative percent error given): superphosphate fertilizer, 0.[illegible]5%, ±2.4; mineral water 2.660 mg B/l., ±2.4.

287

Comparative Study of Various Complexing Agents (Polyols) in the Titration of Boric Acid.

Ronald Belcher, G. W. Tully, and G. Svehla (Univ. Birmingham, Birmingham, Engl.).
Anal. Chim. Acta 50 (2), 261-7 (1970).

Boric acid forms complexes with several polyols, which are acidic enough to be titrated directly with alkali hydroxide solution. A detailed potentiometric study has shown that sorbitol gives slightly sharper end points than the more commonly used mannitol, but both are satisfactory for the titration of 5×10^{-2}–5×10^{-4} *M* H_3BO_3. Fructose, glycerol, and invert sugar are not satisfactory for $<10^{-2}$ *M* H_3BO_3 solution, and very large concentrations of the latter two reagents are needed. Ethylene glycol has limited application; glucose and sucrose cannot be used. The pK values of the complexes formed increase in the order sorbitol < mannitol < fructose ≤ glycerol < ethylene glycol.

288

Determination of Boron in Fertilizers by Emission Flame Photometry in the Air-Hydrogen Flame.

E. E. Pickett, J.C.M. Pau, and S. R. Koirtyohann (Univ. Missouri, Columbia).
J. Ass. Offic. Anal. Chem. 54 (4), 796-800 (1971).

The highly selective extraction of B from acid solutions by 2-ethyl-1,3-hexanediol, recently applied to determination of B in boronated fertilizers by atomic absorption, can be used also in the flame emission mode in the air-H flame with distinct advantage. This convenient and inexpensive flame, although relatively cool, excites B oxide emission intensely and provides superior detection limits, about 0.1 ppm in the extract (time constant, 2 sec). The freedom from interference provided by the extraction permits the background and B oxide emission measurements to be made easily and reliably. Certain older flame photometers can be used satisfactorily, although modern flame emission photometers, including some atomic absorption instruments, equipped with recorders, are preferred. Interferences and extraction conditions were studied further and the method was tried on several fertilizers.

289

Potentiometric Determination of Boron in Agricultural Samples.

R. M. Carlson and J. L. Paul (Univ. California, Davis).
Soil Sci. 108 (4), 266-72 (Oct. 1969).

In this method, B is isolated on a column of Amberlite XE-243 which is specific for B. Addition of hydrofluoric acid converts the B to tetrafluoroborate which is measured potentiometrically with a liquid ion exchange membrane electrode. The calibration curve covers a range of 1–500 micrograms B and is linear between 10–500 micrograms B. B from samples of soil, plant tissue, or water is obtained in solution without regard for pH of the solution. Neutral and alkaline solutions are added directly to the B exchange column but acidic solutions are passed through a weak cation exchange column (BioRex 70, 50–100 mesh) into the Amberlite XE-243. After sample addition, wash the column with 2 ml H_2O, add 2 ml 3*N* NH_4OH, and wash again with 2–3 ml H_2O. Add 2 ml 10% HF and after 10 minutes wash with 5 ml H_2O. Place the Amberlite XE-243 column on top of a strong acid column (Dowex 50W-X8, 50-100 mesh) and add 10 ml 0.3*N* NaOH. Measure the potential of the effluent to determine the B content of the sample. Approximate analysis time is one hour. The procedure can be interrupted at any step and the final effluent is stable for weeks. The method is free from interference by salts, other ions, or dissolved organic matter.

290

Moessbauer Quantitative Analysis of Ferric Ion/Ferrous Ion Ratios in Some Phosphate and Oxide Mixtures: Possibilities and Limitations.

Abraham Lerman, Mariana Stiller, and Erica Hermon (Geol. Surv. Israel, Jerusalem, Israel).
Earth Planet. Sci. Lett. 3 (5), 409-16 (1968).
CA 68, 88929.

Ratios of the peak areas on Moessbauer spectra of mixtures of vivianite and amorphous ferric phosphate vary linearly with the ratios of the proportions of the phases. This makes it possible to use Moessbauer spectrometry for simple quantitative analysis of ferrous-ferric phosphates. The results of the Moessbauer analysis agree to within 3% with conventional chemical methods. Interpretation of the Moessbauer spectra of Fe phosphate mixtures and oxidized vivianite is consistent with magnetic susceptibility measurements. Consideration of the spectra of a number of ferrous and ferric phosphates and

oxides indicates that the Moessbauer analysis may be also applied to some phosphate-oxide mixtures. The slope of the curve of absorption intensities ratio *vs* proportions ratio deviates from the slope predictable by the theory. Hence, for a reasonably accurate estimation of the Fe^{3+}/Fe^{2+} ratios in mixtures of minerals, calibration curves may need to be constructed for each particular case. (16 ref)

291

Photometric Determination of Iron Traces in Hydrofluoric Acid in Antimony Trioxide, and in Diammonium Phosphate.

Yu. L. Lel'chuk, L. L. Skripova, and B. N. Besprozvannykh.
Izv. Tomsk. Politekh. Inst. 163, 127-9 (1970) (Russ).
CA 75, 147443.

The sample is heated with a buffered (pH 3.3-3.5) solution containing tartaric acid, $NaNO_2$, NaCl, and NaOH to form stable complexes with interfering metals and to reduce Fe^{3+} to Fe^{2+}; 2,2'-dipyridyl is added and Fe is determined colorimetrically. The relative error of analysis of HF, Sb_2O_3, and $(NH_4)_2HPO_4$ was ±5, ±10-15, and ±3-5%, respectively.

292

Indicators for EDTA Titrations of Ferric Ions.

M. N. Desai *et al* (Univ. Ahmedabad, Ahmedabad, India).
Chim. Anal. (Paris) 52 (8), 872-8 (1970) (Fr).
CA 73, 136934.

Indicators for direct EDTA titrations of Fe^{3+} are reviewed and 57 phenols are examined for suitability as indicators. Only 24 of the compounds were unsuitable as indicators. Substitution in the phenol ring by Cl, NO_2, or NH_2 gave unsuitable indicators, whereas substitution at the ortho position by OH, CHO, CO_2H, $CONH_2$, or hydroxyiminomethyl groups gave suitable indicators. (160 ref)

293

Determination of Iron and Nickel in Water and Brine by Solvent Extraction and Atomic Absorption Spectroscopy.

Jerry L. Jones and R. D. Eddy (Texas A & M Univ., College Station).
Anal. Chim. Acta 43 (2), 165-71 (Nov. 1968).

A rapid, reliable, and sensitive atomic absorption method for trace amounts of Fe and Ni in concentrated brine and in H_2O is described. A simple single extraction is effective for Fe in H_2O in the range 0.4-200 ppb and in 25% NaCl solutions at 0.8-200 ppb. A similar procedure was developed for Ni concentrations of 2-200 ppb in H_2O and 4-200 ppb in brine. Extraction for 15 minutes with methyl isobutyl ketone (MIBK) from a system buffered at pH 7 yields optimum results. The complexing agents are 0.2% solutions of 8-hydroxyquinoline and dimethylglyoxime for Fe and Ni respectively.

294

Interferences in the Determination of Iron by Atomic-Absorption Spectrophotometry in an Air-Acetylene Flame.

K. E. Curtis (Cresco Fertilizers Pty. Ltd., Bayswater, Western Australia).
Analyst (London) 94 (1125), 1068-71 (Dec. 1969).

Sulfate has been found to interfere in the determination of Fe by atomic-absorption spectrophotometry, when using an air-acetylene flame. The effects of varying the sulfate concentration, the nature of the flame and the path of the light beam through the flame were examined. The effects of PO_4, K, Na, NH_4, Ca, Mg, Mn, and Al ions were also examined.

295

The Interference of Cobalt, Nickel, and Copper in the Determination of Iron by Atomic Absorption Spectrophotometry in an Air-Acetylene Flame.

J. M. Ottaway, *et al* (Univ. Strathclyde, Glasgow, Scot.).
Analyst (London) 95 (1131), 567-73 (June 1970).

An investigation of interferences in the determination of Fe by atomic absorption spectrophotometry in an air-C_2H_2 flame is reported. It was found that three elements, Co, Ni, and Cu, exhibit serious depressive effects, the magnitude of which is strongly dependent on the flame conditions, with respect to both fuel-to-air ratio and the height of the optical path above the burner, and is also dependent on the anion present in the sample solution. The optimization of the flame for both pure Fe solutions and those containing the interfering elements, and means of suppressing these interferences, are discussed. The use of 8-hydroxyquinoline at a concentration ≧ the total concentration of Co, Ni, and Cu is recommended as an effective releasing agent.

296

Determination of Molybdenum in Geological Materials by a Combined Solvent-Extraction–Atomic-Absorption Procedure.

Dawn Hutchison (Inst. Geological Sci., London, England).
Analyst (London) 97 (1151), 118-23 (Feb. 1972).

A method is described for the determination by atomic-absorption spectrophotometry of Mo, up to the 1000 ppm level, in geochemical samples. After attack with acid, the Mo in dilute $HClO_4$ medium is complexed with benzoin α-oxime and extracted into chloroform. The extract is mixed with HNO_3 and $HClO_4$ and evaporated to dryness and the residue is dissolved in ammonia solution. The ammonium molybdate formed is dissolved in a solution containing 1% volume/volume of $HClO_4$ plus 0.5% wt/volume of NH_4Cl and aspirated into a luminous air-acetylene flame.

297

Atomic Absorption Spectrophotometric Determination of Molybdenum in Fertilizers.

S. R. Koirtyohann and Maureen Hamilton (Univ. Missouri, Columbia).
J. Ass. Offic. Anal. Chem. 54 (4), 787-9 (1971).

Molybdenum is extracted into $CHCl_3$ from fertilizer sample solutions at pH 1.6 as the 8-hydroxyquinolate. Atomic absorption in the premixed N_2O–C_2H_2 flame is used for determination. Methyl isoamyl ketone is added to the $CHCl_3$ extract to improve the burning qualities. The method is sensitive and precise but appears to have a positive bias of about 5%.

298

Modification of Dithiol Tests for the Field Determination of Molybdenum.

M. F. Stubbs (Texas Tech. College, Lubbock).
Analyst 93 (1102), 59-60 (Jan. 1968).

Modifications of currently used dithiol tests for the field determination of Mo have been developed. Mo is oxidized and extracted quickly and selectively with sodium hypochlorite at room temperature. The disadvantages of using an alkaline fusion or oxidation with potassium chlorate and hot hydrochloric acid are avoided.

299

The Suppression of Some Interferences in the Determination of Molybdenum by Atomic-Absorption Spectroscopy in an Air-Acetylene Flame.

D. J. David (C.S.I.R.O., Canberra, Australia).

Analyst 93 (1103), 79-82 (Feb. 1968).
Earlier published work on the determination of Mo with an incandescent air-acetylene flame showed that Al could be used effectively to suppress the interferences of such elements as Sr, Ca, Mn, and Fe, but this has not been confirmed for Mn and Fe by other workers. Indications are that this is caused by instrumental characteristics. Ammonium chloride, subsequently shown to be effective in the suppression of Mn and Fe interference in metallurgical analysis, was found to suppress the interferences of alkaline earth chlorides, but to have no effect on a severe interference by Ca ion, sulfate and phosphate in combination. As Al ion was found to suppress this interference, a mixture of Al and ammonium chlorides is suggested for general application.

300
Automatic Determination of Copper in Single- or Multiple-Nutrient Fertilizers.
F. Holz (Landwirtsch, Forsch. Hanninghof, Duelmen, Ger.).
Landwirt. Forsch., Sonderh. 25, 159-65 (1970) (Ger).
CA 74, 124088.
A method was developed for Cu determination in fertilizers by using 2,2'-bicinnamic acid (I) either manually or with an autoanalyzer. Boil 10 g of a finely ground sample with 100 ml 10% H_2SO_4 for 30 min in a 500-ml volumetric flask, cool, dilute to vol with H_2O, and filter. In the automated method reduce Cu(II) in an aliquot with 10% NH_2OH HCl, then add 0.5 *N* citrate buffer of pH 6.0 and add 0.1% I in 100 ml 2% KOH. Measure the absorbance of the violet complex at 570 mμ. In the manual method transfer 10 ml of the solution into a 50-ml volumetric flask, add 5 ml 10% $NH_2OH{\cdot}HCl$, shake for 5-10 min, then add 20 ml citrate buffer and 5 ml I; after 30 min measure the absorbance at 578 mμ. The relative error is ± 0.5%.

301
Collaborative Study of a Zincon Ion-Exchange Method for the Quantitative Determination of Zinc in Fertilizers.
C. E. Jones and L. E. Pracht (Colorado State Dep. Agr., Denver).
J. Ass. Offic. Anal. Chem. 54 (4), 790-5 (1971).
This study represents an attempt to validate the ion-exchange zincon method for the determination of Zn in fertilizers. The values of the standard deviations S_d, S_r, and S_b and the results of the *F*- and *t*-tests are presented as an estimate of the precision, accuracy, and dependability. Atomic absorption measurements were also made and provided reference data for evaluation purposes. In its present form, the method falls short of expectations as an alternative wet approach to the dithizone method. It is recommended that the methods for determining Zn in fertilizers be studied further.

302
Determination of Manganese in Soils and Fertilizers by Amperometric Titration with Sodium Nitrite.
S. M. Yatrudakis *et al* (Inst. Khim., Tashkent, U.S.S.R.).
Uzb. Khim. Zh. 15 (3), 6-8 (1971) (Russ).
CA 75, 109285.
Titration was conducted with $NaNO_2$ using a unit equipped with a rotating (600 rpm) Pt electrode 30 mm long and 0.5 mm in diameter. A calomel electrode was used as standard. The best equivalent point and reproducibility was obtained by acidifying the sample with 2.5-3*N* H_2SO_4 or HNO_3. Both of these acids can be used when the concentration of Mn(VII) is more than 0.006 mg in an initial sample, and only HNO_3 can be used when the concentration of Mn is below 0.0568 mg. The suggested method was used for the determination of total and mobile Mn in serozems of Tashkent region. A difference in results between the photocalorimetric and amperometric methods never exceeded 8%. The method does not require the elimination of H_4SiO_4 and the plotting of a calibration curve: the Mn is determined immediately after decomposition of the sample and oxidation of Mn (II) to Mn(VII).

303
Automatic Determination of Manganese in Trace Element-Containing Major Nutrient Fertilizers with Potassium Diorthoperiodatoargentate (III).
F. Holz (Landwirtsch. Forsch. Hanninghof, Ruhr-Stickstoff A.-G., Duelmen/Westf., Ger.).
Landwirt. Forsch., Sonderh 26 (1), 294-302 (1971) (Ger).
CA 76, 33126.
The diperiodatoargentate (III) reagent solution was made from 28 g KOH and 23 g KIO_4 in 100 ml H_2O to which 8.5 g $AgNO_3$ was added. The solution was heated to boiling and 20 g K_2SO_3 was added in portions with stirring over 30 min. The dark red solution was filtered and the filtrate diluted to 1 l. The orange reagent is stable, but should be stored in the dark. The Ag(III) complex is strongly oxidizing, instantaneously converting Mn(II) to MnO_4^-. Analyses were run on fertilizer solutions manually or automatically with the Technicon Autoanalyzer at a rate of 40/hr for a range of 0-0.25% Mn. The relative standard deviation was ± 0.1 to ± 0.4%. The system was also used for the simultaneous automatic determination of Cu and Mn with a relative standard deviation of ± 0.68%.

SEE ALSO the following numbered abstracts in other sections: 374-75, 378-85, 389-91, 414, 418-19.

TRACE ELEMENTS

304
Direct Spectrographic Determination of Rare Earth Elements in Apatite.
G. M. Mkrtchyan and L. B. Sarukhanyan (Inst. Geol. Nauk, Erevan, USSR).
Izv. Akad. Nauk Arm. SSR, Nauki Zemle 21 (1-2), 136-44 (1968) (Russ).
CA 70, 63973.
A synthetic compound, formed by reaction of $CaCl_2{\cdot}6H_2O$ and H_3PO_4 with CaO, with a composition similar to that of natural apatite, was used to prepare all standards by addition of definite amounts of rare earths. The following analytical lines were selected from literature and study of spectra of various apatites: Ce 2651.01, Ce 2017.20, La 2610.39, La 2893.01, Pr. 4223.00, Nd 3115.17, Nd 4252.44, Nd 4252.44, Sm 4329.02, Eu 2813.95, Gd 3032.85, Gd 3100.58, Dy 3319.89, Y 2894.26, Yb 2891.38, Er 2910.36, Tm 3131.30, Lu 2615.42, Ta 2870.41, and Th 2937.30 angstroms. The similarity of the analyzed samples, the relatively constant total composition, the agreement between the physical-chemical properties of apatites and standards, and satisfactory reproducibility permitted analyses to be made without internal standard. The reproducibility of analysis was 14.2% average. Triplicate analyses improved reproducibility to 8.2%. The control sample of apatite, containing average (for a given deposit) concentrations of rare earth elements, was

photographed on each plate to avoid errors from distortion of calibration graphs.

305

Activation Analysis of Rare Earths. III. The Determination of Rare Earths in Minerals by the Single Comparator Technique.

D. L. Massart and J. Hoste (Ghent Univ., Ghent, Belgium).

Anal. Chim. Acta 42 (1), 21-8 (1968).

The determination of rare earths in minerals by activation is described. The rare earths are separated as a group from the bulk of the material before irradiation. After irradiation the rare earths are separated from each other by gradient elution with ammonium α-hydroxyisobutyrate on a cation-exchange column. The elements are determined by the single comparator technique. This method permits a practical application of activation analysis to the routine determination of rare earths in complex matrixes.

306

Spectrochemical Determination of Rare Earths in Calcium Fluoride.

S. Weisberger (Res. Center Gen. Telephone Electron. Lab., Inc., Bayside, N. Y.).

Appl. Spectrosc. 22 (6), 719-21 (1968).

The development of a spectrochemical method for the determination of type 4f rare earths (except lanthanum and cerium) in amounts usually employed in the activation of calcium fluoride is reported. The method converts the fluoride sample to a common matrix, calcium sulfate, thereby eliminating the possibility of errors in the subsequent arcing of the sample due to previous physical and chemical treatment. Since the "burn" is made in air and recorded in the so-called "metallurgical region," no elaborate apparatus is needed for analysis.

307

Determination of Rare-Earths in Phosphate Rock by Atomic Absorption Flame Photometry.

J. Kinnunen and O. Lindsjo (Outokumpu Oy, Pori Works, Pori, Finland).

Chemist Analyst 56 (1-2), 25-7 (1967).

Europium, Nd, and Y in phosphate rock are measured by atomic absorption spectroscopy. A nitrous oxide-acetylene flame is used, at 4634 Å, 4594 Å, and 4102 Å for Nd, Eu, and Y respectively. The rare earth oxides are separated from the rock by conventional methods, and dissolved in HCl, then 1000 ppm NaCl solution added as ionization buffer. Pure oxides are used for the standard solutions. The sensitivities measured are 20 ppm/1% absorption, 0.6 ppm/1%, and 2 ppm/1% for Nd, Eu, and Y respectively. Silicate, fluoride, and Al interfere seriously with all three elements, Ce interferes slightly with Nd, and acids with Y. Sensitivites agree with reported data, except Eu which is more sensitive.

308

The Atomic-Emission Spectroscopy of the Rare Earth Elements in a Separated Nitrous Oxide-Acetylene Flame.

D. N. Hingle, G. F. Kirkbright, and T. S. West (Imperial Coll., London, Engl.).

Analyst (London) 94 (1123), 864-70 (Oct. 1969).

Flame emission in the interconal zone of a separated nitrous oxide-acetylene flame is shown to provide a sensitive technique for the detection of the rare earth elements, Sc and Y. The relative intensities of the principal atomic lines of these elements emitted in this flame were measured, and the detection limits at the lines most suitable for flame-emission spectroscopy are reported for aqueous and ethanolic sample solutions. The effect on the atomic-emission intensities obtained for each of the 16 elements investigated in the presence of the other 15 elements was investigated. At the concentrations used in this general survey no serious spectral line interferences between the rare earths were observed because of the simple spectra excited by the hot, reducing fuel-rich flame.

309

Determination of Rare Earths in Phosphate Rock by Atomic Absorption Flame Photometry. II.

J. Kinnunen and O. Lindsjo (Pari Works, Pari, Finland).

Chemist-Analyst 56 (4), 76-8 (Oct. 1967).

Procedures for the determination of total rare earths in phosphate rock by chelometric and gravimetric methods, and of Sm, Gd, Dy, Yb, Er, Ho, Tb, Pr, and La by atomic absorption flame photometry are described. A table showing the influence of many interfering elements is included; of these, HF, Si, and Al are the most serious.

310

Rapid Method for the Photometric Determination of Rare Earth Elements in Apatite Concentrate.

T. G. Leshtaeva.

Metody Anal. Rud Kol'sk. Poluostrova, pp. 160-2 (1970) (Russ).

CA 74, 71324.

The method is based on the photometric determination of rare earths with Arsenazo III directly from the concentrate sample dissolved in 1:1 HCl. To an aliquot of solution, containing 10-30 μg of rare earth, is added 1 ml 1% ascorbic acid and the pH is adjusted to 2 against α-dinitrophenol with 1:10 NH_4OH and 1:5 HCl; 5 ml pH 2 buffer solution and 2 ml Arsenazo III (0.1% solution in 0.1*N* HCl) are added and the solution is diluted to 50 ml with 0.01*N* HCl. The absorbance is measured by using a red light filter in a 30-mm cell. The rare earth content is determined from calibration graphs. The sensitivity of the method is 0.01%; 45 min is necessary for analysis. The method is recommended for control of rare earth content in apatite-nephelne concentrate and products of its treatment by HNO_3 and H_2SO_4.

311

Selective Determination of Total Rare Earth Metals and of Thorium in Mineral Material.

L. L. Galkina and E. Yu. Sosnovskaya (Central Asian Res. Inst. of Geol. and Mineral Raw Materials, Tashkent, U.S.S.R.).

Zh. Analit. Khim., 24 (6), 938-41 (1969) (Russ).

Anal. Abstr. 19, 4786.

The method is based on separation of the rare earth metals by extraction with butyric acid in the presence of sulphosalicylic acid. The separated rare-earth metals are determined spectrophotometrically with arsenazo III, complexometrically (xylenol orange as indicator), or gravimetrically (precipitation as oxalates and subsequent ignition to oxides). Similar spectrophotometric or complexometric methods are used for the determination of Th. The error for ≃ 10 to 100 μg of rare earth metals or Th in 2-g samples was within ± 8%.

312

Cathode-Region Method for the Direct Spectrochemical Determination of 50 Trace Elements in Rock Phosphate.

R. Avni and A. Boukobza (Nucl. Res. Center, Negev, Israel).

Appl. Spectr. 23 (5), 483-9 (Sept.-Oct. 1969).

A direct spectrochemical method for 50 trace elements in rock phosphate was developed, exposing only the cathode region

(0.5 and 0.8 mm below the upper electrode) instead of the whole dc arc plasma. In the 0.5-mm region 31 elements were analyzed, while the 0.8-mm region was used for Sc, Y, U, Th, Zr, and the rare earths. The axial gradients of the dc arc, burning in air under atmospheric pressure, were studied in order to find the suitable matrix for the trace element standards. The behavior of the temperature, voltage, electron density, line intensity, and particle concentration indicate calcium metaphosphate as suitable matrix for rock phosphate. When 20% by wt graphite was added to both standards and samples, the detection limits of the traces was in the range of 0.1–10 ppm. An average precision of 20% was calculated for concentrations up to 400 ppm.

313

Fast Way to Analyze Trace Elements.

Am. Machinist 112 (14), 31 (July 1, 1968).

A rapid, sensitive, accurate, and almost universally applicable method of determining trace elements in inorganic and organic materials has been demonstrated by Bell Telephone Laboratories. With the new technique, it is possible to analyze trace elements in less than 15 min, even in bulk samples. The new 'Coprex' (COPREcipitation-x-ray fluorescence spectroscopy) method determines trace amounts of 68 of the 72 elements that are usually determined with a conventional x-ray spectrograph. Coprex procedures are lacking, at present, for osmium, protactinium, promethium, and krypton. The trace elements or elements are quantitatively isolated from interfering elements by precipitation with a suitable reagent. The precipitate is then collected on a filter paper disk and examined using x-ray spectroscopy.

314

Atomic-Fluorescence Spectroscopy. VII. Fluorescence and Analytical Characteristics of Arsenic, with a Microwave Excited Electrodeless Discharge Tube as Source.

R. M. Dagnall, K. C. Thompson, and T. S. West (Imp. Coll., London, England).

Talanta 15 (7), 677-87 (1968).

The construction of an electrodeless As discharge tube and its use for atomic fluorescence studies is described. Cool N-H and Ar-H diffusion flames as well as normal premixed flames are considered as atom reservoirs and the atomic fluorescence emission at 15 different wavelengths is evaluated. The diffusion flames give the largest emission signals at As concentrations < 200 ppm, but show a premature curvature at higher concentrations because of the presence of an abnormally high density of As atoms. Above 200 ppm of As, the premixed air-C_2H_2 flame is superior. The limit of detection at 1890 Å is 0.2 ppm of As in the N-H diffusion flame and 1.0 ppm in the air-C_2H_2 flame. A long path-length diffusion flame is also particularly useful in atomic absorption measurements because it absorbs very little radiation in the far ultraviolet region and gives an abundance of As atoms.

315

Determination of Aluminum by Atomic-Absorption Spectrophotometry with the Nitrous Oxide and Acetylene Flame.

R. C. Mallett, *et al.* (Natl. Inst. Met., Johannesburg, S. Africa).

Natl. Inst. Met., Repub. S. Afr., Res. Rept., No. 137, 19 pp (1967).

CA 70, 92869.

The interference of numerous elements was tested in both aqueous and BuOAc media. An extraction method is described for the determination of Al in silicate materials. Cupferron is used to precipitate the Al, which is then extracted with BuOAc. Al is determined in the organic phase by aspirating into an atomic absorption spectrograph and using the 3092.7 angstrom-line. The method can be applied to many other types of materials and has been used in determining ≤ 20% Al_2O_3. The sensitivity in BuOAc medium is ~0.8 microgram/ml for 1% absorption.

316

Atomic Absorption Spectrophotometric Determination of Strontium in Kola Phosphate Rock.

Andreas Hofer (Haupt-Lab., Oesterr. Stickstoffwerke A.-G., Linz, Austria).

Fresenius' Z. Anal. Chem. 249 (2), 115-17 (1970) (Ger).

CA 72, 74466.

Evaporate a 1 g sample twice with 5 ml concentrated HCl to dryness, dissolve in 1 ml concentrated HCl and 50 ml H_2O, filter, and wash with 50 ml hot H_2O. After cooling, pass the filtrate, through a cation exchange column (Lewatit S 100, 0.3-1 mm, H^+ form) at 3 ml/min, wash with 150 ml 0.01 *N* HCl, elute with 250 ml 4 *N* HCl, dilute the eluate to 500 ml, take aliquots of 25.0 ml, and determine Sr after dilution to 100 ml by the standard addition method by using a C_2H_2-air flame. The Sr content of Kola phosphate by rock is 2.51-2.74%.

317

Determination of Lead in Food-Grade Phosphates and Phosphoric Acid by Atomic Absorption Spectroscopy.

J. Jordan (Albright and Wilson Ltd., Oldbury, England).

At. Absorption Newslett. 7 (3), 48-9 (May-June 1968).

Lead was extracted from 200 ml of 0.5*N* HCl solution by shaking for 30 sec with 5 ml 1% diethylammonium diethyldithiocarbamate in xylene and adding 10% ascorbic acid to prevent Fe interference. The absorbance was measured by using the 2170-Å Pb line and a spectral band pass of 6 Å on an instrument equipped with an air-C_2H_2 burner and a Pb hollow cathode. When 200 μg Cu, Zn, Mn(III), Cr(III), As(III), or Ni was added to a solution containing 25 μg Pb, the recovery of Pb was 25.5-26.8 μg. The method is five times faster than the dithizone colorimetric method and the results are comparable.

318

Spectrochemical Determination of Trace Amounts of Elements in High Purity Phosphorus.

Yasuaki Osumi, Kunishige Higashi, and Yoshizo Miyake (Govt. Ind. Res. Inst., Osaka, Japan).

Bunseki Kagaku 18 (10), 1219-24 (1969) (Japan).

CA 72, 62440.

Dissolve five g P for semiconductors in HNO_3, evaporate several times with H_2O, add Co to give a 40 ppm concentration as an internal standard and 8 ml HCl, dilute to 50 ml and determine >0.1 ppm of Fe, Pb, Cu, Mg, Ca, Al, Cd, B, Bi, and Sn by high voltage spark method.

319

Atomic Absorption Spectroscopy of Selenium.

C. L. Chakrabarti (Carleton Univ., Ottawa, Canada).

Anal. Chim. Acta 42 (3), 379-87 (1968).

The atomic absorption spectroscopy of Se and of its complexes in organic solvents at different wave lengths in air-C_2H_2 flames are discussed. A sensitive procedure has been developed. Se can be determined in aqueous solution at 1960, 2040, 2063, or 2075 Å; the sensitivities for these lines with a Techtron 10-cm air C_2H_2 burner are in the ratio of 1:9.60:93. When a Beckman triple-burner (air-H) and a triple-pass optical system are used, the most sensitive 1960-Å line provides a

sensitivity of 0.5 ppm and a detection limit of 1.0 ppm. With the Se 1960-Å line and a Techtron 10-cm air-C_2H_2 burner, Se extracted into iso-BuCOMe as its diethyldithiocarbamate complex gives a sensitivity of 0.30 ppm, which is a 2.4-fold increase over that found in aqueous solution.

320
Determination of Some Lanthanide Elements in Apatites by Instrumental Neutron Activation Analysis.
E. Steinnes (Kjeller Res. Estab., Kjeller, Norway).
Kjeller Rep., No. KR-120, 7 pp. (1967).
CA 69, 15808.
The concentrations of La, Sm, Eu, and Dy in six apatites from various localities were determined by neutron activation and γ-spectrometry. The γ-activity was measured by a NaI detector. Results are accurate to ± 10%. Three types of systematic error are discussed.

321
Indirect Ultraviolet Spectrophotometric Determination of Vanadium Utilizing Molybdovanadophosphoric Acid.
Robert Jakubiec and D. F. Boltz (Wayne State Univ., Detroit, Mich.).
Anal. Chem. 40 (2), 446-9 (Feb. 1968).
Eight samples, each containing 0.48 ppm of V, gave a mean absorbance value of 0.422 at 288 mμ. The standard deviation was 0.0045 absorbance unit, or relative standard deviation of 1.06%. About 40 min are required for each determination.

SEE ALSO the following numbered abstracts in other sections: 73, 113, 291, 394, 429, 486.

SOIL ANALYSIS

322
Soil Tests for Phosphorus Fertilizer Requirements.
J. D. Colwell.
J. Aust. Inst. Agr. Sci. 33 (4), 289-95 (Dec. 1967).
A variety of soil tests for P based on the simple extraction of a soil with a chemical solution is illustrated. All extract a fraction of the total soil P by dissolution, anion exchange, or complexing displacement, and this fraction is supposedly related to that available to plants. Plant response to P fertilizer is determined not only by P concentration in the soil solution and P reserves in equilibrium with this phase, but also by soil properties such as P sorption capacity, pH, other nutrients, profile form, and profile distribution of these properties, rainfall, temperature, etc. The recent introduction of computer facilities makes practicable for the first time multivalent calibration of all such factors to plant response to P, and they can be regarded as P tests. It is suggested that the next advances is soil testing for P and other nutrients will come from the development of simultaneous test calibrations covering many of these factors. (1 table, 39 ref)

323
Comparisons of Five Soil-Testing Methods for Phosphorus Determination.
Eugen Barkoff and Lars Ohlander (Agr. Res. Center, Dep. Soil Sci., Tikkurila, Finland).
Ann. Agr. Fenn. 6 (2-3), 97-100 (1967).
CA 69, 9916.
The following methods were compared: ion-exchange with Dowex 50 (Na^+) and extraction with pH 4.65 HOAc-NH_4OAc buffer, pH 3.75 NH_4OAc-lactate buffer, pH 7 NH_4F solution, and 0.2*N* H_2SO_4. The best correlation for mineral and organic soils was between the HOAc-NH_4OAc buffer and the NH_4F solution, and the former gave better indication of crop-available P. Factors affecting the results are discussed.

324
Comparison of Radiometric and Colorimetric Methods for the Study of Phosphate Retention and Transformation in Soil.
H. W. Fassbender and K. Igue (Inst. Interamericano Ciencias Agricolas OEA, Turrialba, Costa Rica).
Turrialba 17 (3), 284-7 (1967) (Span).
CA 68, 21230.
Phosphate retention and the form in which the added P is retained by 10 Costa Rican soils was determined using a colorimetric and a tracer technique. The retention varied from 29.9-93.6% when determined colorimetrically and from 26.2-94.2% when determined using ^{32}P. The *N* NH_4Cl-soluble phosphates varied from 0.8-23.6% of the retained P using colorimetry and from 0.8-22.8% using the tracer method. The Al phosphates determined by colorimetry were 54.6-85.7% and by the tracer technique 45.0-77.7%. For Fe phosphates the colorimetric values were 9.0-23.8% and the tracer values were 11.4-35.2%. The Ca phosphates determined by colorimetry varied from 3.5-9.1% and those determined by a tracer from 0.7-3.8% (no significant correlation). Average P recovery was 99% using the tracer method.

325
Anion Exchange Resin as a Means of Assessing Soil Phosphate Status: A Laboratory Technique.
J. Hislop and I. J. Cooke (Levington Res. Sta., Ipswich, England).
Soil Sci. 105 (1), 8-11 (Jan. 1968).
Available P is extracted by shaking 2 ml (vol measurement) of soil with 5 ml of De Acidite FF 510 exchange resin and 100 ml of distilled H_2O for 16 hr at 25°. By using a resin with a particle size >0.5 mm and grinding the soil to a smaller size, the two can be separated on a 0.5-mm filter. Phosphorus is leached from the resin with Na_2SO_4 and determined in the leachate. The method correlates well with 1% citric acid and Olsen's bicarbonate extraction methods on acid soils and with the latter method only on calcareous soils. The resin technique reflects both capacity and intensity/kinetic factors of P status. In agricultural soils with low P levels, the capacity factor is more prominent in the test; for greenhouse soils, the intensity/kinetic component primarily is measured. Altering shaking time shifts the test results to emphasize one or the other of the two components of soil P status.

326
Application of Microprobe Analysis to the Study of Phosphorus in Soils.
R. H. Qureshi, et al (Univ. Coll. North Wales, Bangor).
Nature 221 (5186), 1142-3 (Mar. 22, 1969).
Electron microprobe analysis (L. S. Birks, Electron Probe Micro-analysis, *Interscience*, 1963) was applied to a qualitative study of P distribution in thin sections of soil from a number of profiles. The features studied included a decomposing root section with organic matter diffusing out radially some 100 microns to produce a brown stain visible in thin section by transmitted light. The P concentration was highest near the root margin, where it coincided with a minor Fe peak, and then decreased outward through the stained soil matrix. Another feature studied was preferential association of P with

Fe in a complex Fe-Mn concretion. Under normal soil pH conditions ferric hydroxide develops a positive charge and hydrated manganese dioxide a negative charge which results in selective (chemi-) sorption of phosphate anions on the former. Ordinary soil analysis methods involve destruction of the soil fabric by drying, sieving, and sampling Microprobe analysis does not destroy the soil fabric and can therefore provide valuable information about spatial distribution and mode of occurrence of elements such as P within soil fabric.

327

Applications of Anion Exchange Paper in Soil Phosphorus Studies.

A. G. Sinclair (Invermay Agr. Res. Center, Mosgiel, New Zealand).

Soil Sci. 112 (3), 167-72 (Sept. 1971).

Anion exchange paper was used to extract phosphate by direct contact with wet soil. The phosphate, immobilized on the paper, was reacted with molybdate and reducing solutions to produce phosphomolybdate blue in a pattern corresponding to the distribution of phosphate at the contact surface. The technique was used to measure labile phosphate distribution in soil profiles, to detect phosphate particles in soil and to assess soil phosphate status.

328

Correlation of Soil Test Values for Availabile Phosphorus by Various Methods with the Yield of Rice.

J. D. Naphade and M. V. Bapat.

Riso 17 (4), 303-8 (Dec. 1968).

The amount of available P extracted depends upon the nature and pH of the extracting solution (acidic, alkaline, or buffer), the soil, extractant ratio used, and the duration of extraction. Methods employing acid extractants, narrow soil:water ratio, and short duration of extraction (Spurway's, Jacquet and Le Nir's, and Bray's P_2) gave low value for P. Methods employing buffer extractants (Truog's and Morgan's) gave high value for P Olsen's method employing alkaline extraction gave the best correlation with the response of rice to P fertilization; Bray's P_1 method for absorbed P gave the next best results.

329

Evaluation of Various Methods for the Estimation of Plant Available Phosphorus in the Soils of Caspian Sea Area (Iran).

B. Kacar, F. Didehvar, and E. Shokravi.

Yearbook Faculty Agr. Univ. Ankara Turkey 7, 140-50 (1967).

Sixty-two soil samples, collected from field tests with rice on different land type areas of Caspian Sea, were used to evaluate six different methods for the estimation of plant available P. The soil samples varied in pH from 5.4–7.7. In the order of decreasing precision of the estimating the available P the methods are as follows: Bray and Kurtz No. 2 > Kacar > Bray and Kurtz No. 1 > Olsen, *et al.* > Bingham > "E" valve.

330

Analytical Technique of the Pw Method, Used for the Assessment of the Phosphate Status of Arable Soils in the Netherlands.

H. A. Sissingh [Inst. Soil Fertility, Haren (Groningen), The Netherlands].

Plant Soil 34 (2), 483-6 (Apr. 1971).

The phosphate status of soils has been determined by a new analytical technique that used aqueous extraction at a 60:1 water:soil ratio. Moistening the soil 22 hr prior to P extraction is a novel feature of the procedure. To a measured sample (1.20 ml) of dried, sieved soil in a 125-ml flask, add 2 ml demineralized H_2O, shake by hand, and let stand for 22 hr at 20°. Add 70 ml demineralized H_2O at 20°, shake mechanically for 1 hr, and filter. To 20 ml of Murphy and Riley's potassium antimonyl tartrate colorimetric solution, add 20 ml of the clear filtrate, mix, and measure absorbance at 882 nm. Absorbance remains constant for 12 hr. As^{+5} and Sn^{+4} interfere but As^{+5} can be reduced to As^{+3} and wavelength for measuring absorbance can be changed to 720 nm when Sn^{+4} interferes. (See *FA 4*, 1424)

331

The Determination of Total Phosphorus in Soils and Parent Materials.

J. K. Syers, J. D. H. Williams, and T. W. Walker.

New Zealand J. Agr. Res. 11 (4), 757-62 (Nov. 1968).

The amounts of total P extracted by Na_2CO_3 fusion and by HF and $HClO_4$ digestion procedures from selected New Zealand soils and parent materials were compared. It is suggested that Na_2CO_3 fusion is the most reliable procedure. Digestion with $HClO_4$ gave low results with strongly weathered materials and with samples which contained apatite inclusions within constituent primary minerals, whereas digestion with HF gave slightly low results only with samples which contained included apatite. Incomplete extraction of P by $HClO_4$ and HF digestion procedures from samples which contained apatite inclusions was ascribed to the partial resistance to attack of the host minerals. Because of occlusion within highly crystalline Fe and Al oxides, secondary inorganic P in strongly weathered soils was less readily extracted by $HClO_4$ digestion than by Na_2CO_3 fusion or HF digestion. (13 references)

332

Study of Phosphorus in Central American Soils. III. Comparison of Five Chemical Methods of Analysis of Available Phosphorus.

F. Balerdi, L. Muller, and H. W. Fassbender (Instituto Interamericano de Ciencias Agricola, Turrialba, Costa Rica).

Turrialba 18 (4), 348-60 (Oct.-Dec. 1968).

Available P was determined with Olsen, Bray 1, Mehlich, Saunder, and Egner-Riehm methods in 104 Central American soils. Of these, 75 showed predominance of Ca-phosphates and 29 of Fe- and Al-phosphates. Correlating the phosphate forms found with the available P, it appeared that the NH_4Cl soluble fraction correlated best with the Mehlich (r = 0.754) and Egner-Riehm (r = 0.745) methods. The Ca-phosphates correlated best with the Olsen and Egner-Riehm methods (r = 0.765, r = 0.682), while the Fe- and Al-phosphates correlated best with the Saunder extraction (r = 0.551, r = 0.629). The former tendencies are explained as being due to the different solubility of the phosphates in the soil. Correlations were found between the acid extraction methods. The Olsen technique correlated with the acid extractions but the one of Saunder did not correlate with the other techniques. Dry matter production and P absorption by the indicator plant, tomato, in the non-P-treated pots of the greenhouse experiment gave the following linear correlation coefficients: Egner-Riehm, 0.947 > Olsen 0.870 > Bray 1 0.856 > Mehlich (Carolina del Norte) 0.848 > Saunder 0.340. The statistical data are given for the individual soil groups. It is suggested to use the Egner-Riehm and the Olsen methods in calibration experiments to be undertaken in Central America. (31 references) (For Part II, See *FA 2*, 895)

333

Effect of Different Phosphorus Fertilizers and of the

Carbonate Content of Soil on Results of Available Soil Phosphorus Determinations by Means of Various Extractants.

R. Bucher (Landw. UntersAmt, Wurzburg, German Federal Republic).

Sonderh. Landw. Forsch. 25 (1), 113-27 (1970) (Ger).

Soils Fert. 34, 2010.

The extractants used were (A) double lactate (Egner-Riehm), (B) ammonium lactate + acetic acid (Egner-Riehm-Domingo), (C) calcium lactate (Schuller), (D) $NaHCO_3$ (Olsen), (E) 2-hr shaking with water, and (F) 0.3 *N* NH_4F + 0.025 *N* HCl. The P status of CO_3-free soils was best characterized by (B), followed by (A), (F), and (C); extraction of P in soils that contain CO_3 decreased in the order: (F)>(A)>(B)>(C), and the latter was best suited for soils of pH >6. For insoluble (apatitic) phosphates, (A) and (B) were the most suitable, followed by (C) and (F), while (D) and (E) were quite unsuitable. The extractant (D) was most suitable for CO_3-rich soils; extraction with (E) gave poor indication of fertilizer P remaining in the soil, and yielded for neutral loessic soils values similar to those obtained with (D).

334

The Effect of Certain Types of Fertilizers on Results of P_2O_5 Determinations in Soil.

E Wagner (Landw. Vers St. Annenhof, Hamburg-Sasel, German Federal Republic).

Sonderh. Landw. Forsch. 25 (1), 104-12 (1970) (Ger).

Soils Fert. 34, 2009.

The different methods of determining available P in soil comprised: (A) Neubauer, (B) doublelactate (Egner-Riehm), (C) calcium-lactate, (D) Olsen, and (E) water extraction. High P values were obtained with (B) where soft rock phosphates were applied, and with (D) where superphosphate, basic slag, sintered phosphates, and soft rock phosphates (in this decreasing order of importance) were applied. Extraction by (C) did not dissolve P from soft rock phosphates. Values obtained with (D) were low and were similar to those obtained with (A) or (E); extraction by (B) overestimated P where soft rock phosphates were applied, but not with other P fertilizers (including treated rock phosphate containing amounts of water-soluble P).

335

Correlations Between the Results Obtained from Twenty Methods for Determining the Phosphorus Requirements of Soils and the Effect of Soil pH on the Value for Phosphorus Content Obtained.

E. Rauterberg and D. Ali Dervish (Tech. Univ. Berlin, Berlin, Germany).

Z. Pflanzenernaehr. Bodenk. 118 (2), 85-100 (1967) (Ger).

Eighteen chemical and two biological methods were compared on 30 soils. Soil pH had a considerable effect on the results obtained. Correlation coefficients were calculated for the relations of each method with the other 19, separately for soils with pH <5 and for soils with pH >5. Results from soils with pH > 5 from different methods produced similar values for P requirements of a soil.

336

Chemical and Isotopic Methods for Determinination of Soil Phosphates Readily Available to Plants.

Stanislaw Moskal (SGGW, Warsaw, Poland).

Rocz. Nauk Roln., Ser. A 96 (1), 57-82 (1969) (Pol).

CA 73, 87062.

Pot tests with oats and corn were made on 42 soil samples from Warsaw and Lodz districts, involving 29 samples of podzol, 11 chernozem, and two brown soils, in order to evaluate the effectiveness of isotopic and chemical methods for the determination of available P. Analyses conducted by isotopic methods were compared to those by chemical means, especially with the Egner and Egner-Riehm methods. The results were compared with amounts of P taken up by plants as well as with the reaction of plants to P fertilization. Isotopic methods did not give a better estimation of available P than chemical methods, and did not provide more accurate predictions of increased crop yields by the addition of P in the first yr. Isotopic methods showed much larger amounts of available P in the soil than chemical methods.

337

Phosphorus Soil Tests Based Upon Correlations with Inorganic Phosphorus Fractions and Greenhouse Tests.

N. P. Datta and M. S. Khera (Indian Agr. Res. Inst., New Delhi, India).

J. Indian Soc. Soil Sci. 17 (2), 191-6 (June 1969).

Seventeen methods for determining available P in 22 soils, neutral to alkaline in reaction were evaluated. Extractants–0.3*N* NaOH-0.5*N* $Na_2C_2O_4$, 0.025*N* HCl-0.03*N* NH_4F (1:2 soil solution ratio), 0.5*M* NH_4HCO_3 (pH 7.8) (introduced in this investigation), and 0.5*M* $NaHCO_3$, (pH 8.5) gave highly significant correlation coefficients with P-uptake values by tomato plants. Of the various soil solution ratios investigated in case of 0.025*N* HCl-0.03*N* NH_4F solution, that of using 1:2 soil solution ratio gave the highest correlation, thus proving satisfactory use of this solution for measuring available P in these soils. Fe-P and Al-P explained most of the variations in available P in these soils, although Ca-P was the most abundant fraction present. Fe-P and Al-P were found most significantly correlated with P-uptake by plants/percent yield, as well as with the amounts of soil P extracted by the methods found most satisfactory, thus explaining the basis of their performance.

338

A Method for Determining Mineral Forms of Soil Phosphate.

K. Ye. Ginzburg and L. S. Lebedeva.

Agrokhimiya, No. 2, 125-35 (1971) (Russ).

Sov. Soil Sci. 3 (1), 108-19 (Jan.-Feb. 1971).

A method is described for the determination of mineral forms of soil phosphate. The basic Ca and Mg phosphates are isolated from the original soil, then the fraction of Al and Fe phosphates, and finally the fraction of high-basic Ca phosphate (phosphorite and apatite). The soil sample is treated with several consecutive solvents: (1) 1% $(NH_4)_2SO_4$ + 0.25% $(NH_4)_2MoO_4$, pH about 4.8, (2) 0.5 *N* CH_3COOH + 0.25% $(NH_4)_2MoO_4$, pH about 4.2; (3) 0.5 *N* NH_4F, pH 8.5; (4) 0.1 *N* NaOH, and (5) 0.5 *N* H_2SO_4. The shortcomings in the Chang-Jackson method are overcome in this method by isolating mineral phosphates from soil more fully and in a purer form. The method is recommended for study of the phosphate regime of different soil groups.

339

A Suitable Chemical Method for the Determination of Available Phosphorus for Paddy Growing Soils of Burma.

Myo Thant and Khin Win (Agr. Res. Inst., Gyogon, Burma).

Union Burma J. Life Sci. 1 (1), 4-11 (1968).

Biol. Abstr. 51, 69136.

The isotopic method and five chemical extraction methods were used. The results obtained by each chemical method were correlated against that of the isotopic method. Correlation coefficient analysis showed highest value for Olsen's method for both acid and alkaline soils. Soil samples having

approximately the same amount of organic matter, exchangeable K, pH, and varying amount of available P as determined by Olsen's method were sorted out for further appraisal. The yields from the control plots of these soils were correlated with available P and the comparison showed a close relationship.

340

An Evaluation of Several Soil Tests for Predicting Wheat Yield Response to Superphosphate in Victoria.

J. V. Mullaly, J.K.M. Skene, and R. Jardine (Dep. Agr. Melbourne, Victoria, Australia).

Aust. J. Exp. Agr. Animal Husb. 8 (30), 52-8 (1968).

Superphosphate is applied to 98% of the wheat sown in Victoria. A soil test is needed for predicting rates of P application. Field experiments with superphosphate were conducted in the three main wheat areas (Mallee, Wimmera, and Northern) from 1951 to 1965. Soil samples (0-6 in.) from the experiments were extracted for available P by various methods. Extractants used were 2.5% acetic acid containing 8-hydroxyquinoline, 0.1*N* NaOH (organic P and organic + alkali P), and a modified Olsen bicarbonate extract. No single test was of much practical value for the wide range of soils included in the 157 experiments. The bicarbonate method was superior to the others but a maximum of only 26% of the yield variability could be explained by this form of P.

341

The Estimation of Available Soil Nitrogen.

R. R. Storrier (Dep. Agr., Wagga Wagga, Australia).

J. Aust. Inst. Agr. Sci. 33 (4), 278-83 (Dec. 1967).

The increasing importance of fertilizer N in Australian agriculture is shown by a two- to three-fold increase in usage over the last 5 yr. A brief outline of the chemistry of soil N is given with a discussion of the various method which have been used to measure available soil N. Some observations are noted on the state of N soil testing in Australia. (45 ref)

342

An Aerometric Apparatus for the Evaluation of Gaseous Nitrogen Transformations in Field Soils.

J. W. McGarity (Univ. New England, Armidale, N.S.W., Australia) and R. D. Hauck (Tennessee Valley Authority, Muscle Shoals, Ala.).

Soil Sci. 108 (5), 335-44 (Nov. 1969).

An aerometric apparatus is described which fulfills many of the requirements needed for evaluation of specific reactions involving gaseous products in natural soils in an environment close to that prevailing in the field. Control of O_2 levels has been achieved in a range which is near that of normal atmosphere, CO_2 levels have been kept close to those in normal surface soils, and soil temperature range has approximated that found in nearby field soils. Minor fluctuations in O_2 levels had no measurable influence on general biological activity. Other environmental parameters may be controlled by further modifications of the apparatus. Preliminary tests indicate that the apparatus makes possible limited estimates of total gas evolution from soil and rates of gas diffusion in soil. The equipment can also serve as a respirometer and anaerobic incubator, giving it added flexibility.

343

Automated Determination of Ammonium and Nitrate in Soil Extracts by Distillation.

J. Keay and P. M. A. Menage (Western Australia Lab., Wembley, Western Australia).

Analyst (London) 95 (1129), 379-82 (Apr. 1970).

Automated procedures for the determination of ammonium and nitrate in soil extracts are described. Distillation of the extract with MgO with subsequent determination of NH_3 by the automated indophenol method, is used for ammonium. For ammonium plus nitrate, the nitrate is reduced with titanium (III) sulfate during distillation with MgO and NH_3 determined as before. The method has wider application, for example, to the analysis of fertilizers and water samples.

344

Correlation Studies of Soil Tests for Available Nitrogen and Response of Paddy on Certain Soils of Uttar Pradesh.

R. M. Singh and B. R. Tripathi (Raja Balwant Singh College, Bichpuri, Agra, India).

J. Indian Soc. Soil Sci. 18 (3), 313-18 (Sept. 1970).

Three soil test methods for available N were compared. The alkaline potassium permanganate method was found to be the best as it showed the highest correlation with N uptake by paddy plants in field survey and greenhouse test. The available N content by this method was also highly correlated with percent yield response. The correlation coefficient between plant N (forty days after transplanting) and final yield of crop was positive and highly significant. Available N in soils by alkaline potassium permanganate method at transplanting time may well be utilized for fertilizer recommendations. Other methods evaluated were organic C in soils and mineral N (NH_4 + NO_3) in soils.

345

Sensitivity of the Nitrate-Ion Membrane Electrode in Various Soil Extracts.

A. R. Mack and R. B. Sanderson (Canada Dep. Agr., Ottawa, Ontario).

Can. J. Soil Sci. 51 (1), 95-104 (Feb. 1971).

Measurement of NO_3 concentration in a series of soils with a specific-ion membrane electrode varied with the amount of dispersed colloidal material present in the soil extract. Nitrate-N values with the membrane electrode were in good agreement with those by colorimetric (Phenoldisulfonic acid, PDS) and reduction-diffusion (NO_3 to NH_3) methods for filtered or flocculated water extracts, and for filtered or unfiltered salt extracts (saturated $CaSO_4$). In water extracts having dispersed colloidal material (for example, unfiltered or unflocculated) the measurements were higher (1 to 6 ppm N) with the membrane electrode than by the other two methods, and the discrepancy increased generally with the clay content ($<2\ \mu$ size) of the soil. Removal of the dispersed material by filtration (no. 42 Whatman), addition of a polyacrylamide flocculating agent, or extraction with a salt solution reduced the discrepancy. Improved reproducibility was obtained by adjusting the meter to a standard NO_3 concentration (for example, 100 mV with a 10-ppm standard) and using a larger aliquot of the extract at low concentrations (100 ml for concentration < 2 ppm N). The standard deviation for measurements made on a standard solution of 1 to 100 ppm N repeated over a period of several months was 1.74 mV.

346

Nitrate Determination in Soil Extracts with the Nitrate Electrode.

Asbjoern Oeien and A. R. Selmer-Olsen (Agr. Coll. Norway, Vollebekk, Norway).

Analyst (London) 94 (1123), 888 94 (1969).

Five-g soil samples were shaken for one hr with 100 ml extracting solution, (H_2O, 0.02 *N* $CuSO_4$, and 2 *N* KCl) and the extracts were stored in polyethylene bottles at room

temperature. The nitrate concentration was measured with a nitrate-specific ion electrode and compared with analysis by two colorimetric methods. The stability of soil extracts, the influence of variation in the ratio of g soil/ml extracting agent and in shaking time, interferences caused by ionic strength and anions, accuracy, and reproducibility were evaluated. Nitrate determination with the electrode was reliable both for soil extracts and suspensions. The determinations could be carried out in the same way as pH determinations. Interferences were not serious and the relative standard deviation was ~2%. As little as 9 lb nitrate N/acre could be determined.

347

Nitrate Ion Electrode Method for Soil Nitrate Nitrogen Determination.

R. J. K. Myers and E. A. Paul (Univ. Saskatchewan, Saskatoon, Canada).

Can. J. Soil Sci. 48 (3), 369-71 (1968).

A nitrate ion electrode, together with a calomel reference electrode, and a pH meter with an expanded millivolt scale were used in the determination of soil nitrate N. Soils were shaken with distilled water (1:5 or 1:10 soil-water ratio) for 30 minutes. About 20 ml of supernatant was transferred to a 50-ml beaker, the electrodes were immersed, the mixture was stirred by a laboratory stirrer and the potential in millivolts read 15-30 seconds after drift had ceased. A calibration curve was obtained using standard nitrate solutions. Close agreement was found between soil nitrate by the nitrate electrode and phenol-disulfonic acid methods. The major factor affecting the accuracy of the method was interference by other anions. The technique appears to be suitable for soil testing and routine laboratory analysis of nitrate.

348

Use of the Nitrate Electrode for Determination of Nitrates in Soils.

A. B. Onken and H. D. Sunderman (Texas A&M Univ., Lubbock, Texas).

Communication Soil Sci. Plant Analysis 1 (3), 155-61 (May 1970).

A procedure for the rapid and accurate determination of water-extractable soil nitrates is described. Use of this procedure resulted in quantitative recovery of nitrates added to soil. Reproducibility of results was high, with nitrate-N in 40 soil samples determined on successive days differing by a maximum of 4 ppm with 33 determinations differing by 2 ppm or less. Comparison with a phenoldisulfonic acid method on 513 soil samples had a maximum difference of 7 ppm with a majority of determinations having a difference of 4 ppm or less.

349

Chemical and Isotopic Determination of Small Quantities of Nitrogen in the Soil.

G. Guiraud and Y. Berlier (C.E.N., Cadarache, Belg.).

Chim. Anal. (Paris) 50 (7), 379-84 (1968) (Fr.).

CA 70, 2743.

To determine N and ^{15}N in the soil, first determine total N content by the Kjeldahl method. Then acidify the sample and reduce the NH_4^+ to N_2 with NaOBr as described by D. Rittenberg (1948) and B. D. Sprinson and D. Rittenberg (1949). Determine ^{15}N content of the gas with a mass spectrograph at room temperature: percentage excess ^{15}N = $100\ R/(2 + R)$ where R is the ratio of the peaks of mass 29 3% precision.

350

Automatic Determination of Nitrogen as Indophenol Green in Soils and Plants.

F. Holz and H. Kremers (Landwirtsch. Forsch. Hanninghof, Ruhr-Stickstoff A.-G., West Germany).

Landwirt. Forsch., Sonderh. 26 (1), 177-91 (1971) (Ger).

CA 76, 58119.

Automated methods for the determination of N in plants and of total N in soils were developed using the technicon autoanalyzer. Flow diagram for the automatic determination of N in Kjeldahl digests of plant matter is presented. The rate is 40 samples/hr. The relative standard deviation for the range 1.8-4.8% was 0.32%. The results agree well with those obtained by the distribution method. The determination of N in soils is carried out following the method of Foerster. The addition of Na pentacyanonitrosylferrate increased 10-fold the sensitivity of the determination. The range of concentrations in soils was from 0 to 0.5%. The rate of determination is also 40 samples/hr. For concentrations in soils ranging from 0.15 to 0.35 of the relative standard deviation was 0.81%. Agreement with results obtained by the distillation method is good. The concentrate values are automatically printed by the auxiliary equipment.

351

Use of the Coleman Model 29A Analyzer for Total Nitrogen Analysis of Soils.

D. R. Kenney and J. M. Bremner (Iowa State Univ., Ames).

Soil Sci. 104 (5), 358-63 (Nov. 1967).

Studies to evaluate an automated Dumas procedure (Coleman Model 29A Nitrogen Analyzer) for determination of total soil N showed that maximal total N values were obtained by a procedure involving combustion of soil mixed with wire-form CuO-Pt catalyst at 940° for 12.6 min in a tube filled with this catalyst. This procedure permitted analysis of up to 3 g of mineral soil containing up to 0.4 ml of water and gave almost quantitative recovery of nitrate N and nitrite N added to soil. A comparison of the results obtained in total N analysis of soils by this Dumas procedure and by Kjeldahl and HF-Kjeldahl techniques showed that, when applied to surface samples of mineral and organic soils, these methods gave practically identical results whereas their results with two subsoils containing large amounts of fixed ammonium were in the order HF-Kjeldahl > Dumas > Kjeldahl. The findings reported indicate that total N in most soils can be determined satisfactorily by Dumas or Kjeldahl methods but that these methods do not give complete recovery of native fixed ammonium N in some soils containing high levels of fixed N.

352

Premixed Digestion Salts for Kjeldahl Determination of Total Nitrogen in Selected Forest Soils.

B. C. Blackmon (U.S. Dep. Agr., Stoneville, Miss.).

Commun. Soil Sci. Plant Anal. 2 (3), 201-5 (1971).

Soil analyses for total N by a standard Kjeldahl procedure and a modified method were compared. In the modified method premixed salts (9.9 g K_2SO_4, 0.4 g HgO, and 0.08 g $CuSO_4$) were substituted for the Na_2SO_4 plus catalyst. The amounts of N detected by the two procedures were closely correlated ($r^2 = 0.983$). The modified method is time saving, safer since there is no direct exposure to toxic elements, and is equally reliable for total N determination in forest soil of the Midsouth.

353

Rapid Analysis of Soil Nitrate with Chromotropic Acid.

J. R. Sims and G. D. Jackson (Montana Agr. Exp. Sta., Bozeman).

Soil Sci. Soc. Amer. Proc. 35 (4), 603-6 (July-Aug. 1971).

Colorimetric analysis of nitrate in soil extracts using chromotropic acid (CTA) was studied and compared to the results obtained by the phenoldisulfonic acid (PDA) method. Extracting solutions of 0 5 *M* $MgSO_4$, saturated $CaSO_4$, and a 0 2% $Ca(OH)_2$ suspension were investigated. The three extractants were equally effective in recovering NO_3^-; however, the clearest extracts were obtained with $Ca(OH)_2$. Soil-to-extractant ratios of 1:2.5, 1:5, and 1:10 were studied. The 1:5 ratio effectively extracted NO_3^- and resulted in appropriate NO_3^- concentrations for color development. A shaking time of 15 min was adequate to extract a maximum of NO_3^-. In a NO_3^-–N recovery study, equivalent amounts of NO_3^- were recovered by the CTA and PDA methods. Results of nitrate analyses by the two methods were significantly correlated (p = .01). Nitrate determined by the chromotropic acid procedure was positively correlated (p = .05) with the yield of winter wheat (*Triticum aestivum* L.) and was negatively correlated (p = .01) with response of winter wheat to N fertilizer additions. The new procedure has the advantages of rapidity, simplicity, sensitivity, and relative freedom from interference.

354

Extraction of Soil Organic Nitrogen by Autoclaving in Water: III Diffusible Ammonia, an Index of Soil Nitrogen Availability.

G. Stanford and W. H. Demar (U. S. Dep Agr., Beltsville, Maryland).

Soil Sci. 109 (3), 190-6 (Mar. 1970).

Thirteen soils of widely differing N mineralization capacity were extracted by autoclaving in 0.01 *M* $CaCl_2$. The amounts of diffusible NH_3-N in the extracts, as determined by a modified Conway method, correlated as highly with N mineralized by the soils (r = 0.95) as did alkali-distillable NH_3-N released from the extracts by boiling. In many laboratories, the diffusible component of the distillable N fraction can be determined more conveniently and more rapidly than total distillable N. As an index of soil N availability, the diffusible N fraction is more reliable than the nondistillable or total N extracted. Supplementary studies with glucosamine or chitin showed these substances to be unstable toward autoclaving. Thus, the method used in fractionating the distillable NH_3-N of acid hydrolyzates of soils is not applicable in characterizing boiling water extracts. Hexose sugars in the extracts, expressed as "glucose-equivalent", correlated highly with NaOH-distillable or total N (distillable plus nondistillable), but correlated to a lesser degree with N mineralization than did alkali-diffusible or distillable NH_3-N.

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Interference of CO_2 in Measuring Volatile Loss of NH_3 from Soil.

H. P. Borthakur and N. N. Mahumdar (Coll. Agr. Jorhat, India).

Indian J. Agr. Chem. 3 83-6 (1970).

Soils Fert 34, 4644.

Results of experiments in which NH_3 and CO_2 were generated and absorbed in $Ba(OH)_2$, H_2SO_4, or H_3BO_3 showed that the best procedure for measuring volatile NH_3 loss involved absorption of CO_2 in 0.2*N* $Ba(OH)_2$ solution and absorption of NH_3 in 2% boric acid solution.

356

Determination of the Partial Pressure of Ammonia in Soil Air.

R. W. Blanchar (International Minerals & Chemical Corp., Libertyville, Ill.).

Soil Sci. Soc. Am., Proc. 31 (6), 791-5 (Nov.-Dec. 1967).

A method for determining partial pressures of NH_3 from 0.01 to 0.50 mm Hg in soil air was studied. Soil samples which had been treated with various amounts of ammonium hydroxide were placed in 1-l. polyethylene bottles and allowed to equilibrate. A known vol of air from the bottle was removed by partially compressing the bottle with a press. The air was bubbled through 0.1*N* HCl and the ammonium content of the acid determined by the Nessler reaction. The partial pressure of NH_3 (P_{NH_3}) was calculated from the ideal gas law equation. The method gives a reliable estimate of the partial pressure of NH_3 in soil air. It was shown that the P_{NH_3} of a sample placed in the polyethylene bottle could be determined after a 1-hr equilibration period. Samples which were sealed in the polyethylene bottles for 48 hr had lower P_{NH_3} and higher P_{CO_2} values than samples placed in the bottles for only 1 hr. Reduced P_{NH_3} values in bottles which had been sealed for 1 day or more were attributed to pH reduction due to CO_2 accumulation. Germination of corn seeds (*Zea mays* L.) was damaged when the initial P_{NH_3} value was 0.156 and final values were between 0.077 and 0.104 mm Hg. The germination of corn seeds was not reduced when initial P_{NH_3} values were 0.091 and final values were 0.067 and 0.048 mm Hg. (16 ref)

357

Significance of Errors in ^{15}N Measurements in Soil: Plant Research.

A. E. Martin and P. J. Ross (Cunningham Laboratory, Brisbane, Australia).

Trans. Int. Cong. Soil Sci., 9th, 3, 521-9 (1968).

Many procedures for ^{15}N analysis have been published but most of them lack the adaptability required for tracer studies in plant research. Different kinds of tracer experiments may require different approaches in mass-spectrometric technique, and each technique has its own complement of potential errors. The main sources of error (such as instrumental, contamination by air and other substances, and memory effects) are reviewed, and discussed in relation to three examples commonly encountered in this field of study: highly enriched samples, samples with a ^{15}N abundance close to the natural value, and small samples such as those obtained from soil extracts. The importance of providing a satisfactory estimate of error is emphasized; this can only be achieved by submitting ^{15}N standards at random for isotopic analysis during the course of analyzing a large batch of experimental samples. It is shown that, under routine operating conditions, a coefficient of variation of 1-2% can be expected for samples containing about 1 atom % excess ^{15}N.

358

Soil Testing for Potassium.

I. A. Vimpany (Dep. Agr., Rydalmere, Australia).

J. Aust. Inst. Agr. Sci. 33 (4), 296-301 (Dec. 1967).

A variety of chemical tests intended to extract and measure forms of K available to plants has been proposed. Exchangeable K is considered to be the main source of available K in most soils. Not all exchangeable K is available to plants, and a number of factors can influence its availability. K is mobile. The mobility of K increases the difficulty of soil sampling for K tests. Soil samples taken up to 3 in. in depth are satisfactory for P tests, but 6 in. samples may be needed for K because of its greater downward movement in the soil. Nonexchangeable available K (N.E.A.P.) to plants has been demonstrated but it

is difficult to determine its availability by chemical means. Research on the development of a suitable method for the determination of nonexchangeable available K is being carried out. The level of N.E.A.P. changes very slowly even where soils have been exploited. It would need to be determined only at infrequent intervals, for example, every 10 yr. Each soil test will require individual interpretation. Many factors other than the level of soil K such as paddock history, grazing measurement, cropping economics, and application of other fertilizers will affect the final fertilizers recommendation. (24 ref)

359

Comparison of Different Extractants for Determining Exchangeable Ammonium in the Soils of the Cauca Valley.

Mario Blasco L. and A. H. Cornfield (Suelos Quim., Fac. Agron., Palmira, Colombia).

Acta Agron. (Palmira, Colombia) 17 (1-2), 1-12 (1967) (Span).

CA 68, 28776.

For the determination of NH_4^+ in soils, 5 g samples were extracted for 1, 12, or 24 hr with 100 ml of 0.5*N* or 1.0*N* solutions of KCl, $CaCl_2$, KOAc, $Ca(OAc)_2$, and *N* KCl adjusted to pH 1.0 with HCl. The extracted mixtures wre filtered and mixed with either 7.5*N* NaOH, borate buffer, or MgO, and then distilled for 30 min. The distillate was recovered in 15 ml of 1% H_3BO_3 and titrated against HCl. Solutions of Ca salts always extracted more NH_4^+ than did the corresponding K^+ salts. $CaCl_2$ and KCl nearly always extracted more NH_4^+ than did $Ca(OAc)_2$ and KOAc, respectively. Potassium chloride acidified to pH 1.0 extracted more than did unacidified KCl. Distillation of the extracts with NaOH gave the highest NH_3 values, with borate buffer and MgO giving lower values. The best extraction was with *N* $CaCl_2$, and distilling from NaOH.

360

Use of the Stanford-De Ment Method of Extracting Potassium from the Soil.

J. Quemener and D. Rolland (Alsace Potash Commercial Co., Paris, France).

Ann. Agron. 21 (6), 819-44 (1970) (Fr).

An adaptation of the Stanford-De Ment method is proposed, based on increasing the duration of plant-soil contact up to 20 days and the use of soil diluted by three times its own wt of sand (50 g soil/pot), which, in the environmental conditions imposed, makes it possible to extract up to 1000 ppm of K. In these conditions, however, the plant material produced is no longer entirely independent of the richness of the substratum, in which a second extraction can be carried out with a fresh batch of deficient plants. The scatter of the results appears to depend on the type of soil, as does the reproducibility of results from one series to another, although this seems equally to be connected with the batch of seed used. Potassium from recently applied fertilizer is easily absorbed and the method facilitates study of the breakdown of fertilizers, especially in relation to time, in different types of soil. Improvements that should be studied, particularly those concerned with the rhythm of water supply, are suggested.

361

An Evaluation of Soil Analysis Methods for Nitrogen, Phosphorus, and Potassium, Using Banana.

D. Walmsley, I. T. Twyford, and I. S. Cornforth (Univ. West Indies, Trinidad, West India).

Trop Agr. 48 (2), 141-55 (Apr. 1971).

The value of soil analytical tests for N (seven methods), P (ten methods), and K (six methods) was assessed by correlating test values with yield data from 32 banana fertilizer tests on the main agricultural soils of the Windward Islands. Methods were selected on their ability to predict crop response to fertilizer additions by grouping the soils into 'adequate' and 'deficient' classes. The anaerobic incubation method was best for N but was only able to predict responses correctly 66 times out of 100. Predictions from soil base saturation were better than any of the N tests tried; a critical value of 90% base saturation gave 78% correct predictions of response. A modified Bondorff method (1 g soil shaken for 16.5 hr with 50 ml 0.2 *N* H_2SO_4) is recommended for soil P; this method, and also Olsen's 0.5 *M* $NaHCO_3$ extract, gave 94% correct predictions of crop response to superphosphate. The critical test value is 40 ppm P for Bondorff's method and 2.5 ppm for Olsen's. Exchangeable K removed in a 1 *N* ammonium acetate leachate is recommended for routine measurement. The critical value is 0.40 meq K/100 g soil. Morgan's acetate extract and Pratt's H_2SO_4 method gave an equally good (81% correct) estimate of crop response to potash fertilizer. The recommended methods are suggested for use in routine analysis of farmers' samples as part of an advisory service to banana growers in the Windward Islands.

362

Methods of Extracting Potassium.

F. Lucena Conde and T. Crisan') Herreo.

Ann. Edafol. Agrobiol. 30 (1-2), 137-48 (Jan.-Feb. 1971) (Span).

Eight methods of extracting available K are reviewed. The correlation among these methods gave degrees of significance ranging from less than 1% to 10%. The electrodialysis method results in significant coefficients of less than 1% with the methods Nelson I, Nelson II, Egner, Morgan, and Nehring. Extraction by exchange resins shows a significant degree of correlation with the methods of Nelson I, Nelson II, and Nehring. A critical study of each method is given.

363

Effect of Different Methods of Drying and Storing of Soil Samples on the Content of Available Phosphorus and Potassium in the Soil and its pH.

Konrad Piskula (Stacja Chem.-Roln., Olsztyn, Pol.).

Pamiet. Pulawski 42, 145-58 (1971) (Pol)

CA 75, 139705.

Samples were taken from the arable layer of six soils. After thorough mixing, samples were dried in one of four ways: (1) in cardboard boxes at room temperature until a constant wt was reached, (2) under ir irradiation at a distance of 40 cm from the source; (3) in a lab drier at 60°; (4) in cardboard boxes kept in chests and stored for 3 months in a closed room. Samples were also analyzed before drying. The method of drying and storage had very slight effect on the pH. Light soils had a slightly lower pH than the heavy soils. Exposure to ir increased the P content of the soil, and either increased or decreased the K content. Usually, increases in the average content of P were found in lab dried samples. Soil samples kept in the closed chests had a lower P content; K changes were not significant. All samples analyzed fresh had lower P and K contents. Storage counteracted the effects of drying with regard to P results, but differences in K content remained or increased. During the 5 months storage period a slight increase of available P and K was found. Drying at room temperature is recommended.

364

Simultaneous Determinations of Phosphorus, Potassium, Calcium, and Magnesium in Soil Extracts by AutoAnalyzer.

R. L. Flannery and D. K. Markus (Rutgers State Univ., New Brunswick, N. J.).
Advan. Automat. Anal., Technicon Int. Congr. 1969, 2, 29-37 (Pub. 1970).

Results of the North Carolina extraction method are compared with the NH_4OAc extraction for removal of K, Ca, and Mg and with the Bray P_1 extraction method for removal of P. It compares the AutoAnalyzer with atomic absorption instrumentation for determining K, Ca, and Mg and with manual methods for determining P. Calcium interfered in flame photometry; SO_4^{2-} interference was suppressed by addition of La to soil extracts used for determining Ca by atomic absorption. The same amounts of Ca and Mg were extracted by the various solvents, but NH_4OAc removed 50% more K and the Bray P_1 soil extractant removed more P than the North Carolina extractant.

365

A Comparison of Five Methods for Determining the Sulphur Status of New Zealand Soils.

Margery Cooper (Ruakura Agr. Research Center, Hamilton, New Zealand).
Trans., Int. Cong. Soil Sci., 9th 2, 263-71 (1968).

A preliminary report is presented on a comparison of five chemical methods for the routine determination of S status in soils. The extraction techniques compared were: (1) 0.03*M* $NaH_2PO_4 \cdot 2H_2O$ in 2*N* acetic acid, (Bardsley & Lancaster 1960); (2) 500 ppm P solution as KH_2PO_4, (Ensminger 1954); (3) 0.15% $CaCl_2$, (Williams & Steinbergs 1959); (4) 1% NaCl-Heat-soluble S, (Williams & Steinbergs 1959); and (5) 0.05*M* $NaHCO_3$ at pH 8.5, (Kilmer & Nearpass 1960). Soil S values determined by these methods were compared with results obtained in field trials that were laid down on soils with strongly contrasting parent materials and clay mineralogy and under a wide range of climatic conditions. The sodium phosphate-acetic acid reagent successfully differentiated between responsive and non-responsive soils from 49 field trials. The critical level was about 10 ppm extractable S in air-dry soil. The other methods were effective to a more limited degree.

366

An X-Ray Spectrographic Method of Determining Total Sulfur in Soil Extracts.

S. Roberts and F. E. Koehler (Oregon State Univ., Corvallis).
Soil Sci. 106 (3), 164-71 (Sept. 1968).

Soil is shaken with 5 millimolar $MgCl_2$ solution (1:2.5 ratio) for 30 min and centrifuged for clarification. A 20 ml aliquot is filtered and passed through Dowex 50 x 8 cation exchange resin with water washings. Lithium chloride is added to the filtrate and the solution evaporated to dryness. The residue is taken up in 1 ml of water and 0.5 ml is transferred to a gelatin-coated cupped Mylar film where it is dried for 3 hr in 60°. The sample is irradiated in the x-ray spectrograph using a 50-sec counting interval for peak and background intensity measurement. Precision of the method for samples containing 0.5-14 ppm S is ±2-10% of the amount of S present. (11 ref)

367

Diagnosis of Sulfur Deficiency in Plants by Soil and Plant Analysis.

J. R. Freney and K. Spencer.
J. Aust. Inst. Agr. Sci. 33 (4), 284-8 (Dec. 1967).

Sulfur-deficient soils usually occur in areas of moderate rainfall, away from industrial activity, and away from the influence of the ocean. Plants are not able to use directly organic forms of S which are associated with the organic or mineral colloids in soil. S present in these forms must be converted to inorganic sulfate or to simpler organic S compounds before being assimilated by plants. Transformation is carried out by microorganisms. Factors which affect the release of sulfate from soil organic matter are: temperature, moisture, pH, and nature and availability of food supply. Soil-testing procedures are outlined for: total sulfate, water-soluble sulfate, phosphate-extractable S, heat-soluble S, bicarbonate-soluble S, and reducible S. Suitable plant tests for S status are outlined as: total S, sulfate S, and N/S ratio determinations. The performance of plant tests for diagnosing S deficiency in field trials is far superior to that of soil tests. (45 ref)

368

An Alkaline Oxidation Method for Determination of Total Sulfur in Soils.

M. A. Tabatabai and J. M. Bremner (Iowa State Univ., Ames).
Soil Sci. Soc. Amer., Proc. 34 (1), 62-5 (Jan.-Feb. 1970).

A rapid and precise method of determining total S in soils is described. The soil sample is heated with alkaline sodium hypobromite solution to oxidize soil S compounds to sulfate, and the sulfate thus formed is reduced to hydrogen sulfide by a modified Johnson-Nishita procedure and determined colorimetrically as methylene blue. The method gives quantitative results with pure organic and inorganic S compounds, including amino acids, sulfonic acids, organic sulfates, sulfoxides, thioureas, sulfates, sulfites, sulfides, and elemental S. It gives quantitative recovery of organic and inorganic S added to soils and soil extracts, and its results with soils agree closely with those obtained by other methods proposed for total S analysis of soils.

369

Amperometric Determination of Sulfate Ions in Soil Extracts.

V. D. Skobets, V. A. Chernyi, and G. V. Ruchko (Ukr. Sel'skokhoz. Akad., Kiev, USSR).
Khim. Sel. Khoz. 6 (8), 632-3 (1968) (Russ).
CA 70, 53729.

$SO_4^{=}$ is determined by amperometric titration with $Pb(OAc)_2$. Down to 0.24 mg of sulfate in 25 ml of aqueous soil extract may be determined. The relative difference from gravimetric results is 1.9%.

370

Determination of Sulfur Dioxide with Rosaniline Dyes.

H. G. C. King and G. Pruden (Rothamsted Exp. Sta., Harpenden, Engl.).
Analyst 94 (1114), 43-8 (Jan. 1969).

In order to improve the colorimetric finish to the determination of SO_2 from soil S by Bloomfield's V_2O_5 method (*Analyst 87*, 586, 1962), the relative merits of pararosaniline and rosaniline hydrochloride as colorimetric reagents were reinvestigated. These dyes, purified in small amounts by paper chromatography, each gave a linear calibration up to 80 micrograms SO_2 with the HCl-formaldehyde reaction at pH 1.1. Of the two dyes, pararosaniline hydrochloride is preferred because of its smaller blank value and because impurities can be readily removed by recrystallization.

371

Soil Sulphur Tests Surveyed.

J. D. Beaton (The Sulphur Inst., Washington, D. C.).
Sulphur Inst. J. 4 (4), 13-14 (Winter 1968-69).

The Sulphur Institute surveyed soil testing laboratories in the

U. S. and Canada in late 1968 to determine how many were making soil tests for available S. Idaho and Washington conduct the tests on a routine basis as does also Manitoba. Eight other states make the S test on request. Extractant and method of analysis are listed for each laboratory that performs the test.

372

Determination of Elemental Sulphur in Soils.

N. J. Barrow (C.S.I.R.O., Wembley, Western Australia).

J. Sci. Food Agr. 19 (8), 454-6 (Aug. 1968).

Elemental S was extracted from soil with chloroform and the S was reduced to hydrogen sulfide by Fe powder in the presence of hydrochloric acid, acetone, and chloroform. The hydrogen sulfide was transferred in a stream of N to sodium hydroxide solution and determined by titration with mercuric chloride using dithizone as an indicator. The reduction technique was not specific to elemental S but soils appeared to contain few compounds which were soluble in chloroform and which were also reduced. Wet soils could be extracted without preliminary drying. The analysis is rapid and suitable to routine application. (10 references)

373

Determination of Sulphur in Soils and Plant Material.

James D. Beaton, George R. Burns, and Jan Platou (The Sulphur Inst.).

The Sulphur Inst. (Washington, D. C., U. S. A., and London, England), *Tech. Bull.* No. 14, 56 pp. (Nov. 1968).

Various methods for the determination of S in soils and plant material are reviewed. Total S in field soils may range from 0 to >0.06%, and in organic soils it can be >0.5%. It is present in many different forms, both inorganic and organic. To determine the total amount it is necessary to change all S into one form by either oxidation to sulfate (33 methods are discussed), or by reduction to sulfide (3 methods are discussed). (566 references)

374

Determination of Sulfate in Soils as the $^{133}BaSO_4$ Precipitate.

C. W. Kao, E. R. Graham, and R. W. Blanchar (Missouri Agr. Exp. Sta., Columbia).

Soil Sci. 112 (4), 221-4 (Oct. 1971).

The purpose of this study was to develop a rapid analytical procedure for low levels of S in soils. A 12-g sample of air-dried soil is shaken with 30 ml 5 *mM* $CaCl_2$ in a 50-ml centrifuge tube for 30 min. After centrifuging for 5 min at 2000 rpm, the supernate is passed through a cation exchange resin (Dowex 50W-X8) and 0 1 ml is pipetted into an Al weighing dish. To this is added 0.2 ml of a solution containing 0.08 μCi $^{133}BaCl_2$ in 0.002 *N* $BaCl_2$. After drying under a heat lamp, the precipitate is washed with anhydrous methanol and then treated with 5 ml 0.1 *N* HCl to remove Ba phosphate. Activity of ^{133}Ba is measured for 1 min in a multichannel analyzer and compared to standard solutions. Levels as low as 1 μg SO_4^{2-}/g soil can be determined and about 60 samples per day can be analyzed by this procedure. An analysis of 24 samples ranging from 9 to 134 μg SO_4^{2-}/g soil had a standard deviation of 7.4 μg SO_4^{2-}.

375

Soil and Plant Analysis as Methods for Diagnosing Micronutrient Deficiencies.

J. B. Jones (Univ. Georgia, Athens).

Commun. Soil Sci. Plant Anal. 1 (5), 263-72 (Sept. 1970).

Soil and plant analyses can be effectively used to detect and confirm suspected micronutrient deficiencies. The number of laboratories offering tests for micronutrients has increased substantially in the last 10 yr. Suitable soil tests have been developed for most of the micronutrients. Although plant analysis is relatively new, its use is gaining wide acceptance as an effective means of evaluating the micronutrient status of plants. Considerable improvement in methodology has been a primary factor in the increasing use of soil tests and plant analyses as means of evaluating the micronutrient status of the soil-plant environment.

376

Comparison of Eight Extractants for the Determination of Plant Available Micronutrients in Soils.

Esko Lakanen and Raimo Ervio (Dep. Soil Sci., Agr. Res. Cent., Tikkurila, Finland).

Suom. Maatalous tieteellisen Seuran Julk., No. 123, 223-32 (1971).

CA 76, 58116.

Acid NH_4 acetate/EDTA was suitable for the simultaneous extraction of both macronutrients (K, Ca, Mg, P) and micronutrients (Fe, Mn, Zn, Cu, Co, Mo). A comparison was made of eight extractants for the determination of Fe, Mn, Zn, Cu, Co, and Mo. Highly significant positive correlations existed between the plant and soil Mn, Co, and Zn; for most extractants poor correlations were found between plant and soil-extracted Fe, Cu, or Mo. Comparisons showed that acid NH_4 acetate/EDTA extracted the same amounts of K, Ca, and Mg as acid NH_4 acetate alone. EDTA, acid NH_4 acetate/-EDTA, and the Al reagent were most suitable for trace element extraction, giving good correlations between soil and plant analysis.

377

Activation Analysis in Botany and Agriculture.

H. J. M. Bowen (Univ. Reading, Engl.).

Nuclear Activation Techniques in the Life Sciences, pp. 287-99, Vienna Intern. At. Energy Agency, 1967 (from Symp. in Amsterdam, Netherlands).

Nucl. Sci. Abstr. 23 (3), Abstr. No. 4553 (Feb. 15, 1969).

Applications of activation analysis to the plant sciences are reviewed. It offers a practical method of measuring the concentrations of trace elements such as Co, Cu, Mn, Mo, Se, and Zn in soil solutions. It can also be used to determine P in solutions from P-deficient soils. In pure botany there were many applications, mostly concerned with the behavior of essential trace elements. There were numerous applications in agriculture, though here the sensitivity of the method for essential trace elements was not taken advantage of as much as might be expected. There was, however, particular interest in the determination of Se, mainly because of the difficulty of using conventional analysis for the levels normally found in herbage and fertilizers. The determination of toxic residues, containing such elements as As, Br, Cl, Hg, or Ni was another application of great potential interest. In a recent intercomparison program involving the analysis of standard kale, activation analysis gave results agreeing with those obtained by other techniques in all but one instance. The exception is the determination of K in plant tissue by γ spectrometry.

378

Micronutrient Research in Soil and Plants in India: A Review.

J. S. Kanwar and N. S. Randhawa.

Indian Coun. Agr. Res., New Delhi, 95 pp., 1967 (Price Rs. 5.80).

In this book, all the available literature on micronutrient work in India is summarized in a systematic manner. The research work done so far in India on Fe, Mn, Cu, Zn, B, Mo, and Co is thoroughly discussed. Although S is not a micronutrient, information on the work done on this element is presented, since S as a nutrient is assuming importance in some parts of India. Under each micronutrient, methods of soil, total content in soils, factors affecting total content in soils, availability in Indian soils, factors affecting availability, fixation, role in crop nutrition, symptoms of deficiency and toxicity to plants, contents of plants, effect on uptake of other elements, and soil-test plant-response are presented. Results obtained by the application of micronutrients in the case of rice, wheat, cotton, pulses, maize, millets, sugarcane, potato, oilseeds, berseem, tea, and some fruit trees are summarized. Effort is made to delineate areas of probable micronutrient deficiency in some states. For setting the micronutrient research work on sound footing the authors indicated that intensification of effort on (a) delineation of areas of probable micronutrient deficiency or toxicity, (b) predictability of the availability of micronutrient in the soil (c) development of a plant test to predict the response to the application of micronutrients, (d) relative significance of organic and inorganic finding sites, (e) effect of rhizosphere on the availability of micronutrients, (f) multiple micronutrient deficiencies, (g) long-term equilibrium reactions, (h) effect of heavy fertilization on the availability of micronutrients, (i) toxicity of essential and non-essential micronutrients, and (j) use of chelated compounds of micronutrients for correcting the deficiency should be done.

379

Extraction of Boron from Soils.

Z. E. Deikova.

Dokl. TSKhA (Timiryazev. Sel'skokhoz. Akad.), No. 124, 177-83 (1967) (Russ).

CA 69, 9917.

Various extraction methods were compared for photometric determination of total and available B in soils. For determination of total B, mineralization by fusion with Na_2CO_3 gave best results. The other methods, for example, digestion with $H_2SO_4 + HNO_3$, $HCl + HNO_3$, $H_2SO_4 + HClO_4$, or $H_2SO_4 + NH_4F$ gave lower results due to either incomplete dissolution or volatilization. For extraction of available B, 10 min boiling with 0.02*N* KCl at a soil:solution ratio of 1:2 gave the best results. The main advantage of this method, irrespective of good accuracy and reproducibility, is that the soil colloids are rapidly coagulated and clear filtrates are obtained, even from loamy and clayey soils.

380

Spectrophotometric Determination of Boron in Plant and Soil Samples.

C. C. Weir (Univ. West Indies, St. Augustine, Trinidad) and R. L. Jones (Univ. Illinois, Urbana).

Trop. Agr. 47 (3), 261-4 (July 1970).

The methylene blue method for B analysis has been successfully applied to the determination of B in plant and soil samples. This new solvent extraction procedure offers a relatively rapid, simple, and reliable method for B analysis. The coefficient of variation for B determination in plant and soil samples varied between 4.5 and 11.5%.

381

Relation between Available Boron and Boron Extracted from Soils by Hot Water or Phosphoric Acid.

A. S. Baker (Washington State Univ., Puyallup).

Commun. Soil Sci. Plant Anal. 2 (5), 311-20 (1971).

A measure of biologically available B (BAB) was obtained by assaying the amount of B removed from a small volume of soil by sunflowers grown until they displayed B deficiency symptoms. Four different mineral soils and one organic soil which had been treated in the field with variable lime and B applications 2 yr prior to sampling were compared. The amount of B extracted with hot water from soils before cropping was well correlated with BAB. The B extracted by more intensive hot water extraction methods was closely related to the absolute level of BAB. Digestion of soils with concentrated H_3PO_4 resulted in the dissolution of larger amounts of B than that extracted with hot water. The proportion of H_3PO_4-soluble B that was measured as BAB was quite variable. Thus H_3PO_4 was a less suitable extractant than hot water for assaying the amount of soil B available to plants during a short growing period. In no case was the difference between the B extracted from soils before and after cropping as large as the BAB values.

382

The Determination of Boron in Soil Extracts, Plant Materials, Composts, Manures, Water, and Nutrient Solutions.

Benjamin Wolf (Wolf's Agr. Lab. Ft. Lauderdale, Fla.).

Commun. Soil Sci. Plant Anal. 2 (5), 363-74 (1971).

A colorimetric method based on azomethine-H, is used for the determination of B in various agricultural materials. The method is sensitive to 0-4 ppm B and works well in aqueous media. Interferences by Al, Cu, Fe, and NH_4 are eliminated by using a buffer-masking agent which is prepared by dissolving 250 g ammonium acetate, 25 g of the tetrasodium salt of ethylenediamine tetraacetic acid, and 10 g of the disodium salt of nitriloacetic acid in 400 ml H_2O and adding 125 ml of acetic acid. The azomethine-H is prepared by dissolving 0.9 g of azomethine-H and 2 g of ascorbic acid in 10 ml H_2O, heating gently, cooling, and diluting to 100 ml with water. The azomethine-H is available commercially from Pierce Chemical Co., Rockford, Illinois. The solution is stable for 14 days when refrigerated. From 1-2 hrs are required for the color to develop in sample solutions.

383

Mobilization of Some Forms of Boron in Soil by *d*-Glucose.

P. Cornillon (Sta. Agron., INRA, Avignon-Montfavet, France).

C. R. Hebd. Seanc. Acad. Agr. Fr. 57, 270-7 (1971) (Fr).

Soils Fert. 34, 4653.

The effect of extraction time and solution concentration on the amount of soil B extracted by boiling glucose solutions was determined on different soils. Amount of B extracted from a calcareous alluvial soil by a 5% boiling glucose solution increased with time up to about 10 hr. Under similar conditions, glucose (5%) extracted approximately twice as much B from this soil as did deionized water. Amount of B extracted after 10 min by glucose solutions of different concentrations varied both with concentration and soil type. Maximum amount of B was extracted by a 2.5% solution in a fersiallitic soil, a 10% solution in a calcareous alluvial soil, and a 20% solution in a marsh soil. The organic C content of these three soils was respectively 0.7, 1.92, and 6.89%.

384

EDTA-Ammonium Carbonate Soil Test for Zinc.

J. F. Trierweiler and W. L. Lindsay (Colorado State Univ., Ft. Collins).

Soil Sci. Soc. Am., Proc. 33 (1), 49-54 (Jan.-Feb. 1969).

A soil test was developed for the diagnosis of Zn-deficient

soils. The test consists of shaking 10 g soil with 20 ml of extractant (pH 8.6) containing 0.01*M* EDTA (ethylenediaminetetraacetic acid) and 1*M* $(NH_4)_2CO_3$. After a 30-minute shaking period the suspension is filtered and Zn is determined directly in the filtrate by means of atomic absorption spectrophotometry. The new soil test was evaluated on 42 Colorado neutral and high lime soils whose response to Zn was determined in the greenhouse with corn (*Zea mays*) as the test crop. A critical level of 1.4 ppm of extractable Zn separated the Zn-deficient from the nondeficient soils. The new Zn soil test compares favorably with the dithizone method and is an improvement over the 0.1*N* HCl method. Unlike strong-acid extractants, the new procedure suppresses the dissolution of carbonates and oxides and thereby avoids extraction of occluded Zn. (11 references)

385

A Rapid Method of Evaluating the Zinc Status of Coastal Plain Soils.

H. F. Perkins (Univ. Georgia, Athens).

Commun. Soil Sci. Plant Anal. 1 (1), 35-42 (Jan. 1970).

A study was made to evaluate Zn removed by extraction with a 0.075 *N* acid mixture (0.05 *N* HCl + 0.025 *N* H_2SO_4). A ratio of soil to extracting solution of 1:4 and an extracting time of 15 minutes was selected. Data obtained by the method was significantly correlated with dithizone (0.01%) extraction. The method was found to be acceptable for evaluation of the Zn status of Southern Coastal Plain Soils and easily adapted to routine use in soil testing. A significant correlation was obtained between extractable soil Zn and leaf blade content of Zn for Zn-deficient and non-deficient corn plants.

386

A Comparison of Analytical Methods for Soil Zinc.

A. L. Brown, James Quick, and J. L. Eddings (Univ. California, Davis).

Soil Sci. Soc. Amer. Proc. 35 (1), 105-7 (Jan.-Feb. 1971).

Soils from 92 fields in California were analyzed for extractable Zn by four methods, namely, ammonium acetate-diphenyl-thiocarbazone (dithizone), diethylenetriaminepentaacetic acid (DTPA), 0.1*N* HCl, and disodium ethylenediaminetetraacetate (Na_2EDTA). Each soil was tested in the greenhouse for plant response in relation to Zn applications. All four methods exhibited a high degree of correlation with each other; the highest correlation coefficient was obtained for the comparison of dithizone with DTPA. Calculated predictive values for DTPA, dithizone, 0.1*N* HCl, and Na_2EDTA were 83, 79, 73, and 72%, respectively, for the 92 soils studied. On this basis the DTPA is preferable to the others and the critical level is approximately 0.5 ppm Zn. For some soils, more than one method may be required to properly characterize the Zn status. The choice of method will depend upon the correlation with plant response, equipment and facilities available, and to some extent on the preference of the analyst.

387

Extraction of Zn, Fe, and Mn from Soils with 0.1 *N* Hydrochloric Acid as Affected by Soil Properties, Solution: Soil Ratio, and Length of Extraction Period.

R. C. Sorensen, D. D. Oelsligle, and Delno Knudsen (Univ. Nebraska, Lincoln).

Soil Sci. III (6), 352-9 (June 1971).

Eighteen soils were extracted with 0.1 *N* HCl using 15-, 30-, 100-, and 300-min extraction periods and 25:5, 30:2, and 25:1 solution:soil (volume:wt) ratios. Iron, Mn, and Zn concentrations in the extract were determined by atomic absorption spectrophotometry. The soils varied in pH; organic matter content; cation exchange capacity; quantity of Ca, Mg, K, and H; titratable alkalinity; and total content of Zn, Fe, and Mn. These six variables were related to extractable Zn, Fe, and Mn by regression analysis. Although the relationships differed widely among soils in regard to Zn extraction, little differences among soil types were noted in regard to Mn and Fe extraction. However, the shape of the release curve for Fe was markedly different from that for Mn. Soil organic matter content was closely related to amounts of all three micronutrients released. The importance of total nutrient level, soil pH, and titratable alkalinity varied in regard to the nutrient studied.

388

Multichannel Atomic Fluorescence and Flame Photometric Determination of Calcium, Copper, Magnesium, Manganese, Potassium, and Zinc in Soil Extracts.

R. M. Dagnall *et al* (Dep. Chem., Imp. Coll. Sci. Technol., London, Engl.).

Anal. Chem. 43 (13), 1765-9 (1971)

Exchangeable Ca, Cu, Mg, Mn, K, and Zn in soils were determined in NH_4OAc, HOAc, and EDTA extracts by using a six-channel atomic fluorescence spectrophotometer. Determination of all six elements in a single extract at two dilutions is possible by using this technique. The results obtained compare favorably with the results of single channel atomic absorption analyses for the same extracts. The method permits rapid, sensitive, and accurate analysis for these samples.

389

Evaluation of Atomic Absorption Methods for Determinations of Aluminum, Iron, and Silicon in Clay and Soil Extracts.

T. L. Yuan and H. L. Breland (Florida Agr. Exp. Sta., Gainesville).

Soil Sci. Soc. Amer., Proc. 33 (6), 868-72 (Nov.-Dec 1969).

Atomic absorption methods for Al, Fe, and Si determinations were evaluated in clay and soil extracts obtained with 1*N* NH_4OAc (pH 4.8), 0.1*N* HCl, 0.2*M* $(NH_4)_2C_2O_4$ (pH 3.0), 0.5*N* NaOH, and buffered $Na_2S_2O_4$. The evaluation was made either by correlating the results with those of chemical methods or by calculating the percentage recovery of added Al, Fe, or Si from the extracts. Highly significant correlations and regressions were obtained between the atomic absorption and colorimetric methods for NH_4OAc- and HCl-extractable Al and Fe in soils, dithionite-extractable Fe in clays, NaOH-extractable Al in soils and clays, and NaOH-extractable Si in clays. Recoveries of added Al, Fe, and Si from oxalate, dithionite, and dilute alkali media were successful except that the recovery of Fe in soil extracts exceeded 110% in most cases. The presence of a natural humic acid "Leonardite" did not affect the atomic absorption analyses of Al and Si. However, the Fe results were high as was found in soil extracts, indicating organic matter interference in the determination of Fe by this technique. Removal of humic acid by precipitation reduced the Fe but not Al recovery. The coefficients of variation for 10 determinations were below 3% for all three elements with the exceptions of Si at concentrations below 15 ppm and Fe below 2 ppm. Some difficulties were encountered with the oxalate and dithionite as extractants.

390

Colorado Adopts New Soil Test for Zinc and Iron.

W. L. Lindsay and W. A. Norvell (Colorado State Univ., Fort

Collins).
Farm Chem. 131 (2), 87-8 (Feb. 1968).
An extractant containing diethylenetriaminepentaacetic acid and calcium chloride and buffered at pH 7.3 with triethanolamine is used by Colorado's soil testing laboratory to test for both Zn and Fe. The chemical test correlated well with greenhouse and field tests of Zn deficiency in corn and sorghum and Fe deficiency in sorghum. Corn on soils containing less than 0.8 ppm of extractable Zn responded to Zn fertiliztion; the critical level for sorghum was 0.6 ppm. For Fe the critical level with sorghum was 4.5 ppm of extractable Fe. The test costs less than 50¢/sample and has been in use since Sept. 1, 1967, on both neutral and calcareous soils.

391
Thiocyanate Method of Determination of Gross Molybdenum Content in Soil.
A. V. Glushchenko and I. N. Lyubimova (Mosk Gos. Univ., Moscow).
Agrokhimiya, No. 9, 134-8 (1967) (Russ).
CA 68, 28778.
The thiocyanate method of determination of gross Mo in soil gave satisfactory results only after digestion of soil by HF and H_2SO_4 and additional oxidation by aqua regia. Different samples of soil contained 0.98-2.87 mg/kg of Mo. The higher values were determined in red soils, rich in Fe.

392
Direct Determination of Manganese in Soil Extracts by Atomic-Absorption Spectroscopy.
M. Nadirshaw and A. H. Cornfield.
Analyst 93 (1108), 475 (July 1968).
The preliminary treatment of soil extracts required before Mn can be determined by traditional colorimetric methods is avoided by direct aspiration of the filtered extract for atomic-absorption spectroscopy. Results for Mn extracted into four different reagents used for assessing the Mn status of soils are in close agreement with those found by the colorimetric K periodate method after removal of organic matter.

393
Soil Fluorine.
S. Larsen and A. E. Widdowson (Fisons Ltd., Levington Res. Sta., Ipswich, England).
J. Soil Sci. 22 (2), 210-21 (June 1971).
The development of techniques for measuring soluble and labile soil F using a specific-ion F electrode are described. The methods evolved were used to assess the F status of numerous agricultural soil samples in addition to soils which had received known F additions. Two soil profiles were analyzed with respect to distribution with depth of soluble and labile F. The equilibrium-F concentration was determined after shaking the soil with a 0.01 *M* $CaCl_2$ solution. Isotopically exchangeable (labile) soil F was determined by use of the isotope ^{18}F. These labile F values were well correlated with the amount of soil F extracted by an anion-exchange resin, and the latter method was consequently adopted for further determinations of labile soil F. Nearly half the 100 agricultural soil samples examined gave F concentrations < 0.2 ppm in 0.01 *M* $CaCl_2$ extracts whereas labile F values were evenly distributed around a mean of 20 ppm. For any given pH value, there appeared to be an upper limit to the solubility of soil F. Application to soil of superphosphate (in the field) or of fertilizer containing F (in the laboratory) brought about increases in soluble soil F.

394
Extraction and Colorimetric Determination of Urea in Soils.
L. A. Douglas and J. M. Bremner (Iowa State Univ., Ames).
Soil Sci. Soc. Amer. Proc. 34 (6), 859-62 (Nov.-Dec. 1970).
A simple colorimetric method of determining urea in soils is described. The soil sample is extracted with 2*M* KCl containing a urease inhibitor (phenylmercuric acetate), and the extract is analyzed for urea by measurement of the red color formed when an aliquot is heated with diacetyl monoxime and thiosemicarbazide under acidic conditions (H_3PO_4--H_2SO_4 medium). The method is sensitive and precise, and it gives quantitative recovery of urea added to soils. The extraction performed is satisfactory for determination of exchangeable ammonium, nitrite, and nitrate by steam distillation methods.

395
Determination of Trace Metals in Soils and Rocks by Atomic Absorption Spectrophotometry.
M. Pinta and C. Riandey (Orstom, Laboratoire de Spectrographie, Bondy).
Method. Phys. Anal. 5 (1), 76-85 (1969) (Fr).
At. Absorption Flame Emission Spectrosc. Abstr. 2, 913.
The experimental conditions for the routine analysis of K, Na, Mg, Ca, Mn, Zn, Cu, Cr, Ni, Pb, V, Co, and Sr, which are of importance in geological and agricultural research, are considered. The techniques evolved take into account the diversity of the media, preparation of samples, and evaluation of the results. The main composition range includes silica 40-70, alumina 5-30, oxide or hydroxide of Fe 2-30, Ti oxide 0.1–2, Ca oxide 0.1–5, Mg oxide 0.1–5, Na oxide 0.05–2, and K oxide 0.01–1%. Traces of other elements are also found, as listed above. The preparation of rock samples is based on acid treatment (sulpho-nitro-fluorhydric acid), while soils are subject to H_2SO_4 and HNO_3 attack. The solutions are diluted, to ensure a range of optimum concentrations, and to reduce interference effects. The tabulated results summarize concentrations used, the character of interactions with contaminants, and the correction recommended for the reduction of the interference, as well as the condition of spectra production. Both hollow cathode and a source of high spectral output are cited for an air-C_2H_2 flame, with a cooled burner. The detector is made up of a photo-multiplier with a high sensitivity in uv and ir regions. The results obtained are compared with colorimetric and arc spectrographic methods; differences of less than 10% are observed. (20 ref)

396
Selenium Determination in Soil and Plant Materials.
M. Levesque and E. D. Vendette (Canada Dep. Agr., Ottawa, Ontario).
Can. J. Soil Sci. 51 (1), 85-93 (Feb. 1971).
Selenium was determined in soil and plant samples after wet digestion with HNO_3 and $HClO_4$. The method included the usual steps, namely, the reduction of Se, complexing Se with 2,3-diaminonaphthalene, and the extraction of the piazselenol in cyclohexane followed by fluorometric measurements. The most important step, the stabilization of Se at the oxidative state Se^{+4}, was achieved by reducing Se^{+6} to Se^{+4} with 2 ml of 1 *N* HCl while the system was kept in a boiling water bath. For best results and adequate control of interfering ferric ions, the system was adjusted to pH 1.8, and a stabilizing agent consisting of 10% hydroxylamine hydrochloride in a 0.04 *M* EDTA solution was used. Fluorescence measurements obtained for soil samples gave average coefficients of variation and recovery percentages of 3.35 and 97.4, respectively. For radioactivity counts made on cyclohexane extracts, the coefficients of variation and the recovery percentages were

2.31 and 93.1, respectively. Similar results were obtained for plant materials. Major problems encountered in establishing the modified method are discussed.

397

Soil Testing and Plant Analysis.

Soil Sci. Soc. Amer., Spec. Publ. No. 2 (Madison, Wisc.).

Papers presented by leading scientists in two symposia sponsored by the American Society of Agronomy are included. Part I includes topics on soil testing, including the philosophy of soil testing, methods, and correlation with crop response. Part II includes topics on plant analysis, including principles and practices, methods, interpretation, and field diagnosis.

398

Soil Tests and Fertilizer Recommendations.

J. B. Jones, editor.

Commun. Soil Sci. Plant Anal. 2 (2), 55-144 (1971).

This issue contains the 10 papers presented at a Soil and Plant Analyst Workshop held December 9, 1970, in Chicago, Ill. Titles and authors are: The Philosophy of Soil Testing, John Hanway (Iowa State Univ.); NO_3–N Soil Test–Approaches to Use and Interpretation, R. C. Ward (S. Dak. State Univ.); Use of Nitrate Specific Ion Electrode in Soil Testing, W. C. Dahnke (N.Dak. State Univ.); Rapid Automated Determination of Phosphorus in Bray's P_1 Soil Extracts, C. H. Orr (Custom Farm Services); ASCS Certification for Commercial and Private Soil Testing Laboratories, B. C. Darst (Custom Farm Services); Philosophy and Mechanics of How We Arrive At Fertilizer and Lime Recommendations, R. B. Lockman (AGRICO Chem. Co.); Soil Fertility Recommendations Based On a Balanced Saturation of the Cation Exchange Capacity, R. L. Large (United States Testing Co.); Philosophy and Mechanics of How We Arrive at Fertilizer and Lime Recommendations, C. R. Olson (Olson Laboratories and Olson Management Service); Harris Laboratories' Fertilizer Recommendation Philosophy, R. B. Harris (Harris Laboratories); and Factors in Making Fertilizer Recommendations, R. E. Goff (Minnesota Valley Testing Laboratories, Inc.).

399

A New Approach to Soil Testing.

D. E. Baker (Pennsylvania State Univ., University Park).

Soil Sci. 112 (6), 381-91 (Dec. 1971).

From the theoretical relationships among the concepts of energy of exchange entertained by Woodruff, of the % saturation of the cation exchange capacity (CEC) of Bear and others, and of cationic activities of Marshall and co-workers and Baker and Low, solutions were prepared which differed with respect to the parameters which are related to the availability of K. Twelve widely different soils were equilibrated with these solutions, and from the change in composition of the solutions the K- and Mg-requirements of the soils were calculated. It was concluded that the K and Mg requirement can be determined directly from changes in the concentrations of the respective ions in solution when soils, using a soil:solution ratio of 1:10, are allowed to reach equilibrium with a solution containing 2.4×10^{-4} *M* KCl, 9.6×10^{-4} *M* $MgCl_2$, and 48×10^{-4} *M* $CaCl_2$. A ΔK value of 1×10^{-4} *M* represents about 40 ppm of soil K. A ΔMg value of 1×10^{-4} *M* represents about 25 ppm of soil Mg. Negative ΔK or ΔMg values represent amounts in the soil greater than those required for minimum levels of availability. For most soils, the expected crop removal should be added to the amounts recommended from the ΔK values. The approach to soil testing introduced in this report should find wide application. The soil requirements are determined directly. While the amounts of K and Mg required by a soils are affected by the clay minerals, the CEC, and other properties, these properties need not be measured in order to determine soil requirements.

400

Advisory Soil or Plant Analysis and Fertilizer Use. I. Comparison of Soil Analysis Methods.

J. B. D. Robinson and G. Semb (East African Agr. Forestry Res. Org., Nairobi, Kenya).

East African Agr. Forest. J. 34 (1), 117-39 (July 1968).

From a series of maize fertilizer trials in Western Tanzania, 124 soil samples, representing 16 soil types, were collected during a 3-year period. These were used to compare four analytical methods for extractable P, K, Ca, and Mg. P methods evaluated were. (*I*) an ammonium lactate-acetic acid extraction with ammonium molybdate/stannous chloride color development, (*II*) Truog's weak sulfuric acid extraction with the above color development procedure, (*III*) mixed hydrochloric and sulfuric acid extraction with ammonium vanadate-ammonium molybdate used for color development, and (*IV*) the mixed acid extraction followed by color development using an ascorbic acid reagent *IV* was the least satisfactory method of measuring extractable P. *I* was variable in the amount of P extracted but had the advantage of simultaneous extraction of K, Ca, and Mg. The cations were extracted as in *I* and *III* above and with neutral normal ammonium acetate. Analysis was either by the atomic absorption spectrophotometer or by the flame photometer for K and Ca and thiazol yellow color for Mg. Ammonium acetate was the least variable extractant for Mg while K and Ca were relatively unaffected by extraction method when soil pH was in the acid-neutral range. More suitable analytical methods are needed for alkaline soils. Within the range of soil type and analytical data encountered, it was possible to convert analytical values from any method into equivalent values for any other method. (10 references) (See *FA 2*, 733 for Part II)

401

Various Analytical Results with Dry and Wet Soils.

A. M. Primavesi and A. Primavesi (Dep. Geosci., Univ. Fed. Santa Maria, Santa Maria, Brazil).

Agrochimica 15 (4-5), 454-60 (1971) (Ger).

CA 75, 139710.

To determine whether there is a direct relation between the usual analyses of wet and dry soils and whether a correction can be applied to make the usual analysis values useful in indicating fertilizer requirements of rice soils, 18 crop soils from wheat, potatoes, and paddy rice were analyzed. Soils were analyzed after drying in air and after incubation submerged in water for 4 weeks at 30°. The increase in pH in the wet soils was greater the lower the pH of the dry soil was. The expected increase in P availability was not observed, presumably due to the extraction method. Potassium and Ca tended to increase irregularly, while Mg and Al showed a constant increase. Sulfur increased in crop soils on submerging but not in rice soils. It was concluded that the standard analysis of dried soils offers little useful information on fertilizer requirements for cultivation of submerged soils.

402

Analysis of Greenhouse Soils by Means of Aqueous Extracts.

Ir. J. Van den Ende (Horticultural Exp. Res. Sta. Naaldwijk, Netherlands).

Colloq. Fert. Protected Crops, Proc. Colloq. Int., Potash Inst., 6th, 246-55 (1968).

Routine testing of greenhouse soils is done using a water

extraction method. A common extraction method uses a 1:5 soil: water suspension. The method has the advantage that it can be easily obtained from widely different soils. The disadvantages are: (1) Soils containing gypsum give poor impression of the salinity levels; and (2) Data on electrical conductivity and chloride, nitrate, and K levels have to be interpreted in dependence of the moisture-holding capacities of the soil. Tests were made to compare the 1:5 extract method with a saturation extract (soil samples are saturated with water in a standardized manner). The saturation extract does not yield any important advantages over the 1:5 extract for the determination of salt, nitrate, phosphate, and K levels. The 1:5 extract requires an organic matter and sulfate determination, but this disadvantage is small compared with the difficulty associated with making a saturation extract for routine soil testing purposes.

403

Rapid Wet Digestion Method for the Analysis of Organic Materials and Soils.

C. Abrisqueta and M. Romero (Centro Edafol. Biol. Apl. Segura, Murcia, Spain).

An. Edafol. Agrobiol. 28 (11-12), 855-67 (1969) (Span).

CA 72, 139263.

Wet digestion of soils and organic materials for determination of P, Fe, Mg, Ca, Al, K, and Na was carried out rapidly and more precisely in a system which allowed some refluxing of the reagents during the digestion.

404

Soil Preparation and Sampling Techniques for Studying Ion Movement.

F. E. Khasawneh and J. M. Soileau (Tennessee Valley Authority, Muscle Shoals, Ala.).

Soil Sci. Soc. Am. Proc. 33 (3), 476-77 (May-June 1969).

Techniques were developed for preparing and sampling soil columns and undisturbed soil peds used for ion movement studies. These methods utilize a block of paraffin wax-petrolatum jelly mixture to hold soil peds or to provide a cylindrical cavity for a soil column. A microtome apparatus capable of holding the wax blocks containing the soil is used for precision slicing at increments of 0.5 mm or more.

405

The Determination of Available Nutrient Reserves, P_2O_5, and K_2O, in the Soil Using a Single Extraction.

A. Dostal and M. Pesak (Central Agr. Contr. Expt. Sta., Prague).

Rostl. Vyroba 13 (6), 657-63 (1967) (Czech).

CA 68, 21219.

A single mixed extracting solution containing ammonium lactate, acetic acid, and ammonium sulfate was used for the determination of available P_2O_5 and K_2O in soils. Data on 60 soil samples indicate that comparable values with Egner's method for P_2O_5 and Schachtschabel's method for K_2O were obtained.

406

Atomic Absorption Method of Analysis for Agricultural Samples.

H. L. Breland (Fla. Agr. Expt. Sta., Gainesville).

Soil Crop Sci. Soc. Fla., Proc. 26, (1966), 53-64 (1967).

The atomic absorption method was used for analyzing soil and plant samples and was found to be fast, accurate, and reliable. Soil samples were extracted with 1.0*N* NH_4OAc (pH 4.8) or other suitable solution. Plant samples were ashed to 500° and the ash was dissolved in 0.1*N* HCl. Good reproducibility and precision were obtained over a wide range of concentrations. The maximum variation for Ca did not exceed 5% except in one case. Correlation coefficients for Al, Ca, and Mg by atomic absorption and another method exceeded 0.98 in each case. The regression values obtained for Al, Ca, and Mg were Y = 14.0 + 0.95X; 31.0 + 0.91X; and 2.5 + 0.85X, respectively. It was concluded that atomic absorption is a very satisfactory method for analyzing soils and plants.

SEE ALSO the following numbered abstracts in other sections: 27, 41, 288, 406.

PLANT ANALYSIS

407

Analysis of Plants, Soils, and Waters for Nitrate by Using an Ion-Selective Electrode.

P. J. Milham, *et al* (New South Wales Dep. Agr., Rydalmere, Australia).

Analyst (London) 95 (1135), 751-7 (Aug. 1970).

The use of a commercial anion-exchange electrode permits the rapid determination of nitrate in plant material and in non-saline soils and waters. The buffer used eliminates chloride, nitrite and organic anion interferences. The proposed method gives better recovery and reproducibility than the Devarda method.

408

A Simplified Method for Determining Acetic Acid Soluble Phosphorus in Plant Tissue.

A. S. Baker (Washington State Univ., Puyallup).

Commun. Soil Sci. Plant Anal. 2 (3), 195-200 (1971).

A procedure is proposed for determination of 2% HOAc soluble P in plant tissue Extraction with Darco G 60 eliminates the need to oxidize the extract with H_2O_2. Transfer ~ 250 mg of Darco G 60 and 250 mg of dried sample to a shaking container. Add 25 ml of 2% HOAc, stopper, shake horizontally for 10 min, and filter. Transfer 10 ml of filtrate and standard to 25 ml volumetric flasks. Add ~ 7 ml of water and 5 ml of vanadomolybdic acid and swirl. Build to volume, mix, and allow to set 15 min. Read transmission at 460 mμ for P concentrations of 10μ g/ml or less or for P concentrations greater than 30μ g/ml Read transmission at 445 mμ for P concentrations of 10-30μ g/ml

409

Determination of Mineral Constituents in Plant Materials. III. Photometric Determination of Phosphorus.

Ryszard Schillak (Inst. Uprawy Nawozenia Gleboznawstwa, Bydgoszcz, Poland).

Rocz. Nauk Roln., Ser. A 92 (4), 595-615 (1967) (Pol).

CA 68, 794.

Determinations of P in plant materials, digested with H_2SO_4 and H_2O , were made by the molybdenum blue reaction after addition of 0.2% *p*-methylaminophenol sulfate in sulfite solution and 5.0% NH_4^+ molybdate. Absorbance at 700 mμ increased linearly with temperature between 5-50° and length of time (3-30 hr) after color development. Direct sunlight, especially at the time of reagent addition, increased absorbance. Similarly, concentration of reagents for color development affected absorbance. Boron, K, Ca, Mg, Fe, Mn, and Al had no effect, and Si had no effect at the pH used. Arsenic can

give additional color, but if reduced to arsenite by the reduction solution added before the molybdate solution, the interference is small. The standardized procedure is sensitive, precise, and reproducible.

410

Nitrate Determination in Plant Extracts by the Nitrate Electrode.

J. L. Paul and R. M. Carlson (Univ. California, Davis).

J. Agr. Food Chem. 16 (5), 766-8 (Sept.-Oct. 1968).

The nitrate-specific ion electrode was used to determine nitrate in aqueous extracts of a variety of dried plant tissues. A recommended plant-solution ratio of 1 to 125 gives extract concentrations of 1 to 50 ppm of N for many field-grown crops. Electrode response is linear over this range. The addition of Al resin during extraction eliminates bicarbonate interference and reduces organic anion interference. Ag resin is added if chloride exceeds 2% in the tissue and nitrate concentrations are 5 ppm or less. Nitrate determinations by the phenoldisulfonic acid and electrode methods agreed closely enough that for practical purposes the electrode method could be used in place of the phenoldisulfonic acid method. The average relative standard deviation for 16 plant materials for the electrode method was 3.1%.

411

Automation in Determining Nitrogen by the Kjeldahl Method, with Final Calculations by Computer.

J. Davidson, J. Mathieson, and A. W. Boyne (Rowett Res. Inst., Bucksburn, Aberdeen, Scotland).

Analyst (London) 95 (1127), 181-93 (Feb. 1970)

An account is given of the development of a system making maximum use of automated equipment in the routine determination of N in biological samples when the desired order of precision is better than 1% and the expected number of analyses is greater than 100/day. An automatic digestion unit made by Technicon Instruments Company Ltd. tested for liquids did not achieve the accuracy desired. Results for biological fluids with this digestor tended to be low on occasion by up to 5%. Recovery of N from solutions of the pure compounds creatine and arginine was as low as 70% and alterations in the digestion mixture and digestor heating conditions did not materially improve recovery. For this reason all samples were subsequently digested by a standard Kjeldahl method before automated determination of NH_3 in the diluted digests. Studies were made of the indophenol-blue reaction used in the automated system for determining NH_3 in aqueous solution. Conditions were most stable when the reaction coil was maintained at 22° ± 1° and dwell time in the coil was about 3 min. Effects of mineral content of test solutions, sampling rate, and sampler cam irregularities on the reliability of results were investigated. Results for N determined in acid digests by the automated procedure and by a standard distillation method showed close agreement. The use of an I.B.M. 1130 computer allowed calculation of results to be carried out in half the time taken when using an electronic desk calculator.

412

Application of Sodium Hypobromite Titration with Dead-Stop Indication for the Determination of the Nitrogen Content of Plants and Fertilizers.

Gyorgy Fuleky (Res. Inst. Soil Sci. Agr. Chem., Hung. Acad. Sci., Budapest, Hung.).

Agrokem. Talajtan 19 (3), 339-46 (1970) (Hung).

CA 74, 110930.

The dead-stop NaOBr titration method of Cap and Leonesik (1968) was applied to the determination of ammonium N in corn, wheat, and alfalfa. The method was extended to the analysis of nitrate fertilizers, following prior Raney Ni reduction. Attempts to apply the method to soil analysis failed.

413

Microdetermination of Nitrogen in Plant Tissues.

H. L. Mitchell (Kansas State Univ., Manhattan).

J. Ass. Offic. Anal. Chem. 55 (1), 1-3 (1972).

In the semimicro method for N, the plant sample is digested with $CuSO_4$ or HgO as catalyst in an acid medium, EDTA is added to prevent interference from metals, and the resulting solution is neutralized to pH 7. Sodium nitroprusside is added and the color is allowed to develop 1 hr; the absorbance is measured at 625 nm. The proposed method, with either $CuSO_4$ or HgO, is applicable to dry or fresh plant tissues and yields results which are comparable to those obtained with AOAC 2.049-2.051.

414

Determination of Nitrogen in Plant Seeds by Fast Neutron Activation Analysis.

L. Kosta, V. Ravnik, and J. Dumanovic.

Panel Meeting on New Approaches to Breeding for Improved Plant Protein, Roestanga, Sweden. Vienna, International Atomic Energy Agency, pp. 161-8 (1969).

Nuclear Sci. Abstr. 23, 31307.

With the aim of developing a fast method for the determination of protein in seeds, the activation of N by $^{14}N(n,2n)^{13}N$ was studied using 15-mev. neutrons. Samples were irradiated under well-defined and reproducible geometrical conditions together with monitors calibrated to standard samples. Good agreement was demonstrated between values obtained by the activation technique and by the Kjeldahl method. The N content of single seeds of maize may be determined with sufficient accuracy at neutron doses around 200 rad while leaving the seeds viable.

415

The Determination of Potassium and Manganese in Plant Tissue by Neutron Activation Analysis.

J. W. Dieckert *et al.*

Proc. Symp. Isotopes Plant Nutr. Physiology Sept. 5-9, 1966, Int. Atomic Energy Agency, Vienna, Austria, pp. 81-93 (1967).

Biol. Abstr. 48, 98162.

A technique is described for the determination of K and Mn in plant tissues by nondestructive thermal activation analysis. The source of neutrons was the heterogenous, light-water-moderated and cooled nuclear reactor of the swimming-pool type. Chemistry was not required for the preparation of the samples for neutron irradiation or counting. Samples were irradiated for periods of 10 min to 1 hr at a neutron flux of about 1.5×10^{12} n/cm^2 sec. The gamma-emitting radioactivity generated in the samples by neutron bombardment was measured with a gamma-ray spectrometer consisting of a multichannel analyzer and a shielded thallium-activated sodium iodide detector. The resulting complex gamma-ray spectra were resolved by spectrum stripping; and the quantity of K and Mn in the sample was estimated by the comparator method. Most of the data processing was done by computer techniques. Under the conditions of the analysis and in the energy range of interest, the complex spectra arising from the irradiated plant materials could be accounted for satisfactorily as being the sum of the contributions from ^{24}Na, ^{42}K, and ^{56}Mn. The precision of the method as measured by the

coefficient of variation was routinely better than 3% for both K and Mn. Recovery experiments for each metal demonstrated a linear relationship between the quantity of metal added to a sample of plant materials and the quantity recovered. Interfering reactions were found to be minimal. The method was used to determine the Mn and K content of roots, stems, leaves, and cotyledons of peanut seedlings and seeds. The results of these analyses are in agreement with those made on similar tissues by other methods. Because of the sensitivity and convenience of the method, it proved feasible to analyze individual seeds or seedling parts in experiments involving large numbers of individual plants. The technique permits the repeated analysis of the same sample when this is necessary.

416

Method of Reference for the Determination of Mineral Elements in Plants: N, P, K, Na, Ca, Mg.

Inter-Institute Committee for the Study of Analytical Techniques on Foliar Diagnosis.

Oleagineux 24 (8-9), 487-504 (Aug.-Sept. 1969) (Fr).

The first part of the article enumerates, item by item, the studies undertaken in the last ten years by laboratories interested in this question with a view to increase the accuracy of the analyses in foliar diagnosis and to reduce the coefficient of variation between and within laboratories. After a systematic study of the causes of errors arising at different stages of the analytical techniques, it appeared necessary to perfect the methods of reference which are described in the second part of the article Kjeldahl's method, already adopted by all the participating laboratories, has been retained for N. The dry mineralization method indicated enables the quantitative analysis of P, K, Ca, Mg, and Na. P is quantitatively analyzed by spectrophotometry of the absorption of the phosphovanadomolybdic complex, K and Na by flame photometry, Ca by complexometry and Mg by spectrophotometry of the absorption of the Mg-titan yellow.

417

Automated Procedure for the Simultaneous Determination of Phosphorus and Nitrogen in Plant Tissue.

W. D. Basson, D. A. Stanton, and R. G. Bohmer (South African Co-op Citrus Exchange, Lyttelton, Pretoria, South Africa).

Analyst 93, 166-72 (Mar. 1968).

An automated technique for determining P in plant tissue in an aliquot of the acid-digested sample issuing from the AutoAnalyzer Kjeldahl Analyzer digestor unit, by an adaptation of the molybdovanadophosphoric yellow-color procedure, is described. Optimum reaction conditions have been established, and results indicate that the P determination can be made within the limits of accuracy normally acceptable for similar determinations. (9 ref)

418

A Simple Turbidimetric Method of Determining Total Sulfur in Plant Materials.

M. A. Tabatabai and J. M. Bremner (Iowa State Univ., Ames).

Agron. J. 62 (6), 805-6 (Nov.-Dec. 1970).

A rapid method of determining total S in plant materials is described. The plant material is digested in a volumetric flask with nitric and perchloric acid, and the sulfate content of an aliquot of the digest is determined turbidimetrically as $BaSO_4$ by a barium chloride-gelatin procedure. The method is simple and precise, and its results agree closely with those obtained by the Johnson-Nishita method.

419

Comparison of Flame and Burner Combinations in Atomic Absorption Spectroscopy.

C. H. Perrin and P. A. Ferguson (Canada Packers Ltd., Toronto).

J. Ass. Offic. Anal. Chem. 51 (3), 654-8 (May 1968).

Atomic absorption analyses of Ca, Cu, Fe, Mg, Mn, and Zn in eight animal feeds were conducted in which three different burners and six gas combinations were used under a variety of conditions. Statistical analysis of the data showed in most cases superior accuracy with an O-acetylene flame in a total consumption burner on solutions prepared by dry-ashing the samples.

420

An Automated Procedure for the Determination of Boron in Plant Tissue.

W. D. Basson, R. G. Bohmer, and D. A. Stanton (South Africa Co-op. Citrus Exchange, Verwoerdburg, South Africa).

Analyst (London) 94 (1125), 1135-41 (Dec. 1969).

A routine procedure in which the Technicon AutoAnalyzer is used for the determination of B in plant tissue with azomethine H is described. The preparation of the reagent as the condensation product of H-acid and salicylaldehyde is given. The reagent is highly sensitive to B, and only Cu, Fe, and Al interfere. These interference effects are eliminated with an EDTA solution. The procedure is performed in aqueous medium thus simplifying its adaptation to an automated system and its use for routine determination.

421

Entry and Distribution of Aluminum in *Zea mays*: The Mode of Entry and Distribution of Aluminum in *Zea mays*: Electron Microprobe X-Ray Analysis.

H. P. Rasmussen (Mich. State Univ., East Lansing).

Planta 81 (1), 28-37 (1968).

Biol. Abstr. 49, 107275.

The electron microprobe x-ray analyzer (microprobe) has been used to determine the mode of entry of Al and its distribution and localization in the corn plant. Microprobe analysis is a nondestructive method allowing for multiple element analysis in the same tissues, cells, or cell organelles. Al was found to be precipitated on the surface of the epidermal cells of the root with no penetration into the cortex as long as the root surface remained intact. The root cap was freely permeable and contained the highest concentration of Al. The epidermal layer behind the root cap prevented movement into the cortex and conductive tissue. The penetration of a lateral root through the endodermis, cortex, and epidermis provided a channel of entry for Al into the cortex and conducting tissues of both the lateral and main root. Essentially no Al was found in the transition zone and only small quantities were present in the aboveground plant parts. The localization of P was exactly the same as that of Al. This suggested that there was a precipitation of P by Al. A similar analysis for Ca and P on control plants did not reveal such a precipitation. The method of sample preparation was critical in retaining and localizing the elements in question and is discussed in that light.

422

Instrumental Determination of Trace Elements in Plant Tissue by Neutron Activation Analysis and Ge(Li) Gamma-Ray Spectrometry.

W. A. Haller, L. A. Rancitelli, and J. A. Cooper (Pacific Northwest Lab., Battelle Memorial Inst., Richland, Wash.).

J. Agr. Food Chem. 16 (6), 1036-40 (Nov.-Dec. 1968).
A study was made to develop a reasonably simple and essentially contamination-free scheme for multielement analysis of plant tissue by neutron activation and Ge(Li) spectrometry. This instrumental method, which requires no chemical or ashing treatment, eliminates many inherent errors associated with chemical methods. The samples are freeze-dried, neutron-activated, and analyzed by Ge(Li) gamma-ray spectrometry. The resulting spectra are reduced by standard techniques in which the corrected counts are compared with a system of standards to obtain elemental concentrations. The practicality of the method was demonstrated for determining plant-tissue concentrations of Mn, K, Cu, Na, As, Br, P, Rb, Cr, Fe, Hg, Se, Zn, Cs, and Co. An important feature of the method is that a large number of essential trace elements can be measured simultaneously.

423
Elemental Analyses of Plant Leaf Tissue by Several Laboratories.
J. B. Iones. (Ohio Agr. Res. & Develop. Center, Wooster, Ohio).
J. Ass. Offic. Anal. Chem. 52 (5), 900-903 (1969).
Seven plant tissue referee samples (alfalfa, orchard grass, timothy, bermuda grass, wheat, corn, and tomato plants) were analyzed by 18 laboratories for the elements Al, B, Ca, Cu, Fe, K, Mg, Mn, N, Na, P, and Zn. Various analytical methods were used; several laboratories used atomic absorption spectrometry for determination of Ca, Cu, Fe, K, Mg, Mn, Na, and Zn, and flame photometry for Ca, K, and Na. The samples were all roughly prepared by drying, grinding, and mixing before being sent to the laboratories, but then each laboratory treated the sample in its own way before analysis. The results from the various laboratories were compared and found to differ greatly. It is concluded that sample preparation differences, and lack of adequate standards, are the main reasons for this lack of agreement.

424
Potentiometric Titration of Chloride in Plant Tissue Extracts Using the Chloride Ion Electrode.
R. L. LaCroix, *et al* (Univ. Wisconsin, Madison).
Commun. Soil Sci. Plant Anal. 1 (1), 1-6 (Jan. 1970).
Use of the chloride specific ion electrode to determine chloride in plants was evaluated. Direct potentiometric determination of chloride by the electrode resulted in unreproducible and extremely high chloride values. However, use of this electrode to indicate the end point in titration of the tissue-extract mixture with $AgNO_3$ gave results nearly identical to those obtained by the Mohr procedure. The potentiometric titration procedure developed was found to be a rapid, simple, and accurate method of determining the chloride concentration in plants.

425
The Microdetermination of Fluoride in Vegetation.
M. D. Thomas and R. E. Amtower (Univ. California, Riverside).
Air Pollution Control Assoc. 19 (6), 439-42 (June 1969).
A micro method is described for the determination of the fluoride content of plant materials, particularly the leaves. The samples are dried and ground to a fine powder. Fifty mg samples are burned in O_2 in 250-ml separatory funnels or in 300-ml Erlenmeyer flasks. The gaseous products of the combustion are absorbed in 0.1*N* NaOH in the closed funnel or flask and transferred to a small covered plastic dish in which the fluoride is diffused to tiny droplets of 3*N* sodium hydroxide solution distributed over the lower side of a tight fitting cover. The diffused fluoride is dissolved in water and determined colorimetrically by the SPADNS reagent.

426
Plant Sample Analyses as Affected by Sample Decomposition Prior to Laboratory Processing.
R. B. Lockman (AGRICO Chem. Co., Washington Court House, Ohio).
Commun. Soil Sci. Plant Anal. 1 (1), 13-19 (Jan. 1970).
A study was made to estimate the error that could result from analyzing decayed plant samples. Uniform groups of corn leaves were permitted to reach variable degrees of decomposition. Dry wt losses were calculated. Samples were then dried and analyzed to establish apparent analyses. Appreciable dry wt and N losses can occur with sample rotting. Analyses of decayed samples are distinctly different. The results can be completely and seriously misleading. To prevent sample rotting in shipment, fresh plant samples should be partially dried before packaged for shipment to the laboratory.

SEE ALSO the following numbered abstracts in other sections: 41, 288, 349, 356, 366, 372, 374, 376-77, 379, 381, 395-96, 405.

TECHNIQUES

427
Recent Advances in Atomic Absorption Spectroscopy.
J. B. Willis (C.S.I.R.O., Melbourne, Australia).
Rev. Pure Appl. Chem. (Aust), pp. 111-22 (Sept. 17, 1967).
CA 69, 7970.
The review discusses several of the developments in the atomic absorption technique that have occurred in the last 4 yr, and particularly since the fifth Australian Spectroscopy Conference at Perth in June 1965. Specifically included are discussions of light sources (high-intensity hollow cathode lamps, selectively modulated hollow-cathode lamps, and continuous sources), atomization of the sample (long-tube, heated spray-chamber, and high-temperature flame techniques, and direct atomization of solids), wavelength selectors, detectors, amplifiers, and readout systems. The sensitivities of 34 elements to the atomic absorption method with the N_2O-C_2H_2 flame are tabulated (57 ref)

428
Atomic-Absorption Spectroscopy.
J. W. Robinson (La. State Univ., Baton Rouge).
Purif. Inorg. Org. Mater. 1969, pp. 39-46. Edited by Morris Zief, Marcel Dekker, Inc., New York, N. Y.
Sources, monochromators, detectors, optical slit systems, modulation, calibration curves, interferences, flame composition, solvents, procedures, and sensitivities are reviewed.

429
Trends in Analytical Atomic Absorption Spectroscopy.
Walter Slavin and Sabina Slavin (Perkin-Elmer Corp.,

Norwalk, Conn.).
Appl. Spectrosc. 23 (5), 421-34 (1969).
Atomic absorption spectroscopy is reviewed, especially as to the effect of developments in the past few years on analytical applications. Sources and sampling devices are given special attention. Atomic absorption, flame emission, and atomic fluorescence are compared as to their detection limits and their applicability to analysis. The three methods are in many ways complementary rather than competing. The potentialities of resonance spectroscopy are examined and instrument systems utilizing resonance methods are described. (72 references).

430

Applications of Background Correction to Trace Metal Analysis of Geochemical Samples by Atomic-Absorption Spectrophotometry.

K. Fletcher (Univ. British Columbia, Vancouver, Canada).
Econ. Geol. 65 (5), 588-9 (1970).
The use of H lamp continuum in the determination of trace metals in geochemical samples is reported. Background absorption was measured by replacing the hollow-cathode lamps with a H lamp giving a spectral continuum at 2000-4000 Å. The solutions were reaspirated and absorbance measured. Differences between corrected and uncorrected data are most marked for Co, Ni, and Pb, with uncorrected values up to three times too high.

431

Multielement Lamp Gives Good Precision with Model 403 Atomic Absorption Spectrophotometer.

W. B. Barnett and H. L. Kahn (Perkin-Elmer Corp., Norwalk, Conn.).
Instrum. News 20 (1), 4-5 (1969).
Good precision is obtained with the Model 403 atomic absorption spectrophotometer equipped with the Intensitron multielement hollow cathode lamp; for Al, Si, Ca, Mg, Fe, Cu, and Zn, the repeatability is $\leq 0.3\%$ of the amount present. Meaningful determinations of analysis precision and of detection limit are obtained by using the TR-1 typewriter readout for the Model 403.

432

Interferences of Acids in Atomic Absorption Spectrophotometry.

Toshihisa Maruta, Masami Suzuki, and Tsugio Takeuchi (Fac. Eng., Nagoya Univ., Nagoya, Japan).
Anal. Chim. Acta 51 (3), 381-5 (1970).
CA 73, 83503.
Hydrochloric acid, $HClO_4$, HNO_3, and H_3PO_4 were examined to elucidate the mechanism of their interferences on the atomic absorption spectrophotometry of Cu, Fe, and Cr. The interferences were complex in nature and varied for different elements and for different acids. The mechanism of the interferences is discussed.

433

Atomic Absorption Spectroscopy with High-Temperature Flames.

J. B. Willis (Iowa State Univ., Ames).
Appl. Optics 7 (7), 1295-304 (1968).
An account is given of the history of the development of high temperature flames for the atomic absorption measurement of metals forming refractory oxides. The principles governing the design of premix burners for such flames, and the relative merits of different types of nebulizer burner systems are described. After a brief account of the structure and emission characteristics of the premixed $O\text{-}C_2H_2$ and $N_2O\text{-}C_2H_2$ flames, the scope and limitations of the latter flame in chemical analyses are discussed. (102 ref)

434

Heated Chamber Burner for Atomic Absorption Spectroscopy.

A. A. Venghiattis (Perkin-Elmer Corp., Norwalk, Conn.).
Appl. Optics 7 (7), 1313-16 (1968).
A new heated chamber burner is described. The burner is of the premixed type and burner heads of the types conventionally used in atomic absorption may be readily adapted to it. This new sampling system has been tested for Ag, Al, Ca, Cu, Fe, Mg, Mn, Ni, Pb, Si, Ti, and Zn in aqueous solutions. An improvement of the order of 10 times has been obtained in sensitivity, and in detection limits as well, for the elements determined. Interferences are somewhat more severe than in conventional burners but are controllable.

435

Use of Mixed Air/Nitrous Oxide (N_2O)/Acetylene Flames in Atomic Absorption Spectroscopy.

H. D. Fleming (The Broken Hill Proprietary Co., Ltd., Newcastle, N.S.W., Australia).
Spectrochim. Acta 23B (3), 207-13 (1967).
A system is described in which air and nitrous oxide mixtures are used with acetylene to produce high temperature flames. These flames cover the temperature range between the air/acetylene and nitrous oxide/acetylene flames. The advantages provided by the system are flexibility and safety. An optimum flame setting for the determination of Mg is suggested.

436

Atomic Absorption by the Double Aspiration Method. II. Some Aspects of the Enhancement of Atomic Absorption in the Double Aspiration Method.

Mitsutomo Tsuhako and Eiichi Sekido (Fac. Sci., Kobe Univ., Kobe, Japan).
Bunseki Kagaku 19 (4), 531-6 (1970) (Japan).
CA 73, 51924.
The effects on the atomic absorption intensity of Ca or Mg of substances such as acids, alkalies, salts, and alcohols were examined by use of a glass chamber equipped with two atomizers. Increasing the concentration of $HClO_4$, NaOH, NaCl, NH_4Cl, NH_4NO_3 and alcohols multiplied the atomic absorption intensity at least twice. The sensitivity was increased considerably by increasing the flow rate of C_2H_2. Such an increase of sensitivity was also found in the atomic absorption of Zn and Fe and in the flame emission of Ca and Mg, corresponding to an increase of the atom density in the flame. The increase of atomic absorption intensity is due to various factors including: the ease of dehydration of hydrated metal ion; the enhancement of thermal decomposition of molecules containing a metal atom; and depression of the metal oxide formation of reduction of the oxide in the flame by other substances. (For Part I, See *FA 3*, 1773)

437

Laser-Microanalysis by Atomic Absorption.

V. G. Mossotti, K. Laqua, and W. D. Hagenah.
Spectrochim. Acta 23B (3), 197-206 (1967).
A technique for estimating the concentration of trace constituents in microanalytical samples by atomic absorption is described. Material from a preselected area of an analytical specimen is laser evaporated into the optical path of an atomic absorption spectrometer. The peak absorption in the time-

resolved absorption spectrum is used for the analytical signal. Working curves and detection limits are presented for several elements in a variety of matrices. Analytical sensitivities are on the ppm level for some elements, but they are highly dependent on the host material.

438

Electronically Modulated Microwave – Excited Electrodeless Discharge Tubes as Sources in Atomic Absorption Spectroscopy.

R. F. Browner, R. M. Dagnall, and T. S. West (Imperial Coll., London, Engl.).

Anal. Chim. Acta 45 (1), 163-70 (Mar. 1969).

Electronic modulation of a selected range of electrodeless discharge tubes is achieved by superimposing a 50 Hz component on the d.c. potential of the anode of the magnetron valve. The effect of modulation is favorable and the usual methods of tube preparation are satisfactory. The source spectra for Pb, Hg, Ag, Tl, and Sn are compared with those for the corresponding hollow-cathode lamps and the analytical atomic absorption working curves obtained with the various sources are compared. The sources for Pb and Sn give considerably higher sensitivity and a wider working range than the hollow-cathode lamps because of the absence of continuous background or non-absorbing lines near the resonance line. The Hg source behaves similarly, probably because of less self-reversal.

439

Trace Analysis by Atomic Absorption Spectrophotometry – A Sequential Multi-Element Approach by Solvent Extraction.

B. Montford (Whiteshell Nuclear Res. Estab., Pinawa, Manitoba, Canada).

Can. Spectrosc. 13 (5), 126-30 (1968).

The use of solvent extraction in conjunction with atomic absorption spectroscopy was investigated as a sensitive method of analysis. Six different chelating agents and six organic solvents were studied and compared. A sodium diethyl dithiocarbamate (NaDDC)-methyl isobutyl ketone (MIBK) system showed a 100-fold gain in sensitivities compared to aqueous solutions for Fe, Cu, Co, Cr, Mn, and Ni. The metals are pre-concentrated simultaneously and determined sequentially using a multi-element hollow cathode lamp. A procedure is described for analysis in the concentration range 0-50 micrograms/liter. Eight samples can be analyzed for six metals in 90 minutes.

440

The Use of Water-Miscible Organic Solvents in Atomic Absorption Spectrophotometry.

V. K. Panday and A. K. Ganguly (Bhabha Atomic Res. Center, Trombay, India).

Anal. Chim. Acta 52 (3), 417-23 (Dec. 1970).

The enhancement of the absorption signal of an element obtained through the use of organic solvents in the sample solution is well known and is believed to arise, among other factors, because of an increase in the proportion of finer droplets. Although chemical interferences are usually expected to be a function of droplet size, the effectiveness of organic solvents in reducing many of these interferences did not receive much attention until recently. The purpose of the work was to study the use of some water-miscible organic solvents for reducing chemical interferences in addition to increasing analtyical sensitivities by atomic absorption methods.

441

Automated Methods for Total Nitrogen, Direct Available Phosphorus Pentoxide, and Potassium Oxide in Fertilizers.

C. W. Gehrke, F. E. Kaiser, and J. P. Ussary (Univ. Missouri, Columbia).

Automat. Anal. Chem. Technicon Symp., 3rd, 1, 239-51 (1967) (Pub. 1968); Mediad Inc.: White Plains, N. Y.

Precise and accurate automated methods are given for the spectrophotometric determination of total N and direct available P, and the flame photometric determination of K in fertilizers. The methods are applicable to all types of fertilizers. The sampling rates give 40 analyses/hour. (22 references)

442

Determination of Phosphorus and Sulfur in Fuel-Rich Air-Hydrogen Flames.

A. Syty and J. A. Dean (Univ. Tennessee, Knoxville).

Appl. Optics 7 (7), 1331-6 (1968).

Excitation conditions for the green HPO bands, the uv PO bands, and the violet S_2 bands were explored. A cylindrical glass shield placed around the tip of a Beckman (sprayer) burner provided a simple arrangement to isolate a fuel rich environment of a reversed air-hydrogen flame. Samples were converted to aerosol in a separate nebulization chamber. The HPO band at 5262 Å gave a detection limit of 6 micrograms/ml; the S_2 band, 5 micrograms/ml. Owing to low flame noise, both detection limits could be improved with interference filters in place of the Beckman small quartz monochromator. The PO bands are emitted best from fuel rich oxygen-acetylene flames with the normal Beckman sprayer burner. The significant aspect of this study lies in the introduction of liquid samples and circumvention of lengthy, and often uncertain, decomposition steps when handling many types of organic and biochemical compounds containing P and S.

443

A Molecular Emission Method for Determining Anions Containing Phosphorus and Sulfur.

K. G. Brodie (Varian Techtron Pty. Ltd., Walnut Creek, California).

Resonance Lines 1 (3), 1-4 (1970).

At. Absorption Flame Emission Spectrosc. Abstr. 2, 653.

A method is described for the determination of anions containing P and S using a conventional atomic absorption spectroscopy unit with flame emission facility. A flat top Techtron burner with a shield prevents air being entrained in the fuel rich air/H_2 flame. Molecular emission takes place in the cool regions of the flame near the shield. The detection limit using air-hydrogen flame is about 1 ppm for P, and about 10 ppm for S. Difficulties arise in the analysis of P or S when a large excess of metal ions or certain anions are present. Amberlite cation exchange resin is used to remove cationic interferences. Analysis of coal ash by this method gives results within 10% of those obtained by the $BaSO_4$ precipitation method.

444

Determination of Phosphorus, Arsenic, or Silicon by Atomic Absorption Spectrometry of Molybdenum Heteropoly Acids.

T. V. Ramakrishna, J. W. Robinson, and P. W. West (Louisiana State Univ., Baton Rouge).

Anal. Chim. Acta 45 (1), 43-9 (Mar. 1969).

Trace amounts of P, As, or Si were determined by the title method. The heteropoly-molybdo acids of P, As, and Si were formed and selectively separated by means of organic solvent

extraction; the Mo present in the organic phase was determined by atomic absorption spectroscopy with an N_2O–C_2H_2 flame. The method is rapid, simple, and accurate and is essentially free from interferences.

445

Analysis of Inorganic Siliceous Materials by Atomic Absorption Spectrophotometry and the Hydrofluoric Acid Decomposition Technique. Part I. Analysis of Silicate Rocks

F. J. Langmyhr and P. E. Paus (Univ. Oslo, Norway).

Anal. Chim. Acta 43 (3), 397-408 (Dec. 1968).

Analysis of various inorganic siliceous materials of geological and industrial interest is discussed. The methods proposed are based on decomposition of a single sample by HF and determination of up to 10 constituents by atomic absorption spectrophotometry using a Perkin-Elmer model 303 atomic absorption spectrophotometer. Two types of burners were employed: a 3-slot Boling burner for C_2H_2-air flames and a N_2O burner for C_2H_2-N_2O flames. General procedures are described and details are given for determination of Si, Al, total Fe, Mg, Ca, Na, K, Ti, and Mn in silicate rocks. Analytical data are given for the analysis of reference rocks G-2 and W-1. (23 references)

446

Atomic Absorption Analysis of Silicates Employing $LiBO_2$ Fusion.

J. H. Medlin, N. H. Suhr, and J. B. Bodkin (Pennsylvania State Univ., University Park).

At. Absorption Newslett. 8 (2), 25-9 (March-Apr. 1969).

A rapid and simple atomic absorption procedure for the determination of Si, Al, Fe, Mg, Ca, K, Na, Mn, Cr, Sr, Ti, Cu, and Zn in silicate rock and mineral samples from one solution has been developed. The samples are fused with $LiBO_2$ and dissolved in a dilute nitric acid solution followed by a variable dilution with a La solution or water. There are no chemical separations or modifications of the instrument or special apparatus involved. Comparison of the results with fourteen rock and mineral standards shows good agreement.

447

Analysis of Rocks and Minerals by Atomic Absorption Spectroscopy. III. Lithium-Fluoroborate Scheme for Seven Major Elements.

Sydney Abbey (Geol. Surv. Canada, Ottawa, Can.).

Geol. Surv. Can., Pap., No. 70-23, 20 pp (1970).

A new analytical scheme is proposed, whereby SiO_2, Al_2O_3, total Fe, Mg, Ca, Na, and K are determined in silicate rocks and minerals by atomic absorption spectroscopy. Samples are decomposed by fusion with Li metaborate, the fusion is dissolved in dilute HF, and excess fluoride is complexed by the addition of H_3BO_3. The resulting stable solution contains all of the nonvolatile components of the sample, and aliquots are analyzed by comparison with solutions similarly prepared from international reference samples of rocks. Possible extension of the method to other components is discussed.

448

Determination of Nonmetals by Atomic Absorption Spectrophotometry.

G. D. Christian and F. J. Feldman (Walter Reed Army Medical Center, Washington, D.C.).

Anal. Chim. Acta 40 (2), 173-9 (Feb. 1968).

Inorganic anions and organic compounds were determined using conventional atomic absorption apparatus. Several methods were studied in which the desired compound either limits or interferes with the determination or absorption of a metal. A direct relationship was obtained between the absorption by the metal and the amount of substance sought. Substances determined include orthophosphate, sulfate, iodide, sulfide, iodate, glucose, protein, 8-hydroxyquinoline, EDTA, and ammonium pyrrolidine dithiocarbamate. (18 ref)

449

A New Type of Interference in Atomic Absorption or Emission Measurements with the Premixed Nitrous Oxide-Acetylene Flame.

S. R. Koirtyohann and E. E. Pickett (Univ. Missouri, Columbia).

Anal. Chem. 40 (13), 2068-70 (Nov. 1968).

Interference caused by the presence of mineral acids in sample solutions is discussed. Data are given for the change in emission signals for a number of elements as a function of the perchloric acid concentration.

450

Atomic Emission Characteristics of a Premixed Acetylene-Nitrous Oxide, Total Consumption Flame.

V. G. Mossotti and Marjorie Duggan (Univ. Illinois, Urbana).

Appl. Optics 7 (7), 1325-30 (1968).

Most of the burners presently used to produce high temperature, premixed flames have the tendency to be discouragingly wasteful of the sample solution, often bringing only a small fraction of the amount used into the flame. The construction and performance are described of a highly efficient total consumption burner that produces a nonturbulent C_2H_2-N_2O flame from premixed gases. The 18 flame emission detection limits tabulated for a select group of elements compare favorably with the best values heretofore reported in the literature, and the apparent freedom of alkaline earth emission from phosphate interference indicates the total consumption flame here described to be less subject to chemical interference than is the conventional diffusion flame. The relative low cost burner that has been developed is convenient to operate and can be quickly assembled from commercially available components. (19 ref)

451

Interelement Interferences in Atomic Absorption Analyses with the Nitrous Oxide-Acetylene Flame.

J. Y. Marks and G. G. Welcher (Advan. Mater. Res. and Develop. Lab., Pratt and Whitney Aircraft, Middletown, Conn.).

Anal. Chem. 42 (9), 1033-40 (1970).

The effects of flame and instrumental variables on cation interference effects were evaluated. The variables most critical in determining the magnitude of cation interferences are the height of measurement, fuel to oxidant ratio, and concentration of analyte in the salt matrix. Many of the observed interferences were reduced with the proper selection of operating parameters. Possible interference mechanisms, such as lateral diffusion of analyte in the flame and competition for O were studied. Salt vaporization effects were the most critical in determining interference effects. A new, more pertinent method of expressing flame conditions is presented. The new parameter expresses the oxidant to fuel mole ratio as a fraction of the stoichiometric ratio of three moles of N_2O to 1 mole of C_2H_2.

452

Atomic Fluorescence Flame Spectrometry.

J. D. Winefordner and J. M. Mansfield (Univ. Florida, Gainesville).

Fluorescence, pp. 565-625 (1967).

CA 69, 7960.

Atomic fluorescence flame spectrometry (A.F.) is based on absorption of radiation, in a flame cell, by an atomic vapor producing excited atoms and the measurement of the radiation emitted when a fraction of these atoms lose their energy by a radiation process. The development of A.F. is reviewed, and the various processes of resonance, direct line, stepwise line, and sensitized fluorescence and their applications are discussed. The theory of A.F. is discussed with particular attention to the profile of atomic absorption lines, including broadening of these lines by Doppler, collisional, and resonance effects. Expressions for total absorption and intensity of atomic fluorescence are given. The effect of flame temperature and sample concentration on atomic concentrations are considered. A.F. has been found useful for only a limited number of elements. These are Zr, Cd, Hg, Cu, Pb, Tl, Ag, Au, Bi, Ga, Mg, Ni, Co, and In. (40 ref)

453

Atomic Fluorescence Flame Spectrometry: Potential Tool for Trace Analysis.

D. R. Demers (Univ. New Hampshire, Durham).

Appl. Spectrosc. 22 (6), 797-9 (1968).

The technique of atomic fluorescence flame spectrometry as a tool for trace analysis of metal was studied. When the O-H flame was used the signal intensity increased as the O_2 flow rate decreased; the greatest signal was obtained when only a H_2/entrained-air gas mixture is used. A high-intensity line source gave significantly lower detection limits than a continuum source and were equal or superior to those obtained with atomic absorption or thermal emission methods. Most interferences can be eliminated by making sample solution 1% $SrCl_2$.

454

Flame Emission Spectroscopy with the Nitrous Oxide-Acetylene Flame.

G. D. Christian (Univ. Kentucky, Lexington) and F. J. Feldman (Instrumentation Lab. Inc., Lexington, Mass.).

Abstr. Pittsburgh Conf. on Anal. Chem. and Appl. Spectrosc. 1970, March 1-6, 107.

At. Absorption Flame Emission Spectrosc. 2 (4), 189 (Abstr. No. 512) (July-Aug. 1970).

The optimum conditions for the use of the nitrous oxide-acetylene flame in the flame emission spectroscopic analysis of 68 elements are investigated. An Instrumentation Laboratory Model 153 atomic absorption emission spectrometer is used. Optimum wavelengths, slit widths, photomultiplier voltages, flame composition, "red feather" height, height of observations, and signal interpretation are found for each element. Detection limits are given and compared with those from atomic absorption spectroscopic analysis.

455

Analytical Flame Spectroscopy.

R. I. Bystroff (Lawrence Radiat. Lab., Univ. of California, Livermore).

Tech. Metals Res. 3 (Pt. 1), 185-223 (1970).

CA 73, 83452.

A review of the title subject is given. Introduction of the sample, the burner and flame, principles of flame emission and of atomic absorption, and sources for atomic absorption spectroscopy are discussed. Processes in the flame which affect the analyte are discussed as well as a general explanation of the spectrometer. An arrangement of the detection limits by groups in the Periodic Table is given. (118 ref)

456

Rapid Consecutive Determination of Ammonium, Calcium, and Magnesium Ions in a Single Sample of Fertilizer.

D. Ceausescu and Ana Sirbu (Univ. Timisoara, Romania).

Z. Chemie, Lpz. 10 (7), 272 (1970) (Ger).

Anal. Abstr. 20, 4376.

Detailed instructions are given for determining NH_4^+ by displacement of NH_3 with formaldehyde and titration of liberated acid with NaOH solution (thymolphthalein as indicator). EDTA is used for the subsequent complexometric titration of Ca^{2+} (murexide as indicator) and then of Mg^{2+} (Eriochrome black T as indicator) with use of a 'background' of methyl orange to give sharper end-points.

457

Complete Chemical Analysis of Khibin Apatite-Nepheline Rocks.

L. D. Nikitina.

Metody Anal. Rud Kol'sk. Poluostrova, pp. 188-95 (1970) (Russ).

CA 76, 10064.

A system for separation of elements with subsequent determination of Mg; the sum of Al_2O_3, Fe_2O_3, and TiO_2; Ca, Sr, and rare earth elements in nepheline-apatite rocks with various mineralogical composition was developed. A sample (0.5 g) was dissolved in a mixture of 10 ml HF, 6 ml H_2SO_4 (1:1), and 2-4 ml HNO_3. The salts were dissolved in dilute HCl, diluted with ~150 ml H_2O. Oxalic acid (10%) and 50 ml saturated $(NH_4)_2C_2O_4$ solution were added and the solution was heated to 50° (pH 7). The precipitate was washed with 0.2% $(NH_4)_2C_2O_4$. The filtrate (*A*) was kept. The precipitate was dissolved in 25 ml HCl (1.4), diluted with H_2O to ~100 ml, 5-10 ml saturated $(NH_4)_2C_2O_4$ and 2 ml 10% Complexon III were added The precipitate (*B*) was rinsed with 0.2% $(NH_4)_2C_2O_4$ and kept. The filtrate was combined with filtrate *A* and 5 ml 10% Complexon III and 7-50 ml 6% hydroxyquinoline in 5% HCl were added The precipitate was washed with 2% NH_4OAc, filtered, and the sum of Al_2O_3, Fe_2O_3, and TiO_2 was weighed. Nitric acid (20 ml) and 10 ml H_2O_2 were added to the filtrate and the solution was boiled to remove N oxides. Diammonium phosphate (10 ml 10%) and 2-3 drops methyl red indicator were added and the solution was neutralized with 10% NH_4OH to a yellow color. The precipitate (*C*) was washed with NH_4OH (1 25), filtered off, and added to precipitate *B*. Hydrochloric acid (4 ml), 1-2 ml 10% $(NH_4)_2HPO_4$, and 0.1 g citric acid were added to the filtrate and precipitation occurred with the dropwise addition of NH_4OH. The precipitate was washed with NH_4OH (1:95), calcined at 1000-100°, and MgO was weighed. The sum of rare earth elements was determined in the combined precipitates *B* and *C*. The weighed precipitate was dissolved in HNO_3 and 2-4 drops H_2O_2 and diluted to 100 ml with H_2O Arsenazo III (10 ml 0.005%) and 8 ml 25% urotropine were added to an aliquot containing 10-30 μg rare earth elements, the solution was diluted to 100 ml with H_2O and analyzed photometrically. Strontium and Ca contents were established by difference.

458

Rapid Chemical Analysis Method for Gypsum Stone and Gypsum-Containing Rocks.

A. G. Gegenava and A. M. Chkhikvadze.

Sb. Tr., Tbilis. Gos. Nauch.-Issled. Inst. Stroit. Mater., No. 3, 311-17 (1968) (Russ).

CA 74, 60513.

A method for rapid chemical analysis of gypsum stone or gypsum-containing rocks by using a complexometric method for determination of Fe, Al, Ca, Mg, and SO_3 is proposed. The

method is applicable for analysis of gypsum-containing rocks in the presence of Glauber's salt and other impurities in a sample. For separation of Na_2SO_4, 50% Et_2O solution was used.

459

Analysis of a Solution Containing Ammonium Sulfate, Sulfite, Nitrate and Nitrite, Free Ammonia, and a Complex of Ammonium Sulfite with Nitric Oxide.

M. L. Varlamov, G. A. Manakin, and L. S. Zbrozhek (Odess. Politekh. Inst., Odessa, USSR).

Izv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol. 11 (11), 1261-4 (1968) (Russ).

CA 70, 92940.

A complex salt solution resulting from the ammoniacal treatment of the gas from a nitrose-H_2SO_4 system was analyzed. Free alkali or acid is determined acidimetrically by using methyl red. Total NH_4^+ (not bound to SO_3^{--}) is determined by the HCHO method. After preliminary removal of SO_3^{--} with HCHO in an alkaline medium, EtOH is used to determine the NO_2^- concentration as $EtNO_2$. $(NH_4)_2SO_3$ is determined with alkaline $KMnO_4$. Total N oxides are determined with a nitrometer, and NO_3 is calculated by difference between the nitrometer data and NO_2^-. The total content of S compounds is determined gravimetrically after oxidation with Br. The sum of the sulfate and the complex is calculated by the difference between the gravimetric value and the alkaline $KMnO_4$ value. The average error in this method of analysis is $\leq 5\%$.

460

Methods for Preparing Samples for the X-Ray Quantitative Analysis of Mineral Fertilizers.

B. M. Maslennikov and A. I. Soklakov (Nauchno-Issled. Inst. Udobr., Insektofungits., Moscow, U.S.S.R.).

Rentgenogr. Miner. Syr'ya, No. 7, 144-7 (1970) (Russ).

CA 76, 58127.

Instead of using an internal standard (*CA 62*:15379h), mechanical standard mixtures were used to give a much higher accuracy in the determination of mixed fertilizer phase composition. (Relative error ± 10% as compared with ±25% for the method with the internal standard.) To obtain reproducible results, a very precise standardization of the conditions of preparing initial substances and standard mixtures is necessary as well as a strict control of the degree of disintegration of standards and their moisture content. Preparation of standard mixtures in a dry chamber is recommended. Introduction of various disintegrating additives (especially 1-1.5% graphite) has an inhibiting effect on the course of the chemical reaction, the occurrence of recrystallization phenomena, and other secondary processes.

461

Thermographic Analysis of Ammonium Phosphates.

M. N. Nabiev, *et al.*

Zh. Neorg. Khim. 14 (11), 2950-3 (1969) (Russ).

CA 72, 62390.

X-ray diffraction patterns are given for $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, and $(NH_4)_3PO_4 \cdot 3H_2O$. The latter compound loses one NH_3 easily and is converted to a diammonium phosphate which has a different powder diffraction pattern than that of $(NH_4)_2HPO_4$. Differential thermal analysis of $NH_4H_2PO_4$ shows only one endothermic effect (at 200°) corresponding to melting. When (NH_4) HPO_4 is heated it partially loses NH_3 at 155° and melts at 185°; $(NH_4)_3PO_4 \cdot 3H_2O$ melts incongruently at 60° and loses H_2O at 110° with simultaneous decomposition to $(NH_4)_2HPO_4$ which subsequently melts at 180°.

462

Simultaneous X-Ray Emission Analysis of Phosphorus, Silicon, Calcium, Iron, Aluminum, and Magnesium in Phosphate Rock Using a Small Computer to Correct for Matrix Variations.

C. N. McKinney and A. S. Rosenberg (Continental Oil Co., Ponca City, Okla.).

Advances in X-Ray Analysis. B. L. Henke (Univ. Hawaii, Honolulu), J. B. Newkirk and G. R. Mallett (Univ. Denver, Colorado) (Editors) Vol. 13, 681 pp (1970).

Phosphate rock from different sources varies widely in composition; this results in a large interelement effect. A mathematical model was developed to correct for matrix variations in each sample. This model utilizes the x-ray intensity from each of the six elements considered and the mass absorption coefficients of the elements to calculate concentrations. Accurate analyses for P, Si, Ca, Fe, Al, and Mg are obtained by using this model. The x-ray instrument is interfaced with a small computer that performs the calculations on each sample and prints the results. Sample preparation, standardization, and the computer programs used for the sample calculation and standardization are discussed.

463

X-Ray Fluorescence Analysis of Ferrophosphorus and Slag from the Electric-Reduction Furnace Manufacture of Elemental Phosphorus.

F. M. Yelinek, A. J. Graffeo, and R. L. Carroll (Mobil Chem. Co., Richmond, Va.).

Appl. Spectrosc. 24 (2), 247-9 (1970).

X-ray fluorescence analysis has been applied to the determination of Si, P, and Fe in the ferrophosphorus and slag which are by-products in the manufacture of elemental P by reduction of phosphate rock in the electric furnace. Accuracy comparable to chemical analysis is obtained in a considerably shorter time, a factor important in production control.

464

Infrared and X-Ray Studies of Urea-Monocalcium Phosphate Complex.

M. K. Sen, *et al.* (Fertilizer Corp. India Ltd., Bihar).

Technology (Sindri) 5 (3), 181-5 (July-Sept. 1968).

The system urea-$Ca(H_2PO_4)_2 \cdot H_2O$ was studied by x-ray and infrared spectroscopy to gain information on the mechanism of reactions occurring between urea and $Ca(H_2PO_4)_2$ in fertilizer mixtures. The results indicated that urea probably replaces the water of crystallization of $Ca(H_2PO_4)_2 \cdot H_2O$ in forming the complex $Ca(H_2PO_4)_2 4CO(NH_2)_2$. This is corroborated by the fact that anhydrous $Ca(H_2PO_4)_2$ does not form the complex [Frazier, Lehr, and Smith, *J. Agr. Food Chem. 15*, 345 (1967)].

465

Thermographic and X-Ray Diffraction Methods for Analyzing Complex Fertilizers.

M. T. Saibova, *et al.* (Inst. Khim., Tashkent, USSR).

Uzb. Khim. Zh. 12 (5), 3-7 (1968) (Russ).

CA 70, 105459.

Formation of various components of the commercial fertilizer, SUM-III, containing N, P, and K was studied by x-ray and D.T.A. Thermograms were obtained for the following mixtures: $Ca(NO_3)_2 \cdot 4H_2O + H_3PO_4$, $KCl + H_3PO_4$, $KH_2PO_4 + Ca(NO_3)_2 \cdot 4H_2O$ (1:1), and $KH_2PO_4 + Ca(NO_3)_2 \cdot 4H_2O$ (1:1) by heating them to 500° at 15-17°/minute. The thermal decomposition curves indicated the formation of monocalcium phosphate: $Ca(H_2PO_4)_2 \cdot H_2O \xrightarrow[160\text{-}180^\circ]{-H_2O} Ca(H_2PO_4)_2$, then $Ca(H_2PO_4)_2 \xrightarrow[250\text{-}270^\circ]{-H_2O} Ca_2H_2P_2O_7$. The observed effects at 130-140° for the KH_2PO_4-$Ca(NO_3)_2 \cdot 4H_2O$ mixture indicate

the formation of $CaHPO_4$ and KNO_3. Calculated thermodynamic parameters for the reaction of H_3PO_4 with KCl and $Ca(NO_3)_2$ with KH_2PO_4 are tabulated and analyzed.

466

Characterization of Phases Formed in Acidulated Rock Phosphate and Their Estimation by X-ray Diffraction Method.

S. C. Chatterjee, A. Guha, and S. K. Ghosh (Fertilizer Corp. India Ltd., Sindri, India).

Technology (Sindri) 5 (2), 92-7 (Apr.-June 1968).

Jordan phosphate rock (P_2O_5 34.45, CaO 52.40, F 5.68, CO_2 4.75, SiO_2 2.5, and R_2O_3 0.22%) was acidulated with H_2SO_4 in varying degrees from 5-100% acidulation. The reaction products were examined by x-ray diffraction. It was found that mono-, di-, and tricalcium phosphate could be estimated directly in the acidulated rock by x-ray diffraction. The compositions computed by x-ray analysis were usually lower than those determined by chemical analysis where citrate-insoluble P_2O_5 is assumed to be tricalcium. citrate-soluble as dicalcium, and H_2O-soluble as monocalcium phosphate.

467

Ion-Selective Electrodes.

Nat. Bur. Stand. (U. S.) Spec. Publ. 314, 474 pp. (1969). R. A. Durst, Editor. Available GPO $3.50. Ch. 2, Solid-State and Liquid Membrane Ion-Selective Electrodes. J. W. Ross (Orion Res., Inc., Cambridge, Mass.) pp. 57-58.

Measurement of ion activities by ion-selective membrane electrodes is rapid and nondestructive and avoids pretreatment of sample or complicated equipment. Disadvantages are inaccuracy and uncertainty in the definition of ion activity. The mechanism and theory of membrane electrodes are discussed. Phosphate ester systems are good for Ca^{2+} determination. A table of ion selectivities and the required liquid systems is given. The selectivity and low resistance of solid state systems depends on the properties of the crystals alone. La fluoride is a good detector for F^-, as is Ag_2S for S^{2-}. The Ag_2S-Ag halide mixed system is a good detector for the halides, and Ag_2S-metal sulfide mixed system is good for S^{2-}.

468

Ion-Selective Electrodes.

Nat. Bur. Stand. (U.S.) Spec. Publ. 314, 474 pp. (1969). R. A. Durst, Editor. Available GPO $3.50. Ch. 10, Industrial Analysis and Control with Ion-Selective Electrodes. T. S. Light (Foxboro Co.; Foxboro, Mass.) pp. 349-74.

The principles and operation of ion-selective electrodes, related to their use in industrial analytical instrumentation, are discussed in detail. Principle interferences and pH ranges suitable for analyses are listed for the ions for which electrodes are currently available. Many applications for monitoring liquid and gaseous streams are described. (26 ref)

469

Ion-Selective Electrodes.

Nat. Bur. Stand. (U. S.) Spec. Publ. 314, 474 pp. (1969). R. A. Durst, Editor. Available GPO $3.50. Ch. 9, Analytical Studies on Ion-Selective Membrane Electrodes. G. A. Rechnitz (State Univ. New York, Buffalo, New York). pp. 313-48.

The various analytical studies which may be performed by using ion-selective membrane electrodes are discussed, including theoretical aspects of the principles of operations, studies of complex formation, and kinetic studies.

470

Ion-Selective Electrodes.

Nat. Bur. Stand (U. S.) Spec. Publ. 314, 474 pp. (1969). R. A. Durst, Editor. Available GPO $3.50. Ch. 11, Analytical Techniques and Applications of Ion-Selective Electrodes. R. A. Durst (Inst. Mater. Res., Nat. Bur. Stand., Washington, D. C.) pp. 375-414.

Various techniques including direct potentiometry and specific applications for the determinations of F^-, Ca^{++} NO_3^-, BF_4^-, ClO_4^-, CN^-, Ag_2S, Mg^{++}, Cu^{++}, Pb^{++}, Cd^{++}, SCN^-, and halides are discussed.

471

Ion-Selective Electrodes: Theory and Applications in Water Analysis.

J. B. Andelman (Univ. of Pittsburgh, Pa.).

J. Water Pollut. Contr. Fed. 40 (11), Pt. 1, 1844-60 (1968).

Anal. Abstr. 18, 1299.

The principles of operation of membrane-type ion-selective electrodes for the determination of a wide range of ions, including F^-, NO_3^-, S^{2-}, Na^+, K^+, and Ca^{2+}, and total hardness (bivalent ions), are considered, together with the use of these electrodes for sensing equivalence-points in potentiometric titrations. The effects of ion-binding, electrode selectivity and methods of calibration, the precision of direct potential measurements with these electrodes, and the sensitivity of membrane-electrodes and their applications in water analysis are also reviewed and discussed. (35 ref)

472

Ion Electrodes Make Control Easier.

Can. Chem. Process 54 (2), 35-6 (Feb. 1970).

Glass membranes that allow both ion exchange and interstitial chain movement of cations are used as sensors for univalent cations such as Na^+, K^+, H^+, Ag^+, Cs^+, Rb^+, and NH_4^+. Newer electrodes that use organic anion or cation exchange liquids in conjunction with such membranes as ultrafine fritted glass, inorganic crystals, and neutron-bombarded regenerative cellulose films and polycarbonates are finding application in pollution and oceanographic monitoring and in industrial control. A limitation is that they usually are only moderately selective for the ion of interest. New electrodes permit measurement of the concentrations of F^-, Cl^-, Ca^{2+}, and the partial pressure of O_2 dissolved in a liquid or mixed with other gases.

473

New Directions for ion-selective electrodes. Comments.

R. H. Mueller.

Anal. Chem. 41 (12), 113A-114A, 116A (1969).

An empirical approach is described for graphically predicting the equilibrium, electromotive force and the half-time (time required for the electromotive force to reach half the final equilibrium value) of an electrode from experimental data. The calculated values agree with observed values, with the same precision with which the experimental data are known.

474

New Directions for Ion-Selective Electrodes.

G. A. Rechnitz (State Univ. New York, Buffalo).

Anal. Chem. 41 (12), 109A-113A (1969).

Electrode development and applications mutually stimulate one another. The outlook for the future indicates that ion-selective electrodes will play an important part in measurement in science. The development of the following types of ion-selective electrodes is reviewed: immobilized (matrix) liquid membrane electrodes; mixed-crystal membrane electrodes; enzyme electrodes; antibiotic electrodes.

Applications of the electrodes are discussed briefly. (19 references)

475

Analytical Studies with Ion-Sensitive Electrodes.

Friedrich Oehme.

Galvanotechnik 61 (2), 133-41 (1970) (Ger).

CA 72, 139194.

A review of the title subject is given. Properties of ion-sensitive electrodes, commercial available ion-sensitive electrodes, ion meters, analytical methods for ion-sensitive electrodes, activity measurements, measurements according to the total-ionic-strength-adjustment-buffer method, and double measurements according to a method in which the electrode is used for measurements of a sample solution both before and after addition of a standard are discussed. (11 ref)

476

Ion-Selective Electrodes in Science, Medicine, and Technology.

R. A. Durst (Natl. Bur. Stand., Washington, D.C.).

Amer. Sci. 59 (3), 353-61 (1971).

The applications of ion-selective electrodes are reviewed. The species detectable by commercially available electrodes are Cd, Ca, Cu, H^+, Pb, Hg, K, Ag, NH_4^+, Br^-, Cl^-, CN^-, F^- BF_4^-, I^-, NO_3^-, ClO_4^-, S^{2-}, SCN^-. Several specific electrode assemblies such as F^-:Cl^- detectors, Ca^{++} flowthrough electrodes, and enzyme substrate electrodes are described.

477

The Sample, The Procedure, and The Laboratory.

W. J. Youden (Nat. Bur. of Stand., Washington, D. C.)

Nat. Bur. Stand. (U.S.), Spec. Publ. 1 (300), 138-45 (1969).

The viewpoint is taken that an analytical procedure has an inherent accuracy and precision. Systematic errors are present and are major problems. Interlaboratory differences are discussed.

478

Automated Sampling and Analysis of Wet-Process Phosphoric Acid Digestion Systems.

A. N. Baumann and H. H. Roberts (International Minerals & Chemical Corp., Bartow, Fla.).

Automat. Anal. Chem. Technicon Symp., 3rd, 1, 257-60 (1967) (Pub. 1968); Mediad Inc.: White Plains, N. Y.

A discussion is given of various methods for sampling wet-process H_3PO_4 digestion systems. A process of continuous sampling, combined with intermittent sulfate determinations, was developed. Baseline drift caused by the precipitate coating the flow cell walls in turbidimetric equipment is prevented by washing between the sulfate readouts.

479

Automatic Sampling and Analysis of Compound Fertilizers.

A. C. Docherty (Agr. Div., Imp. Chem. Ind. Ltd., Billingham, England).

Chem. Ind., No. 7, 216-20 (Feb. 17, 1968).

An automatic analysis system based on commercially available samplers, dividers, balances, and the AutoAnalyzer, and which made the sampling and dissolution process fully automatic, was devised for fertilizers. The coefficient of variation of 1-2% achieved with this system was about 2-fold greater than that obtained for analysis by the AutoAnalyzer in the laboratory, but this was considered to be quite adequate for plant control purposes. Setups are described for determinations of NH_4^+, K, NO_3^-, and PO_4^{3-}.

480

Sampling Bulk Fertilizers in Railroad Cars and Piles.

C. W. Gehrke, *et al* (Agr. Exp. Sta., Univ. of Missouri, Columbia).

J. Ass. Offic. Anal. Chem. 52 (3), 592-9 (1969).

The three official sampling devices used obtained samples of NPK fertilizers at all locations in railroad cars and warehouse piles that on analysis gave results well within the permitted tolerances. Dry blended fertilizers could not be sampled, but recommendations are made for sampling fluid fertilizers.

481

Analytical Control of the Manufacture of Phosphate Fertilizers.

G. E. Mapstone (Swinburne Coll. Technol., Hawthorn, Aust.).

Aust. Chem. Process. Eng. 23 (8), 28-9 (1970).

CA 74, 31229.

Phosphate fertilizers such as single superphosphate and triple superphosphate are manufactured by reacting phosphate rocks with H_2SO_4 and H_3PO_4, respectively, under controlled ratios. Various equations were examined for calculating these ratios with reference to the composition of the phosphate rocks.

482

A Hardness Test.

Charles Dirdak (American Potash and Chem. Corp., Trona, Calif.).

Fertilizer Ind. Round Table, Proc. 19th, pp. 33-6 (1969).

A procedure is described for the determination of the hardness of granular materials. The significance of variables is explained in order to help users select appropriate adjustments to the procedure that make it suitable for a great variety of products. The precision of the procedure is expressed in terms of standard deviation. The test is useful in the evaluation of mixed fertilizer.

483

Separation and Preconcentration Techniques.

Atsushi Mizuike (Nagoya Univ., Nagoya, Japan).

Tech. Metals Res. 3 (Pt. 1), 25-67 (1970).

CA 73, 83446.

Although modern instrumental techniques, specific organic reagents, or masking agents overcome difficulties in selectivity and sensitivity, separation or preconcentration techniques are often necessary to obtain maximum accuracy or sensitivity (for example, determination of ppb of traces). Preparation of standards is very difficult and should be omitted whenever possible. Separation techniques based on volatilization, liquid-liquid extraction, selective dissolution, precipitation, electrode position, and ion exchange are recommended. A review is given. (169 ref)

484

Method for Determining the Effectiveness of Anti-Caking Agent.

James Passmore (to Petrochemicals Company, Inc.).

U. S. 3,481,187, Dec. 2, 1969, Appl. Dec. 19, 1966; 3 pp.

An apparatus for the determination of effectiveness of an anti-caking agent is described. Test results of the penetrometer to accurately predict the anti-caking results when a predetermined quantity of agent is added are given. Samples of materials containing various amounts of agents are subjected to pressure, using the hydraulic fluid Carver laboratory press.

The maximum pressure of the material in storage is normally the pressure used in the test. The samples are placed in a storage area at ambient temperatures and left for seven days. The penetrometer is then used to determine the force necessary to penetrate the caked portion of each sample. This is an indication of the degree of caking that takes place commercially.

485

Application of an AutoAnalyzer System to the Control of a Complex Fertilizer Plant.

S. Fassari (SINCAT, S.p.A., Syracuse, Italy).

Automat. Anal. Chem., Technicon Symp., 3rd 1967, 2, 303-8 (Publ. 1968) Mediad, Inc.: White Plains, N. Y.

CA 70,105520.

An automatic analytical control system permitting simultaneous analysis of total P_2O_5, ammoniacal N, nitrate N, and K_2O present in fertilizers was described. The system used was previously described (A.C. Docherty, 1964) and utilizes a flame spectrophotometer and three calorimeters with the modifications that an actual crushed fertilizer and a different sampler were used. The method was suitable for determining the content of fertilizers containing 4-25% P_2O_5, 4-22% K_2O, 2-7.5% nitrate N, and 4-14% ammoniacal N; reproducibility of the analysis was within 1-1.5% of the absolute value.

486

Automatic Analysis in Fertilizer Plants.

G. H. King and A. G. Scobie (Technicon Instruments Co Ltd.).

Chem. Process Eng. (London) 51 (5), 62-3 (May 1970).

A brief general description is given of the AutoAnalyzer system as applied to analysis of raw materials, intermediates, products, and effluents in the manufacture of N-P-K granular fertilizers. See *FA 1*, 834 and *2*, 1231.

487

Automatic Methods for Trace Element Analysis.

L. G. Andren (Technicon AB, Swed.).

Mod. Kemi, No. 4, 34-6 (1970) (Swed).

CA 74, 134360.

The following automatic analytical procedures are described and the apparatus schematically represented: orthophosphates in soil analysis; orthophosphates in boiler feed water; orthophosphates in detergents; total phosphates in pesticides; Fe in water; Cu in boiler feed water; fluorides; and Hg. Analogous methods of analysis can be developed for Cd, Zn, Ag, Pb, and Cu. The procedures described are based upon using the Technicon AutoAnalyzer.

488

Instrumental Methods in the Chemical Analysis of Minerals.

G. Dijkstra (Utrecht Univ., Utrecht, Netherlands).

Geol. Mijnbouw 47 (6), 379-93 (1968).

CA 70, 83849.

Instrumental methods of minerals analysis are reviewed, including emission and absorption spectrography, excitation and de-excitation at high temperatures, flame photometry and flame emission spectroscopy, arc or spark emission spectrography, atomic absorption and atomic fluorescence spectrometry, mass spectrometry, neutron activation analysis, x-ray emission analysis, and infra-red absorption spectroscopy.

489

Use of Programmable Desktop Computers in a Research Laboratory. I. Use in Analytical Procedures Based on Calibration Curves.

Siegfried Ebel and Guenter Herold (Inst. Pharm. Chem. Lebensmittelchem., Marburg/Lahn, Germany).

Deut. Lebensm.-Rundsch. 67 (9), 301-3 (1971) (Ger).

CA 76, 30376.

Programmable desk computers are used for the colorimetric determination such as NO_3^- in water, which is based on a linear relation between the absorbance value and the concentration. Water containing 5.50-95.00 mg NO_3^-/l. as determined from calibration curves was calculated to contain 4.93-94.85 mg NO_3^-/l. with a relative error of 10.29 to 0.16%; the relative standard deviation was 0.0376. Various computer programs are given. This method of evaluation is more rapid than the conventional graphic evaluation with calibration curves and is applicable to the colorimetric titration of various types of compounds.

490

Criterion for Judging Acceptability of Analytical Methods.

E. F. McFarren, R. J. Lishka, and John H. Parker (Bureau Water Hygiene, Public Health Service Cincinnati, Ohio).

Anal. Chem. 42 (3), 358-65 (Mar. 1970).

A procedure is developed for calculating the so-called total error of a method. On the basis of this total error, it is suggested that methods be divided into three categories: excellent (total error 25% or less), acceptable (total error 50% or less), and unacceptable (total error greater than 50%). This system is then applied to the results obtained in some recent ARS collaborative studies in order to categorize the methods objectively.

491

Industrial pH Measurements.

Ted R. Barben (Universal Interloc Inc., USA).

Instrum. Contr. Syst. 41 (8), 85-6 (1968).

A flow chamber and electrodes are presented for industrial pH measurements. In the reference cell, the liquid junction is generally made of hardwood or porous ceramic. The reference potential is constant within 0.025 pH units. A cell can be renewed completely by replacing the liquid junction, the half-cell assembly, and the electrolyte.

492

The Collaborative Test.

W. J. Youden (Nat. Bur. of Stand., Washington, D. C.).

Nat. Bur. Stand. (U.S.) Spec. Publ. 1 (300), 151-8 (1969).

The interlaboratory test is an indispensable scrutiny of an analytical procedure. The planning of collaborative tests, a technique to establish that a procedure is ready for a collaborative test, and the interpretation of the results of a collaborative test are discussed.

493

Precision Standardization of Ceric Sulfate Solutions.

A. J. Zielen (Argonne Natl. Lab., Argonne, Ill.).

Anal. Chem. 40 (1), 139-45 (Jan. 1968).

Standardization procedures for ceric sulfate solution accurate to 0.01% were verified by agreement between the National Bureau of Standards redox reagents: arsenious oxide, sodium oxalate, and potassium dichromate. Particular attention was paid to the catalyst role of osmium tetroxide in the As(III)-Ce(IV) reaction. Incomplete reoxidation of the osmium to the VIII state was found to cause serious errors. Depending on the amount of osmium, titration direction, and potentiometric *vs* indicator end point detection, these errors ranged as high as 0.3-0.4% for a 2-meq sample. The only error-free method was found to be the potentiometric titration of Ce(IV) by As(III), which is the reverse of the customary procedure. The redox indicator ferroin can also be used if a blank correction is

applied. A similar direction dependence was observed in the potentiometric standardization of Fe(III) with dichromate. Here, dichromate as the titrating agent avoids a small error.

494

Simultaneous Determination of Phosphorus, Iron, and Aluminum in Phosphate Rock and Fertilizer Systems by Automated Colorimetric Analysis.

J. L. Hoyt and D. E. Jordan (Continental Oil Co., Ponca City, Okla.).

J. Assoc. Offic. Anal. Chemists 52 (6), 1121 (Nov. 1969).

An automated colorimetric method is used to simultaneously determine P, Fe, and Al in phosphate rock and various solid and liquid fertilizer systems. Combination of an *in situ* dilution technique for P with a sample splitting technique results in an effective analysis rate of 60, 90, or 120 determinations/hour (20, 30, or 40 samples/hour three elements/sample). P is determined as the molybdovanadophosphate complex at 420 milli-microns; Fe and Al are both determined as "Ferron" (8-hydroxy-7-iodo-5-quinoline sulfonic acid) complexes with the Fe complex determined at 610 milli-microns and combined Fe and Al complexes determined at 366 milli-microns. The precision and accuracy are better than ±1% relative throughout the total range of 0.1-75% P_2O_5, and up to 10% Fe_2O_3 and 10% Al_2O_3.

495

Phosphorites Analysis by Complexometry and Colorimetry.

I. B. Moizhes and E. A. Alikeeva.

Tr. Leningrad. Nauch.-Issled. Proekt. Inst. Osn. Khim. Prom., No. 1, 323-8 (1967) (Russ). From *Ref. Zh., Khim. 1968*, Abstr. No. 13G125.

CA 70, 111312.

A fast method based on the combination of photometry, complexometry, flame photometry, and differential photometry was used in determining SiO_2, P_2O_5, CaO, MgO, Fe_2O_3, Al_2O_3, TiO_2, MnO, Na_2O, K_2O, F, and CO_2 in stripped phosphorites. After decomposing the specimen with HCl and HNO_3 and removing the insoluble residue, SiO_2 was determined by difference in wt before and after HF treatment. P_2O_5 was determined by differential photometry in the form of a P-V-Mo complex. TiO_2 was reduced by ascorbic acid and then determined photometrically with diantipyrylmethane. CaO, MgO, Fe_2O_3, and Al_2O_3 were determined by Complexon III titration. Low Fe and Al concentrations (<1%) were found photometrically with sulfosalicylic acid and aluminon. Mn^{++} was oxidized by $S_2O_8^{--}$ to MnO^{4--} and measured at ~530 millimicrons. Na_2O and K_2O contents were determined by the flame-photometric method after the decomposition of the suspension by HF and H_2SO_4. In working with a low-temperature flame PO_4^{3-} had a small effect on the results for determining the K and Na. F was separated by distillation with HCl and HNO_3 and Th^{4+} by complexation and coloration with arsenazo. CO_2 was determined gravimetrically by decomposing the sample with 10% AcOH or by the gas volumetric analysis during acid processing of the sample.

496

Practical Use of Nuclear Magnetic Resonance for the Elemental Analysis of Material.

A. M. Sazonov.

Geofiz. Appl., No. 35, 109-17 (1968) (Russ).

CA 69, 73631.

Factors affecting the shape and signal-to-noise ratio in N.M.R. spectra of solutions and solids are discussed with respect to elemental analysis. Results of the determinations of D in mixtures of D_2O-H_2O and ^{19}F in apatite and fluorite are given.

497

Electroanalytical Methods for the Analysis of Fertilizers.

K. S. A. Gnanasekaran and K. C. Narasimham (Central Electrochemical Research Inst., Karaikudi, India).

Trans. Soc. Advan. Electrochem. Sci. Technol. 4 (2), 33-7 (1969).

CA 72, 65901.

Determination of N, P, K, and moisture in fertilizers by potentiometry, conductometry, polarography, and amperometry are reviewed. (30 ref)

498

Analysis of Nutrient Solutions Used in Plant Culture by Means of the AIP-2 Device.

B. P. Konstantinov and O. V. Oshurkova (Fiz.-Tekh. Inst. im. Ioffe, Leningrad).

Agrokhimiya, No. 9, 99-106 (1967) (Russ).

CA 68, 21317.

An apparatus is described that uses the principle of moving boundary electrophoresis with an opposing movement of the supporting electrolyte solutions for the analysis of aqueous fertilizer solutions. The analysis of fertilizer cations requires that the electrophoretic mobility of the cation in the cathode electrolyte solution be higher than that of cations present in the test solution, whose mobilities, in turn, should be higher than that of the cation in the anodic electrolyte solution. An analogous situation must exist with respect to the mobilities of anions when the anion content of fertilizer solutions is examined. The moving boundaries can be visualized and quantitated by a diffraction plate.

499

Complexes and Analytical Chemistry.

Hayami Yoneda (Wakayama Univ., Wakayama, Japan).

Kagaku No Ryoiki, Zokan, No. 90, 295-319 (1970) (Japan).

CA 73, 83443.

A review is given of configurations of dimethylglyoxime complexes, acetylacetonato complexes, oxine complexes, EDTA complexes, and chromatographic behavior of anionic and cationic complexes (Rf values), ion associations, and resolution of optically active complexes by electrophoresis. (61 ref)

500

Determination of Copper, Arsenic, and Antimony in Pure Phosphorus by Neutron Activation Analysis.

Shoji Bando and Hajime Kishi (Jap. At. Energy Res. Inst., Oarai, Japan).

Bunseki Kagaku 19 (1), 17-22 (1970) (Japan).

CA 72, 117365.

A neutron activation method using $^{63}Cu(n,\gamma)^{64}Cu$, $^{75}As(n,\gamma)^{76}As$, and $^{121}Sb(n,\gamma)^{122}Sb$ reactions is developed for determining Cu, As, and Sb traces in pure red P for doping Si semiconductors. Samples (0.2 g, in 100-50 mesh powder) were sealed into polyethylene bottles (5 mm in diameter, 40 mm long). The bottles and a bottle containing standard solution were transferred by a pneumatic tube system and were irradiated for 20 min in a thermal neutron flux of 8 x 10^{13} neutrons/cm^2-sec. As chemical carriers, 10 mg of Cu, As, and Sb, respectively, were added to the irradiated sample, and the sample was dissolved with HNO_3. The elements being determined were precipitated as sulfides by $MeCSNH_2$ solution from 1-2*N* HCl sample solution, and were separated

by anion exchange chromatography. Activity measurements of ^{64}Cu(0.51 MeV), ^{76}As (0.56 MeV), and ^{122}Sb(0.57 MeV) were made on a gas-flow counter and a 3 x 3 in. NaI(Tl) scintillator with a 400-channel pulse height analyzer. Lower limits of 7 x 10^{-4} μg Cu, 5 x 10^{-4} μg As, and 9 x 10^{-4} μg Sb were attained. The time for analysis is ~6 hr.

501

Fluoride Method for Separating Rare Earth Elements During an Analysis of Minerals and Ores.

V. S. Bykova.

Khim. Anal. Formuly Mincr. pp. 13-19 (1969) (Russ). Edited by Borneman-Starynkevich. Izd. "Nauka": Moscow, U.S.S.R.

CA 73, 94278.

The conditions for quantitative separation of rare earths (RE) by the fluoride method were studied, especially for determination in minerals, where the ratio of rare earths to Fe + Al was 1:7. The oxides $(RE)_2O_3$, formed after precipitation of the decomposed sample with NH_3 and calcination were treated with HF. The losses observed are caused by the conversion of Ce^{3+} to Ce^{4+} giving soluble CeF_4. Reduction of Ce^{4+} requires addition of H_2O_2 during the treatment with HF. Al and Fe interfere with the separation of fluorides. Results are practically quantitative when the solution is evaporated with concentrated HF in the presence of NH_4^+ salts. To prevent the precipitation of Al, HF is added in several portions, the solution is heated on a gently boiling water bath, and is not evaporated to a very small vol. A large excess of NH_4^+ salts causes coprecipitation of Al. For separation of 9-10 mg rare earths from 200 mg Al_2O_3 + Fe_2O_3, (1:1), after conversion of $(RE)_2O_3$ to fluorides and evaporation to 2-3 ml, the solution is evaporated twice in the presence of 200 mg NH_4NO_3 with 5-7 ml concentrated HF to 2-3 ml. After dilution with H_2O the vol should not exceed 20 ml.

502

Thin-Layer Chromatographic Behavior of a Number of Metal Ions on DEAE-Cellulose in Thiocyanic Acid-Organic Solvent Mixtures.

K. Oguma and R. Kuroda (Univ. Chiba, Chiba, Japan).

J. Chromatogr. 52 (2), 339-46 (Oct. 1970).

The thin-layer chromatographic behavior of 48 metals was investigated on a weakly basic anion exchanger, DEAE-cellulose, in binary solvent mixtures consisting of HSCN (0.1-2.1 *M*) and an organic solvent such as methanol, acetic acid, acetone, dioxane, and others. For the sake of comparison, the R_F values for the same metals on a microcrystalline cellulose, Avicel SF, in three solvent mixtures involving methanol, acetic acid, and acetone are also presented. The addition of a protic solvent to the aqueous HSCN solution enhances the adsorption of many metals, in so far as the metals form stable thiocyanatocomplexes and their R_F values may be controlled predominantly by the ion-exchange mechanism. This is not the case for the nonprotic acetone-HSCN system, where mechanisms other than ion exchange may prevail to influence the R_F values of the metals. Useful multicomponent separations on DEAE-cellulose are presented to demonstrate the use of R_F measurements for predicting separations in these solvent systems.

503

"Channel" Thin-Layer Chromatography - A New Method for the Quantitative Evaluation of Thin-Layer Chromatograms.

I. Berthold (Forschungslab., ESSO A.-G., Hamburg-Harburg, Ger.).

Fresenius' Z. Anal. Chem. 240 (5), 320-2 (1968) (Ger).

CA 69, 102825.

The title method comprises the use of sheets coated with silica in designs shaped like an inverted funnel. The edges of the silica-coated areas are confined so that the developing solvent in ascending chromatography is guided from the flared end, on which the sample is spotted, into the narrow, constant width portion of the silica coating. Confinement of the resulting spots on the developed chromatogram permits the accurate determination of hydrocarbons, for example, the spot size for some sample determinations was related to the hydrocarbon concentration by the constant relation 2.33 sq mm/0.1 mg hydrocarbon.

504

Electron Microprobe Analysis of Precipitates in the Laser Crystal Material Fluorapatite.

P. J. Walitsky (Westinghouse Electric Corp., Bloomfield, New Jersey) and R. H. Hopkins (Westinghouse Electric Corp., Pittsburgh, Pa.).

Appl. Spectr. 23 (5), 490-2 (Sept.-Oct. 1969).

Electron probe microanalysis has been used to identify precipitates in calcium fluroapatite $Ca_5(PO_4)_3F$. Crystals grown from nonstoichiometric melts were found to have defects of either CaF_2 or $Ca_3(PO_4)_2$ depending on the melt composition.

505

Application of Some Thermoanalytical Techniques to Study the Normal Superphosphates.

Carlo Giavarini and Fausto Pochetti (Univ. Roma, Rome, Italy).

Ann. Chim. (Rome) 61 (10), 682-94 (1971) (Ital).

CA 76, 80763.

Thermogravimetric methods are given for determining $Ca(H_2PO_4)_2$ and $CaHPO_4$ in normal superphosphates made by treating mineral phosphate with H_2SO_4. Use of differential scanning calorimetry is also described.

506

Composition of Gases Prepared from Kara-Tau Phosphorites and Metaphosphoric Acid Studied by Infrared and Mass Spectroscopic Methods.

M. A. Dykanbaev, *et al.*

Tr. Inst. Khim. Nauk, Akad. Nauk Kaz. SSR 25, 39-41 (1969) (Russ).

CA 72, 128348.

The composition of gases prepared from phosphorites and metaphosphoric acid was studied by ir and mass spectrometry. The ir spectra were recorded on IK-10 spectrometer by using 100-mm cells. The MI-1305 mass spectrometer was used and the spectra recorded for 15-105 *m/e*. The results were compared with standard spectra of CO_2, CO, HF, SiF_4, etc. The ir data showed that the main components are CO_2 and HF; the CO concentration is negligible. The mass spectral data showed that HF is present mainly as dimeric $(HF)_2$, and only ~5% as monomeric HF.

507

Quantitative Analysis of Water-Soluble Fertilizers by Aqueous Solution Infra-red Spectroscopy.

J.D.S. Goulden and D. J. Manning (Natl. Inst. Res. Dairying, Reading, England).

J. Sci. Food Agr. 18 (10), 466-9 (Oct. 1967).

A method is described for determination of NH_4, NO_3, PO_4, and SO_4 in water-soluble synthetic fertilizers. The infra-red absorption spectra of suitably-prepared aqueous extracts of fertilizers were recorded and the absorbences measured at the

appropriate four wavelengths. Results calculated from these absorbances gave NH_4 concentrations that agreed with chemical analyses to an accuracy of about 0.1% at the 10.0% level, while the NO_3 and PO_4 results agreed to about 0.3%.

508

Thermal Studies of Some Indian Rock Phosphates With or Without Additives.

S. K. Adhya, *et al* (Fertilizer Corp. of India Ltd., Sindri, Bihar).

Technology (Sindri) 6 (2-3), 91-5 (1969).

Differential thermal studies were made on three Indian rock phosphates and on a sample of imported Makatea rock, to determine mineralogical composition and thermal behavior with and without additives. With rock phosphates containing calcite, clayey, and Fe minerals, there is some increase in, citrate solubility on heating up to 950° but no further increase on heating to higher temperatures. However, on mixing with mica, Na_2SO_4, and C and heating up to 1250° the citrate solubility is increased. Mica is the most effective additive for Fe-rich phosphates whereas Na_2SO_4 and C are the most effective for those containing calcite and clay minerals. Iron compounds aid fusion in the presence of mica and favor crystallization of citrate-soluble α-tricalcium phosphate from the melt. In the presence of Na_2SO_4 and C the apatite develops another citrate-soluble compound, like $10\text{-}CaO{\cdot}2Na_2O{\cdot}3P_2O_5{\cdot}SO_3{\cdot}2SiO_2$, which is promoted when calcite or clayey minerals are present. The constitution of the apatite seems to influence the development of citrate-soluble compounds, with or without additives.

509

Analysis of Slightly Soluble Magnesium and Calcium Polyphosphates.

V. A. Pechkovskii, L. N. Shchegrov, and A. S. Shul'man.

Izv. Akad. Nauk Kaz. SSR, Ser. Khim. 18 (3), 13-18 (1968) (Russ).

CA 69, 70520.

To dissolve slightly soluble Mg and Ca polyphosphates without changing their composition suspensions of the polyphosphates were contacted with the Dowex 50 X 12 cation exchanger in the H^+ form. The optimum amounts of the resin, polyphosphate, and H_2O are 5 g, 0.15 g, and 15 ml, respectively. The contact time depends on the heating temperature during preparation of the respective polyphosphate and is 0.16 and 3 hr for Mg compounds heated at 100 and 450°, respectively, and 0.16 and 1 hr for Ca compounds heated at 100 and 360°, respectively. In the obtained solution, the polyphosphates were analyzed by paper chromatography; 0.08 ml of each solution was used. No hydrolysis of the polyphosphate anions occurred during the dissolution or during the subsequent standing of the solutions for several days.

510

Ion Exchange Dissolution Method for Silicate Analysis.

Kuppusami Govindaraju (Centre de Recherches Petrographiques et Geochimiques, Nancy, France).

Anal. Chem. 40 (1), 24-6 (Jan. 1968).

A simple procedure for dissolving silicate rock samples and eliminating the Si is described. The sample is fused with an alkali borate and the powdered fusion product is stirred for a few min in H_2O with a strongly acidic cation exchanger (column or batch technique). The effluent contains only B and Si, whereas all other elements are recovered by elution with diluted HCl. Analytical applications for the determination of major and trace elements in silicates are discussed using atomic absorption, and chemical and spectrochemical methods. Particularly attractive is the analysis of the resin itself (after the adsorption step) using a tape machine for determining trace elements and even major and minor elements.

511

Chemical Analysis of Phosphorites.

L. N. Podgornyi.

Geokhim. Geol. Fosforitonosn. Medenosn. Otlozh. Tatarii, pp. 57-65 (1970) (Russ).

CA 76, 67783.

A system for analysis of phosphorites and more effective methods for determination of the components included in the composition of natural phosphorites are proposed. A sample was dissolved in HF + HCl, the solution was filtered, the undissolved residue was fused with NaOH, the melt was leached, both solutions were combined, and Si was determined as SiO_2 gravimetrically. Phosphorus was determined titrimetrically and Ca, Mg, Fe, and Al complexometrically in the solution after Si separation. Small amounts of Al were determined photometrically with aluminon. From separate samples, Ti was determined by a peroxide method, Fe^{2+} by titration with $K_2Cr_2O_7$, Mn photometrically as MnO_4^-, F^- photometrically by using Zr-alizarin complex as a reagent, Cl^- by argentometric titration of HNO_3 extract. CO_3^{2-}, $S_{(total)}$, and SO_4^{2-} were determined by well-known methods, and S^{2-} was calculated by the difference of $S_{(total)}$ and SO_4^{2-}. For determination of quartz in phosphorites, they were treated with H_3PO_4, and the undissolved residue was leached with 5% Na_2CO_3. The quartz did not decompose in these conditions and is determined gravimetrically.

512

Rapid Determination of Nitrogen, Phosphorus, and Potassium in Peat and Peat-Mineral Fertilizers.

A. V. Tishkovich, T. D. Prasolova, and R. P. Shurygina.

Fiz.-Khim. Torfa Torf. Mekh., pp. 141-5 (1970) (Russ). Edited by N. S. Pankratov. "Nauka i Tekhnika": Minsk, Beloruss. SSR.

CA 74, 140120.

Place 1 g of peat in an ignition flask, add 25 ml concentrated H_2SO_4, or 25 ml phenylsulfuric acid in the case of a large concentration of nitrate N, plug it with a stopper and let it stand overnight. After 24 hr heat it till the appearance of white vapors, add 1 ml $HClO_4$, burn it over low flame while agitating. If the flask content did not become clear in 30-40 min add a few drops of $HClO_4$ and continue to burn until a complete clarification of liquid takes place. Then cool the flask, filter its content into a 250-500 ml flask, wash the filter with hot water, cool the filtrate, and add water to a required level. The obtained extract is used for the determination of total N, P, and K. Nitrogen is determined by distillation of a certain vol of the extract with 33% NaOH. The evolving NH_3 is absorbed by 0.1 *N* H_2SO_4 followed by a titration with 0.1 *N* NaOH. Phosphorus is determined by the calorimetric method, and K, by flame photometry.

513

High-Precision Coulometric Iodimetry.

George Marinenks and J. K. Taylor (Natl. Bur. of Std., Washington, D.C.).

Anal. Chem. 39 (13), 1568-71 (Nov. 1967).

On the basis of measurement of the potential of the working Pt anode as a function of current density and concentration of KI in solution, conditions were established for 99.9999 + % efficient generation of I. NBS Standard Reference Material As_2O_3 was analyzed utilizing optimum conditions for generation of I and for the stoichiometric reaction of arsenious acid with I. The precision of the method for titration of 0.5 g samples as As_2O_3 is approximately 0.003%. Analysis of data

for the assay of samples ranging in size from 100 mg to 1 g indicates no basis in the method.

514

Chemical Determination of Some Major Constituents in Rocks and Minerals.

E. Kiss (Australian Natl. Univ., Canberra, Australia).

Anal. Chim. Acta 39 (2), 223-34 (Oct. 1967).

Macro-analytical schemes are described for the determination of Al, total Fe and Fe(II) as part of the complete analysis of silicate rocks and minerals. Solvent extraction eliminates interferences before titration of Al with DCTA. Iron(III) is extracted with MIBK and determined indirectly with EDTA. Iron(II) is determined by potentiometric titration under an inert atm. Interferences are removed with 2,4-pentanedione and carbone tetrachloride before the determination of Ca and Mg.

515

Use of an Electrical Conductivity Method for Characterizing the Properties and Composition of Fertilizers.

V. S. Vyzgo, et al. (Inst. Khim., Tashkent, USSR).

Dokl. Akad. Nauk Uzb. SSR 25 (5), 23-4 (1968) (Russ).

CA 69, 76029.

The softening which occurs in the preparation of N-P fertilizer in a fluidized bed was studied by electric conductivity methods. The appearance of a liquid phase was due to the presence of $Ca(NO_3)_2$. The temperature at which the liquid phase appears depends on the proportion of $Ca(NO_3)_2$ in the mixture.

516

Precipitation Titrations with Electrochemically Generated Lanthanum Ion. Potentiometric Titration of Fluoride and Turbidimetric Titration of Oxalate.

D. J. Curran and K. S. Fletcher (Univ. Massachusetts, Amherst).

Anal. Chem. 41 (2), 267-73 (Feb. 1969).

Lanthanum ion electrochemically generated from a lanthanum hexaboride anode has been used as a precipitant for fluoride and oxalate ions. A lanthanum fluoride membrane electrode was used for end point detection in the fluoride work and a turbidimetric end point technique was used in the oxalate titrations. The pH conditions for the fluoride reaction were studied and 0.5-2.0 mg of fluoride in about 100 ml of solution have been determined with a precision and accuracy of a part per thousand at a pH electrochemically controlled at 5.0. The techniques of pretitration and titration back to a predetermined end point potential were used. An equation for the fluoride titration curve is discussed. Approximately 0.5-2.6-mg samples of oxalate ion in acidic solution (approximately 20-ml volumes) have been titrated with a precision and accuracy in the 1-2% range.

517

Separation of Silicon and Phosphorus with Ammonium Molybdate and Their Successive Determinations.

A.M.G. MacDonald and F. H. Van Der Voort (Univ. Birmingham, England).

Analyst 93 (1103), 65 (Feb. 1968).

A method for the successive determinations of Si and P is described. Phosphate is separated cleanly from silicate as ammonium molybdophosphate; phosphate in the precipitate and silicate in the filtrate are determined by conventional quinoline procedures. The method is suitable for the separation and determination of 0.2-2.0 mg of each of the ions. The separation method can be applied to organic materials, after decomposition with peroxide. A study of organic bases for the precipitation of molybdosilicate showed that none is preferable to quinoline.

518

Characterization of Ureaform Fertilizers by Differential Thermal Analysis.

H. Roy, A. K. Datta, and H. Acharyya (Fertilizer Corp. India, Sindri, Bihar, India).

Technology 6 (2-3), 143-5 (1969).

The composition of a range of such fertilizers has been studied by DTA. The method is claimed to be superior to others, as amorphous materials and condensation products that do not give an x-ray diffraction pattern can be studied.

519

Thermal Analysis of Magnesium Phosphate at Low Pressures.

M. T. Saibova, *et al* (Inst. Khim., Tashkent, U.S.S.R.).

Uzb. Khim. Zh. 14 (3), 38-40 (1970) (Russ).

CA 73, 115923.

In the thermal anlaysis of $Mg(H_2PO_4)_2 \cdot 2H_2O$ the rate of heating was 15°/min and the pressure was varied from atmospheric to 1 mm Hg. Evolution of gas and the electrical conductivity were measured simultaneously. The thermograms of $Mg(H_2PO_4)_2 \cdot 2H_2O$ at 250 mm Hg and 20 mm Hg and the x-ray diffraction patterns after DTA at atmospheric pressure and at 100 mm Hg are given. The first endothermic effect (115-150°) corresponds to the melting of $Mg(H_2PO_4)_2 \cdot 2H_2O$ with simultaneous evaporation of H_2O. The wt loss in the interval 20-200° was 14.4%. The temperatures of formation of pyrophosphate (270-280°) and of tetrametaphosphate (450-470°) are independent of pressure. The endothermic peak at 450-470° and not over 250 mm Hg splits because of the dependence on pressure of the exothermic peak of crystallization.

520

Chromium(III)-Eriochrome Blue Black R: Chelometric Indicator.

G. L. Silver and R. C. Bowman (Mound Laboratory, Miamisburg, Ohio).

U. S. At. Energy Comm. MLM-1536, (1968), 8 pp.

The preparation and some properties of a new indicator suitable for the determination of metal ions with ethylenediaminetetraacetic acid (EDTA) is described. Titrations of Ca, Cd, Mn, and Zn illustrate the applicability of the indicator in chelometry.

521

Analysis of Inorganic Substances by an Automatic Carbon-Hydrogen-Nitrogen Analyzer.

Makoto Noshiro and Kiyoshi Matsumoto (Asahi Glass Co., Ltd., Yokohama, Japan).

Bunseki Kagaku 20 (9), 1069-75 (1971) (Japan).

CA 75, 147362.

An automatic organic C-H-N analyzer (Yanagimoto MT-2) was used to determine several kinds of inorganic compounds and substances. Most inorganic compounds which decompose <900 to form CO_2, H_2O, and N, such as $CaCO_3$, $KHCO_3$, $LiNO_3$, $NaNO_3$, KNO_3, $NaNO_2$, $K_4[Fe(CN)_6]$, KSCN, NH_4SCN, NH_4Cl, and $(NH_4)_2Cr_2O_7$, could be easily analyzed for C, H, and N with ≤0.3% absolute error with the apparatus under conditions generally used for the analysis of organic compounds. Hydrated H_2O in some compounds, such as $CaSO_4 \cdot 2H_2O$, $BaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, $Na_2B_4O_7 \cdot 10H_2O$, $Al_2(SO_4)_3 \cdot 18H_2O$, $MgSO_4 \cdot 7H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$, was determined by decomposing them at 850°, hydrated H_2O and adsorbed H_2O in amorphous SiO_2 were determined separately at 160 and 900°, respectively. The results agreed well with

those obtained by thermogravimetry. Water and CO_2 in clay minerals and CO_2 in limestone and dolomite were also determined easily by decomposing them at 900°. Those samples which have higher decomposition temperatures, >900°, which is the upper limit of the working temperature of the apparatus, such as Li_2CO_3, Na_2CO_3, $SrCO_3$, and $BaCO_3$, could be analyzed for C by adding B_2O_3 or P_2O_5 to the samples as a flux to lower the decomposition temperature to <900°.

SEE ALSO the following numbered abstract in another section: 359.

MISCELLANEOUS

522

Fertilizers.

C. W. Gehrke (Univ. Missouri, Columbia).

Anal. Chem. 43 (5), 64R-69R (Apr. 1971).

The literature in 1969 and 1970 concerning the analysis of fertilizers for H_2O, N, P, K, and micronutrients is reviewed. (79 ref)

523

Free and Total Water in Fertilizers.

R. D. Duncan (Tennessee Valley Authority, Muscle Shoals, Ala.).

J. Ass. Offic. Anal. Chem. 54 (4), 988 (1971).

Methods for the determination of free and total water in fertilizers are based on the Karl Fischer titration. Free water is extracted with 1,4-dioxane, and total water is separated by azeotropic distillation with amyl alcohol. Results of a preliminary collaborative study were in wide disagreement. It is recommended that the method be written in more explicit detail before further collaborative study. **Water in Granular Triple Superphosphate.** *Ibid.* 989-90. The gain or loss of moisture by samples of granular triple superphosphate during grinding in preparation for analysis depends upon both the conditions of manufacture of the material and the humidity of the atmosphere in the grinding room. Care should be exercised in the preparation of superphosphate samples for analysis, and the relative humidity in the grinding room probably should be ≤40%.

524

Determination of Free and Total Water in Fertilizers by Karl Fischer Titration.

R. D. Duncan and J. A. Brabson (Tennessee Valley Authority, Muscle Shoals, Ala.).

J. Assoc. Offic. Anal. Chemists 52 (6), 1127 (Nov. 1969).

Free water in fertilizers is determined by extraction of the sample with 1,4-dioxane and titration of the extract with Karl Fischer reagent. Total water is determined by distillation of *n*-amyl alcohol from its mixture with the sample and titration of the distillate with Karl Fischer reagent. Hydrate water is taken as the difference between the total water and the free water.

525

Determination of Free Water in Fertilizers.

J. C. Alcarde, R. A. Catani, and P. R. Furlani (Cadeira Quim. Anal. Fis. Quim., ESALQ, Brazil).

An. Esc. Super. Agr. "Luiz de Queiroz." Univ. Sao Paulo 24, 239-45 (1967) (Port).

CA 73, 2999.

Fertilizer blends and fertilizer components were dried in an oven at 100-105° for two hr or in a vacuum oven at 50°, using a vacuum of 20 inches, for the same period. The comparative percentage wt losses by the two methods were: simple superphosphate 6.304 and 1.224; triple superphosphate 7.430 and 1.496; KCl 0.604 and 0.396; $(NH_4)_2SO_4$ 0.210 and 0.074; Chile saltpeter 0.642 and 0.523; nitro lime 6.130 and 4.760; and urea 0.374 and 0.175. The losses of the fertilizer blends all showed greater losses in the 105° oven. A greater difference than calculated occurred in the two blends which contained urea, thought to result from decomposition. The vacuum oven method is preferred.

526

New and Improved Automatic Dead-Stop Apparatus for Water Determination in Mixtures by the Karl Fischer Method.

A. Bellomo, A. De Robertis, and D. De Marco (Inst. Anal. Chem., Univ. Messina, Messina, Italy).

Proc. Conf. Appl. Phys. Chem., 2nd, No. 1, 535-42 (1971). Edited by Ilona Buzas, Akad. Kiado: Budapest, Hungary.

CA 76, 67635.

Apparatus for the automatic determination of H_2O by the Karl Fischer method employing the dead-stop titration system is described. A transistorized circuit is described which activates a solenoid for the control of the titration. The average of eight determinations with this apparatus was 6.22 g/100 ml with a standard deviation of 3.7×10^{-2} for a sample of EtOH which contained H_2O.

527

Experimental Evaluation of the Karl Fischer Method for Determining Water in Potassium Salts.

Siegfried Vielhauer (Hanover, Ger.).

Kali Steinsalz 5 (8), 279-84 (1970) (Ger).

CA 74, 60638.

Potassium-containing minerals and the accompanying salts (gypsum; loeweite) were analyzed for H_2O content. Shaking the sample with dioxane and titrating an aliquot of the solution gives good results for adsorbed H_2O. In the presence of substances containing crystallization H_2O small quantities of that H_2O are dissolved by the dioxane; the results can be corrected for these quantities mathematically. The results of the Karl Fischer method are specific for adsorbed H_2O; drying of the salts at 105° gives unspecific H_2O losses. Suspending and dissolving the sample in the pyridine–SO_2–MeOH mixture and $HCONH_2$, and determination of H_2O by titration with I + MeOH gives all H_2O whose binding-energy does not exceed a certain level. In the absence of kieserite, polyhalite, syngenite, and loeweite, this is the total H_2O. In the presence of these minerals the difference between total H_2O and crystallization H_2O is obtained. This value coincides with the easily lost H_2O, the most practical information during storage of the salts. In the presence of kainite or of gypsum (a rare case) the second method is rather time consuming. Both methods gave reproducible results and are very sensitive. At the 0.004% level the relative standard deviation (standard deviation/medium value) is ±2.5%; at the 0.02% level it is 6%; at the 0.5% level only 1%.

528

Automated Coulometric Determination of Water.

J. L. Hoyt (Continental Oil Co., Ponca City, Okla.).

Anal. Chim Acta 44 (2) 369-75 (1969).
An automated coulometric titrator and its successful application to the determination of water by a Karl Fischer-type reaction is described. Coulometric *in situ* generation of the highly moisture-sensitive Karl Fischer reagent is used to determine accurately the water content of a variety of compounds. The titrator is applicable to all levels of water, from hydrocarbons containing a few ppm water to samples consisting of pure water.

529

Determination of Water in Fertilizer Materials by Microwave Absorption.

F. W. Bennett.

Proc., Fert. Soc., No. 104, 81-96 (1968).

In a fluctuating electrical field, the time for reorientation of the dipole in the free water molecule is short compared to the time for other substances, and at this frequency the absorption of energy is specific to water. An x-band microwave moisture meter was used to measure the attenuation. A linear plot of attenuation against water content is obtained. The smaller the water content to be measured, the thicker the sample must be. The age of the sample, the temperature, the size and distribution of the granules, and the chemical variation between granules affect the attenuation. Experimentally, the results for compounds of similar formation can be combined into a composite line. When this technique is used to determine the water content of H_3PO_4, the attenuation/water plot shows a maximum at 50-60% water. The technique can also be used for hydrated Ca sulfates, slurry intermediates, and compressed bulk peat.

530

Application of an Automated Coulometric Titrator to the Determination of Water in Phosphoric Acids.

D. E. Jordan and J. L. Hoyt (Cont. Oil Co., Ponca City, Okla.).

J. Assoc. Offic. Anal. Chem. 52 (3), 569-77 (May 1969).

In the described method, water in phosphoric acid is determined by *in situ* coulometric generation of Karl Fischer reagent with automated end point detection. The variables associated with visual end point detection among different operators are eliminated. Sample size is limited by the generation rate of available coulometers and is 50 mg for samples containing more than 20% water and 100–150 mg for samples containing less than 20% water for a 20 minute analysis time. The precision at 99% confidence ranges from 0.43 ± 0.05% for superphosphoric acid to 36.8 ± 0.81% for untreated 10-34-0 base solution; for polished wet-process phosphoric acid the precision is 16.49 ± 0.19% compared to 16.70 ± 0.64% by azeotropic distillation. The method is applicable in all systems which do not normally interfere with Karl Fischer reagent; the generating efficiency at the 100% water level is $>99\%$. Coulometer power tube fatigue is the most serious limitation unless a careful check and replacement program is initiated.

531

Moisture and pH Determination of Ammonium Nitrate Containing Melts or Concentrated Solutions.

D. Bennett, J. K. Bradley, and K. A. Sherwin (to Fisons Fertilizers Ltd.).

Brit. 1,159,612, July 30, 1969, Appl. Aug. 25, 1966; 3 pp.

CA 71, 108878.

Air or another gas is brought into contact with a melt or concentrated solution of NH_4NO_3 at a constant elevated temperature above room temperature. A sample of the gas is subsequently obtained and the moisture and NH_3 contents are determined by gas chromatography.

532

Determination of Moisture in Fertilizers and Materials Insoluble in Methanol.

A. M. Heslop, J. M. Skinner, and A. C. Docherty (I.C.I. Ltd., Agr. Div. Res. and Dev. Dep., Billingham, Engl.).

Analyst (London) 94 (1121), 681-7 (1969).

An apparatus is described in which a sample can be ground under methanol, the H_2O being titrated automatically with Karl Fischer reagent with use of platinum indicator-electrodes. Results in good agreement with those obtained by gravimetric and Dean and Stark methods are reported. The method and apparatus are the subject of British Patent 1,021,745.

533

Determination of Water in Hydroxyapatite at High Temperature.

P. V. Riboud (Inst. Rech. Siderurg., Maizieres-les-Metz, Fr.).

C. R. Acad. Sci., Ser. C 269 (13), 691-4 (1969) (Fr).

CA 72, 18064.

Loss of H_2O by hydroxyapatite (room-temperature formula, $10CaO{\cdot}3P_2O_5{\cdot}H_2O$, 1.8 wt % H_2O) at high temperatures was studied by thermogravimetry in an O_2 atmosphere over P_2O_5, by the R. Wallaeys method (1952) of F^- substitution for OH^-, and by thermal decomposition of the products at 1650°. H_2O (0.47-0.54 wt %) was lost gradually and reversibly on increasing temperature from 1150 to 1440° under 55 mm water vapor pressure without alteration of the lattice. The remaining H_2O was lost abruptly with thermal decomposition at 1458°.

534

Polarographic Estimation of Biuret in Commercial Urea.

M. B. Mishra and B. K. Banerjee (Fert. Corp. India Ltd., Sindri, India).

Technology 6 (1), 35-6 (1969).

Biuret is determined from the decrease it produces in the height of the polarographic wave for Cd^{2+} in aqueous NH_3-NH_4Cl buffer solution of pH 9.2; this decrease is proportional to the biuret concentration. Urea in large excess has no effect. Recoveries of biuret (1 to 100 mg) ranged from 98 to 100%.

535

Determination of Biuret in Complex Fertilizers.

V. M. Makarevich and A. E. Koyander (Nauch.-Issl. Inst. Udobr. Insektofungits., Moscow, U.S.S.R.).

Agrokhimiya, No. 1, 139-43 (1970) (Russ).

CA 73, 2998.

The commonly used method for determination of biuret by reaction with Cu salts in alkaline solutions cannot be used for analysis of complex fertilizers containing large amounts of NH_4^+, Ca^{2+}, Mg^{2+}, K^+, Fe^{3+}, NO_3^-, SO_4^{2-}, PO_4^{3-}, and Cl^-. Therefore, a method was developed for determination of biuret on the basis of the formation of a yellow complex with Ni. The sample of fertilizer (10 g) was dissolved in distilled water and made up to 500 ml. The solution was thoroughly mixed and filtered, and 15 ml of filtrate was transferred into a 50-ml volumetric flask. Then 5 ml of alkaline Ni-tartrate reagent (1:1 solutions of 1.36 g $NiSO_4{\cdot}7H_2O$/500 ml and 133 g NaOH + 137 g Na-K tartrate/500 ml of H_2O) and 5 ml 10% (saturated) $Na_4P_2O_7$ were added and the flask was kept for 30 min in a water bath at 72-75°. After cooling to room temperature and diluting with distilled water, the absorbance

was determined at 265 mμ. The content of biuret was read from standard curves.

536

Determination of Chloride in Calcium Phosphates with a Chloride-Selective Electrode.

E. J. Duff and J. L. Stuart (Univ. Manchester, Manchester, England).

Anal. Chim. Acta 57 (1), 233-5 (1971).

Chloride, 24-22,000 ppm is determined in commercial and laboratory-prepared Ca, Cu(II), and Zn phosphates, with a Cl^--selective electrode in pH 2.5 solution where $(a_{Cl^-}) = 10^{-2}$-$10^{-5}M$. A Radiometer selective ion meter, an Orion solid-state Cl^- electrode and a $Hg/HgSO_4$ reference electrode were used. Calcium phosphate, 0.1-0.2 g, is dissolved at 25° with 5 ml 2*M* $HClO_4$-2*M* citric acid. The pH of the solution is adjusted to ~2.5 by adding 5 ml 2*M* $(HOC_2H_4)_3N$ and 5 ml H_2O, the potential is measured, and the Cl^- content obtained from a calibration curve prepared from standard NaCl solutions using the same buffer solution. The (a_{Cl^-}) vs electrode potential (mV) curve for pH 2.5 solution is linear for 0.05-$10^{-4}M$ Cl^-. The Cl^- values determined (8 replicates/determination) in the metal phosphates, and the average percent deviation, are: commercial $CaHPO_4$ 24.2, 5.27; commercial $CaHPO_4 \cdot 2H_2O$ 30.1, 3.16; $Ca_5OH(PO_4)_3$ 242, 1.04; $Ca_5F(PO_4)_3$ 520, 0.97; Cu(II) fluoride phosphate 2366, 0.76; Cu(II) phosphate chloride 22047, 1.03; $Zn_5OH(PO_4)_3$ 330 ppm, 1.10%, respectively. For $(a_{Cl^-}) = 10^{-4}M$, 5 min is sufficient to obtain equilibrium; at lower activities, 20-30 min may be needed. Ca^{2+}, $H_2PO_4^-$, NO_3^-, F^- at $F^-/Cl^- = 500$, and Br^- at $Cl^-/Br^- = 300$ do not interfere.

537

Voltametric Determination of Chloride Ion in Phorphoric Acid and its Salts.

G. S. Bikmatova, N. F. Zakharchuk, and I. G. Yudelevich (Inst. Neorg. Khim., Novosibirsk, U.S.S.R.).

Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, No. 1, 154-7 (1970) (Russ).

CA 73, 52057.

Determination of Cl^- in H_3PO_4 and its salts with a Ag electrode is described. The effect of potential during the preelectrolysis step and of Cl^- concentration on the dissolution current, I_p, of AgCl film was studied. The sensitivity for a 1-g sample of H_3PO_4 is 2×10^{-6}% and for phosphates is 8×10^{-6}%. The relative standard deviation was < 6%. To determine Cl^- in phosphates transfer 10 ml of 0.5 *M* H_3PO_4 buffer solution to a cell and electrolyze for 5 min while bubbling with N or Ar. Record the polarogram at 0.0 to 0.4V with consecutive additions of 2×10^{-6}, 4×10^{-6}, 6×10^{-6}, 8×10^{-6}, and 1×10^{-5} *M* Cl^-. To determine Cl^- in H_3PO_4, neutralize 2.5% H_3PO_4 solution to pH 5. Record the polarogram of a 10-ml aliquot by using additions of 1×10^{-7}-1×10^{-6} *M* Cl^-. Calculate Cl^- content from calibration graphs or by the addition method.

538

Determination of Low Concentrations of Organic Carbon in Phosphoric Acid and Phosphate Rock.

J. Wimberley (Continental Oil Co., Ponca City, Okla.).

Analytica Chim. Acta 52 (1), 142-5 (1970).

The sample (up to 26 g and containing down to 50 ppm of organic C) is heated under reflux with a known amount of $K_2Cr_2O_7$ in the presence of H_2SO_4. The unconsumed $K_2Cr_2O_7$ is determined by titration with $(NH_4)_2SO_4 \cdot FeSO_4$ solution. A blank determination, and a determination without the heating under reflux (to correct for easily oxidized compounds), are also carried out. Results agree well with those obtained by dry-combustion in a Leco apparatus. The precision for three samples known to contain 89 to 760 ppm of C ranged from 0.7 to 1.6% (5 to 6 determinations each). Chloride interferes, but F^- does not.

539

Preparation of High-Purity Phosphorus. III. Determination of Microamounts of Carbon in Phosphorus.

M. Nakane, *et al.* (Govt. Ind. Res. Inst., Osaka, Japan).

Kogyo Kagaku Zasshi 71 (8), 1147-9 (1968) (Japan).

CA 70, 34018. (See *FA 2*, 154 for Part IV)

As little as 8 ppm C in P is determined by gas chromatography on a silica gel column after combustion in O_2 and passage through a heated zone of CuO, and collection of the CO_2 in a U-tube chilled with liquid O_2. Relative standard deviations are 6.7 and 4.6% for 33 and 366 ppm C, respectively.

540

A Nonaqueous Titrimetric Determination of Acid-Evolved Carbon Dioxide in Silicate Rocks.

J. I. Read (Dep. Trade Industry, Cornwall House, London, England).

Analyst (London) 97 (1151), 134-7 (Feb. 1972).

A method is described for the determination of carbonate in silicate rocks at concentrations, expressed as CO_2, down to 0.01%. After treatment with acid the CO_2 liberated is absorbed into a dimethylformamide solution and titrated directly with a solution of tetrabutylammonium hydroxide.

541

Gas Chromatographic Determination of Carbonate Carbon in Rocks and Minerals.

John Marinenko and Irving May (Washington, D.C.).

U.S., Geol. Surv., Prof. Pap., No. 700-D, 103-5 (1970).

A simple, rapid, and direct gas chromatographic method for determining carbonate C in rocks and minerals was developed. Powdered samples are heated with H_3PO_4, and evolved gases are separated on a silica-gel column. Carbon dioxide is detected by thermal conductivity using He as a carrier gas. The method is most applicable for determining CO_2 when only a limited quantity of sample is available. As little as 2 μg of CO_2 can be determined.

542

Infrared Spectra of Mineral Apatites.

V. M. Bhatnagar (Fisk Univ., Nashville, Tenn.).

Technology (Sindri) 5 (3), 189-91 (July-Sept. 1968).

The infrared absorption spectra of 17 samples of apatites from different localities are given. The frequencies and assignments of the bands are provided. The OH-band at 3578 cm was absent or very weak in many apatites. This may be due to their high contents of F or Cl.

543

Routine Determination of Major Constituents in Geologic Samples by Atomic Absorption.

O. Karmie Galle (State Geol. Survey, Univ. Kansas, Lawrence).

Applied Spectroscopy 22 (5), 404-8 (Sept.-Oct. 1968).

A method for determining Al, Fe, Ti, Mn, Ca, and Mg in minerals by atomic absorption is described. A sample weighing 0.5-1.0 g is put into solution by treatment with HF, fusion of the residue with $K_2S_2O_7$, and dissolution of the fusion with HCl. Determination of the various elements is then made using an acetylene-nitrous oxide flame and a premix type of burner. The method was developed to eliminate the necessity of changing flame parameters because of the refractory and

nonrefractory elements involved. Results obtained in analyzing NBS samples, 1-A, G-1, and W-1, and USGS standard samples BRC-1 and PCC-1 agreed within 0.1% or less with the listed values. Standard deviations and coefficients of variation calculated for all determinations were within acceptable limits.

544

Hygroscopicity of Complex Fertilizers—Determination of Critical Relative Humidity of Multicomponent Systems.

P. R. Geissler (Esso Res. & Engineering Co., Linden, N.J.).

J. Agr. Food Chem. 16 (3), 378-83 (May-June 1968).

A new vacuum line technique for the measurement of the equilibrium relative humidity of complex fertilizers consists of determing the vapor pressure of the saturated solutions that are formed on the surfaces of such fertilizers by the absorption of small amounts of water vapor. Applications of this method to systems of binary mixtures, reciprocal salt pairs, and commercial fertilizers containing several components are discussed. The main advantage is that the method can measure critical relative humidities of samples over a range of measurable water concentrations at the low concentrations usually found under storage conditions. (10 ref)

545

Investigation of the Calcium Sulfate-Water System by Infrared Spectroscopy.

John Bensted and Satya Prakash (Res. Lab., Assoc. Portland Cem. Mfr. Ltd., Greenhithe, England).

Nature 219 (5149), 60-1 (1968).

The $CaSO_4$-H_2O system was investigated by using infrared spectroscopy. Also thermogravimetric analyses and x-ray diffraction techniques were used where necessary. Calcium sulfate dihydrate was used as the starting material. The products of its thermal dehydration were prepared at temperatures in the range 97-700°. Many new infrared bands, not reported earlier, have been established. The spectra for the α and β forms of hemihydrate are identical as are those of α- and β-soluble anhydrite. The spectrum of gypsum shows four vibration bands in the H-O-H stretching region at 3245, 3410, 3500, and 3555 cm^{-1}. The two vibrations at 3560 and 3615 cm^{-1} in the spectrum of hemihydrate are υ_1 and υ_3 vibrations, respectively The frequencies at 3410 cm^{-1} in gypsum and 3615 cm^{-1} in hemihydrate can be used for analytical purposes. In the H-O-H bending region, the vibrational band 1688 cm^{-1} (υ_2, H_2O) can serve the same purpose, for it is absent in hemihydrate. The vibration is 1623 cm^{-1} is present in both gypsum and hemihydrate and is assigned to the υ_2 mode of H_2O. These frequencies are absent in both soluble and insoluble anhydrite. The existence of only three different products on thermal dehydration of $CaSO_4 \cdot 2H_2O$ is shown. The frequencies due to the sulfate group are again different and are important in distinguishing gypsum and all three types of dehydration products.

546

The Collection of Slurry Samples on a Field Scale and Their Subsequent Storage for Chemical Analysis.

T. A. Stewart (Greenmount Agr. Hort. College, Muckamore, Co. Antrim).

Rec. Agr. Res. Minist. Agr. Nth. Ire. 17, 97-100 (1968).

A simple and effective method of collecting slurry samples on a field scale where application is made by vacuum tanker, is described. This involves the attachment of buckets to the tanker in the vicinity of the spreading mechanism. Two buckets placed on either side of the tanker outlet were found to reduce sample variation compared with a single bucket suspended directly under the tanker outlet. Total-N, soluble-N, P_2O_5, and K_2O contents of fresh slurry samples collected by the two bucket method were similar to those obtained from samples collected in shallow trays placed at random around the field. The percentage dry matter and pH were significantly lower when collected in buckets attached to the tanker compared with field trays. The effects of a brief storage period on the chemical composition of slurry samples was examined in a single laboratory study. Storage at room temperature, in one-liter polythene bottles with tightly fitting screw-on lids, had the least effect on chemical composition when compared with storage of samples at room temperature after acidification and at temperatures below zero Centigrade. This was also the most convenient of the storage methods considered. Total and soluble N contents were unaffected after one week, and phosphate and potash contents after eight weeks storage at room temperature in this type of bottle.

547

General Referee Reports: Report on Fertilizer.

R. C. Rund (Purdue Univ. Lafayette, Ind.).

J. Ass. Offic. Anal. Chem. 54 (2), 270-1 (Mar. 1971).

The 84th annual meeting of the AOAC was held Oct. 12-15, 1970, at Washington, D. C. The recommendations of the General Referee as adopted by the Association are reported for fertilizers. **Automated Flame Photometric Method** *Ibid.* pp. 447-8. The automated flame photometric for K_2O in fertilizer as described in *J. Ass. Offic. Anal. Chem. 53*, pp. 456-60 (1970) was adopted. The analytical method is given.

548

General Referee Reports: Subcommittee A. Report on Fertilizers.

E. D. Schall (Purdue Univ., Lafayette, Ind.).

J. Assoc. Office Anal. Chemists 52 (2), 217-8 (Mar. 1969).

It is recommended that the alkalimetric quimociac method for total P, citrate-insoluble P, and available P by the direct method be adopted as official first action and that the method of sample preparation for citrate-insoluble and for available P by direct and indirect methods be continued. A collaborative study was conducted on a modification of the official STPB method for K. The modified procedure uses an aliquot from the direct available P_2O_5 sample solution rather than from the usual oxalate solution, thereby eliminating the need for a separate sample weighing and solution preparation. The collaborative results support the adoption of this modification as an official first action method.

SEE ALSO the following numbered abstract in another section: 423.

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