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RECENT ADVANCES IN FERTILIZER ANALYTICAL METHODS*

by

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SUMMARY

The developments in analytical methods for the determination of nitrogen, phosphorus, potassium, secondary elements, micronutrients, and a few miscellaneous constituents in fertilizers are traced over the last few years.

In the area of nitrogen analysis, studies on reductants for nitrate and salt-acid ratios in macro-Kjeldahl procedures are discussed. The use of the ammonia selective-ion electrode is cited in completed investigations as well as mention of its future potential. The adaptation of colorimetric methods for ammonia, nitrate, and urea nitrogen to automated analysis systems is discussed. The determination of biuret in urea and urea-based mixed fertilizers is also covered.

Phosphate methods development follows three concepts or approaches to the determination of P_2O_5 in fertilizers and materials. The gravimetric, alkalimetric and spectrophotometric methods are brought to their latest state of development. The adaptation of the spectrophotometric method to automated analysis also is reported. Different methods of extraction to simulate "availability" are mentioned, as well as problems associated with the introduction of polyphosphates in modern fertilizers.

Potassium methods discussed include gravimetric and titrametric tetraphenyl borate methods, and flame absorption and emission techniques. An automated flame method also is reported.

The analysis of fertilizers for the secondary elements calcium, magnesium, and sulfur is discussed only briefly. Chelometric and atomic absorption methods are cited for calcium and magnesium and an indirect chelometric method for sulfur is mentioned.

Methods for micronutrients in fertilizer have become almost totally dependent on atomic absorption spectrophotometry and are so reported. Boron is one exception and a colorimetric method is discussed for this important element.

*Prepared for presentation at the CENTO Seminar on Fertilizer Analytical Methods, Sampling, and Quality Control, Lahore, Pakistan, March 11-16, 1974.

Trace elements, such as cadmium, lead, chromium, vanadium, mercury, uranium, arsenic and selenium are discussed because of their contribution to pollution and their toxicity. Methods included for these elements employ flame absorption and emission, flameless atomic absorption and fluorimetry.

The last section of the paper includes methods for miscellaneous constituents such as water, fluorine and chlorine.

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The most widely used and most often cited methods for fertilizer analysis in the world today are probably those published by the Association of Official Analytical Chemists (AOAC) (1). These official methods are continually being modified, and new methods are being proposed by individual investigators. These new and modified methods are tested collaboratively and many are adopted as official. The AOAC sequence of investigator publications, associate referee collaborative studies, and finally adoption as official methods is the source for most of the information presented in this paper. In some areas, such as trace metals, the AOAC has not been active and other sources are cited.

For organization of this report it has been divided into five sections: Determination of Primary Nutrients, Secondary Nutrients, Micronutrients, Trace Metals, and Miscellaneous Constituents. Each element is discussed under the general classifications. Details of methods have not been included since these can be found in the primary references.

Determination of Primary Nutrients

Nitrogen: Since Kjeldahl (2) first proposed a sulfuric acid with catalyst digestion of materials to convert all nitrogen to ammonia, analytical chemists have modified this concept to fit their own products. Two of the most recent attempts to improve the Kjeldahl-type methods

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applicable to fertilizers are the Comprehensive Nitrogen Method (CNM) and the Raney Powder Catalyst Method (RPCM). The CNM proposed by Gehrke, et al., (3) employs chromium powder in a hydrochloric acid medium to reduce nitrates to ammonia prior to the sulfuric acid with mercuric oxide and potassium sulfate digestion to convert all other nitrogen to ammonia. The RPCM reported by Brabson and Woodis (4) used a Raney powder catalyst to reduce nitrates in a dilute sulfuric acid solution, followed by a digestion with concentrated sulfuric acid and catalysts. Both of these methods were studied by the AOAC and adopted as official methods (5). Within the past year the RPCM has been revised (6) to make it applicable to nitric-phosphate containing non-sulfate sulfur, to remove mercury as a catalyst, and to decrease the digestion time.

Data are presented in Tables 1 and 2 comparing nitrogen content of selected fertilizers and organic materials obtained by the modified RPCM and the CNM.

Historically, fertilizer chemists have used Devarda alloy to distill nitrogen from materials containing only ammoniacal and nitrate nitrogen. Recently Johnson and Miller (7) reported a method using a Raney powder catalyst as a substitute for Devarda alloy. It was shown that the Raney metal was as effective as Devarda in an alkaline solution. Table 3 compares the analysis of potassium nitrate by the Devarda, Raney, and a third extremely reliable method.

The determination of ammoniacal nitrogen in the presence of urea has been a tedious task because of the partial hydrolysis of urea in either acid or alkaline solutions. Woodis and Cummings (8) developed a method using an ammonia selective-ion electrode that gave very satisfactory

results for ammoniacal nitrogen in the presence of urea. The ammonia electrode also holds considerable potential for the analysis of Kjeldahl distillates instead of the normal titration. The results by the electrode method are compared in Table 4 with an acceptable distillation method.

The use of automated instrumental equipment has been the primary objective of at least two research papers. Gehrke, Killingley, and Wall (9) published a comprehensive report on their development of an automated method using equipment designed and marketed by Technicon, Inc. The chemical basis for this work was conversion of all nitrogen to ammonia by either reduction or digestion and finally measuring the ammonia by a spectrophotometric method. Herz (10) reported on an automated method based on combustion of materials to form nitrogen gas which was trapped and measured in a nitrometer. Both methods have been applied to fertilizers, and representative data from the latter study are presented in Table 5.

Phosphorus: Since the adaptation of the quinoline molybdate method to a gravimetric procedure by Ferrin (11) there has been no method for total phosphorus that has rivaled its accuracy. When the precipitate is dried at 200°C and weighed, it has the formula of $(C_8H_7N)_3Mo_7[PO_4 \cdot 12MO_3]$ and a molecular weight of 3212.69. This compound is 3.20% P_2O_5 , which gives a very favorable gravimetric factor. Several modifications have been made in the gravimetric quinoline method, and it remains the best referee method available.

To eliminate the objection to gravimetry, Duncan and Brabson (12) adapted the quinoline method to a titrimetric procedure. Previous attempts at titrating the quinoline molybdophosphate had been fraught with problems in dissolving the insoluble precipitate. The addition of an excess of citric acid prior to the precipitation prevented the formation of insoluble

lumps and instead produced large crystals of quinoline molybdophosphate. These crystals dissolved much easier and made the final titration feasible. Comparison of gravimetric and alkalimetric results on selected fertilizers is shown in Table 7.

The vanadomolybdate method is the most acceptable spectrophotometric method for the determination of phosphorus in fertilizers. It was adopted as an official method by the AOAC in 1958 (13). Several investigators (14, 15, 16, 17) have used this basic procedure to develop automated methods with equipment from Technicon. The two most recent papers have reported on methods to determine P_2O_5 in citrate extractions directly, with no digestion to destroy the citrate. The method proposed by Gehrke, et al., (15) was the basis for two AOAC collaborative studies (18, 19). In both of the studies, results of the gravimetric quinoline method were compared with the automated vanadomolybdate method. The results indicated that the automated method gave comparable average values but was significantly less reliable than the gravimetric method. A summary of the statistics of the last study is presented in Table 8.

The introduction of polyphosphate technology in the fertilizer industry has made it necessary for the chemists to find methods to determine the polyphosphate content of these products. Two approaches have been taken: to analyze the material for orthophosphate and total phosphate and assign the difference to polyphosphate content, and to separate the different individual phosphate species by ascending paper chromatography. Both methods are described by Johnson (20) in a monograph edited by M. Halmann. Improvements have been made in the chromatographic method by Woodis, Trimm, and Duncan (21). These improvements include a new solvent that causes less hydrolysis of the phosphate species. Typical chromatographic analyses are shown in Table 9.

Potassium: The development of a method for the analysis of potassium in fertilizers using sodium tetraphenylboron (STPB) was first reported by Schall (22). The method was a titrametric procedure in which excess STPB was added to precipitate the potassium and the excess was back-titrated with a quaternary ammonium solution. This method, or some slight modification, is used extensively today.

A gravimetric procedure based on the precipitation of potassium with STPB, drying at 120°C, and subsequent weighing is used in Japan (23). A comparison of a gravimetric STPB method and the AOAC titrametric method (1) was made by Melton, Hoover, and Howard (24). The data obtained by the two methods are comparable and are presented in Table 10.

Flame photometry is the instrumental technique used for the analysis of potassium. The official AOAC method (1) has been used successfully for a number of years. Recently the flame procedure has been automated (25) and, after two collaborative studies (26, 27), was adopted as an official method. The automated method utilizes Technicon equipment and when compared to the titrametric STPB in the collaborative studies yielded accepted results. A summary of the statistics from the latest collaborative study is shown in Table 11.

Determination of Secondary Elements

Calcium: Normally, analyses for calcium are not made on finished fertilizers. Occasionally, calcium is determined on phosphate rock in a quality control laboratory of a wet-process acid plant and sometimes it is useful to know the calcium impurity level of wet-process phosphoric acid.

There are two approaches to determine macro amounts of calcium in the presence of phosphorus; the classical oxalate precipitation method similar to that listed by AOAC (1) and complexometric titration methods. Several methods have been proposed to determine calcium in fertilizers with the chelating agent EDTA. Many of these are fraught with interference problems and some are too cumbersome for routine analyses. The method currently used in Japan (23) is probably adequate for most samples.

The analyses of fertilizer or related materials for low concentrations of calcium are most effectively done by atomic absorption spectrophotometry (AAS). McBride (28) summarized the results of three collaborative studies which included calcium by AAS. His recommendations were that the method for calcium gave acceptable results. In our own laboratory at TVA we have effectively used the AAS method to determine many elements including calcium at levels below 0.1% in wet-process phosphoric acid.

Magnesium: The concentration of magnesium in fertilizers or related materials is almost always at levels below 2%, either as an impurity or as an added micronutrient. As an impurity in wet-process phosphoric acid, magnesium can cause precipitation of various compounds that produce an objectionable "sludge." This impurity, of course, originates in the rock phosphate and this necessitates analysis of the rock prior to wet-process acid production.

Two methods of analysis are most frequently used to determine magnesium--titration with EDTA and AAS. Several chelometric methods have been proposed that are similar to the one used in Japan (23). To obtain good results by the EDTA methods it is generally necessary to previously remove the interfering ions; this can be done by ion exchange resins.

Since the introduction of AAS methods this has been the most popular approach. It has extreme sensitivity and is relatively free of all interferences. McBride (28) included magnesium in his studies; this method has been accepted as an official method by the AOAC.

The EDTA titration and AAS analysis of thirteen wet-process acids for calcium and magnesium are compared in Table 12. All EDTA titrations were made on previously treated sample solutions to remove phosphate and interfering cations. The AAS results were obtained on solutions after ion exchange and on untreated solutions.

Sulfur: Recent developments in the analysis of sulfur in the presence of phosphate have included titration with barium perchlorate, precipitation with lead and back-titrating the lead with EDTA, turbidimetric measurement of barium sulfate suspensions, and indirect AAS techniques. Archer, White, and Mackison (29) titrated sulfate with $\text{Ba}(\text{ClO}_4)_2$ using the indicator carboxyarsenazo, after removal of large amounts of cations by ion-exchange resins. After removal of phosphate and divalent cations with ion-exchange resins, Woodis, Johnson, and Cummings (30) precipitated sulfate with excess lead and then back-titrated the lead with EDTA. Turbidimetric measurements of a glycerol-stabilized suspension of BaSO_4 were made by Panteleeva and Krupina (31) on samples of phosphoric acid. The measurement of excess barium used to precipitate sulfate by AAS was proposed by Magyar and Santos (32). The four methods cited above should be applicable to fertilizers if the sulfur is present in the sulfate form or is converted to sulfate by oxidative preparation.

Data obtained by the lead precipitation method (30) on selected metal sulfates that may be found in fertilizers are presented in Table 13.

Determination of Micronutrients

The methods for the determination of metallic micronutrients have been dominated in recent years by atomic absorption spectrophotometry (AAS). Several investigators (28, 33, 34, 35) have published AAS methods that included manganese, copper, zinc, and iron. These methods differ mostly by the techniques used in preparation of the sample solution. Preparation of the sample solution is relatively easy for all materials except frits; these require special precautions if total metal content is desired. The AAS methods are excellent because of their good sensitivity, rapidity, and relative freedom from interferences.

Boron is one micronutrient that has had special attention by researchers recently. Weger, Hossner, and Ferrara (36) extracted boron from an acid fertilizer solution with 2-ethyl-1, 3-hexanediol, and then made the final determination with AAS. They claim good sensitivity, good signal-to-noise ratio, and negligible interferences. Experience in our laboratory, however, indicates the boron, hollow-cathode lamp to be noisy and to have a short usable life.

Pickett, Pau, and Koirtjohann (37) also used 2-ethyl-1, 3-hexanediol to extract boron but claims a distinct advantage for flame emission measurement over AAS. An air-hydrogen flame was used which increased sensitivity by 10 over AAS.

Perhaps the most convenient and reliable method for boron in fertilizers is a spectrophotometric method reported by Hofer, Brosche, and Heidinger (38). The 2-ethyl-1, 3-hexanediol is again used as the extractant; boron is reextracted with 0.5 N NaOH and determined spectrophotometrically with the color being formed by Azomethine-H. They claim 0.001 to 0.006% boron can be determined in complex fertilizers. This method has been successfully applied in our laboratory.

The determination of molybdenum in fertilizers continues to pose problems. One proposed method (39) utilized AAS with a nitrous oxide-acetylene flame after complexation with 8-hydroxyquinoline and extraction into chloroform. The method proved to be sensitive and precise but appeared to have a positive bias of about 5%; this positive bias was confirmed in our laboratory.

Determination of Trace Metals

This section has been included because of the toxicity of many trace elements and the need for emphasis on their determination in fertilizer plant pollution studies. The elements selected are all present in phosphate rock but the list is not intended to be complete.

Examples of the concentrations of trace metals in phosphate rock and wet-process phosphoric acid are shown in Table 14 (unpublished TVA data). The rocks analyzed were randomly selected and are not intended to be representative of major U.S. deposits. The acids and gypsum samples also were randomly selected and do not correspond to the respective rocks from the same geographic area. Methods of analysis used to obtain the data were as follows: mercury--flameless atomic absorption modified from the method of Hatch and Ott (40); cadmium and lead--AAS with prior organic solvent extraction for lead; vanadium and chromium--flame emission as reported by Johnson, Woodis, and Cummings (41); selenium--modification of the fluorometric method reported by Levesque and Vendette (42); and arsenic--distillation of arsenic as $AsCl_3$ followed by spectrophotometric measurement.

Another trace element that is commonly associated with phosphate rock is uranium. Analytical methods for uranium are not abundant and those that are available are cumbersome and tedious. A spectrophotometric method reported several years ago (43) has been found, in our laboratory, to give good results with a minimum of trouble.

Determination of Miscellaneous Constituents

Fluorine: For some forty years, distillation-titration methods based on the work of Willard and Winter (44) have been dominant in the selection of methods to determine fluorine in fertilizers. These methods involve the distillation of fluorine with perchloric or sulfuric acid as hydrofluosilicic acid and its subsequent titration with thorium nitrate using various indicators to detect the endpoint. They are excellent methods but are rather long and tedious.

The development of the fluoride selective-ion electrode has led to several methods for fluorine in fertilizer materials. Duff and Stuart (45) used the fluoride electrode to determine fluorine in calcium phosphates with sodium citrate as a buffer to reduce interferences. Yamazoe (46) applied the electrode to perchloric acid distillates of fertilizers and plant material. Fluorine in phosphoric acid was determined directly by Hanson and Lloyd (47) utilizing the fluoride electrode. The application of these selective-ion electrodes is the most promising development for fluorine analysis in recent years and has been used in our laboratory with great success.

Biuret: Spectrophotometric methods based on biuret-metal complexes have been in use for some time. Copper has been the most commonly used metal and is specified in the official AOAC method (1). Nickel was substituted for copper by Makerevich and Koyander (48) and they claimed that the nickel tartrate-biuret complex was not affected by free ammonia or phosphate as is the copper complex.

In 1973 Corominas (49) conducted an AOAC collaborative study comparing the official method, the nickel method, and a modification of the official method. The main modifications made in the official method were: the size of the sample was increased to ensure a representative sample, and the biuret used for preparation of the calibration curve was recrystallized. On the basis of 515 individual results from seven laboratories, the modified official method yielded the best results.

Chloride: The determination of chloride in fertilizer materials is generally required for one of two reasons: to ascertain why a liquid is corrosive or to guard against the toxic effect of chloride on certain plants. Historically, the classical silver nitrate titration method has been used, but it does not work well for very small quantities of chloride and it requires considerable time. A chloride selective-ion electrode was used by Duff and Stuart (50) to determine chloride in calcium phosphates. They used the electrode with a Hg/HgSO_4 reference electrode and made their measurements in a buffered solution at a pH of 2.5.

Voltametric titrations of chloride in phosphoric acid were made with a silver electrode by three Russian workers (51). After the sample of acid was neutralized to pH 5, known additions of chloride were made and polarograms were recorded. Chloride content was determined from calibration graphs.

Water: The determination of water is very important in assessing the physical and storage properties of fertilizers. Two approaches to this analysis have been vacuum methods and heating at temperatures of about 100°C . Vacuum techniques suffer from the time it takes to complete an analysis, generally from 4 to 15 hours; and heating methods very often give erroneous results by volatilizing constituents other than water.

The AOAC Associate Referee for water has made four reports (52, 53, 54, 55) recently on different aspects of water in fertilizers. In the first of this series of papers, methods for the determination of free and total water are proposed. The free water is obtained by extraction of the sample with 1,4-dioxane and titrating the extract with Karl Fischer reagent. Total water was determined by separation of water (including water of crystallization) by azeotropic distillation with n-amyl alcohol and titrating the distillate with Karl Fischer reagent. The results obtained on several compounds normally found in fertilizers are presented in Table 15. The last paper in the series from the Associate Referee recommended adoption of the method for free water as an official method. The method for total water was not recommended because it was found that nitrate seriously interfered, causing high results.

Closing Remarks

Recent advances for the determination of primary nutrients in fertilizers have been mainly in the area of automated systems. Equipment necessary for automation is expensive but when compared to manpower saved, it is generally justified. I expect this trend to continue with more instrument companies designing acceptable systems.

Flame spectroscopy has made the determination of micronutrients and trace elements in fertilizers and materials quite easy. Atomic absorption and flame emission spectrophotometric methods are relatively free of interferences and are simple to apply. Improved flames and other sample atomization techniques will dominate future advance in this field of analysis.

The measurement of the quality of fertilizers by analytical chemists throughout the world will continue to be an important contribution to the production of food for mankind.

References

- ✓ 1. Official Methods of Analysis, 11th Ed., AOAC, Washington, DC, 1970.
2. Kjeldahl, J., Z. Anal. Chem. 22, 366 (1883).
3. Gehrke, C. W., Ussary, J. P., Perrin, C. H., Rexroad, P. R., and Spangler, W. L., J. Assoc. Official Anal. Chem. 50 (4), 965-975 (1967).
4. Brabson, J. A., and Woodis, T. C., Jr., J. Assoc. Official Anal. Chem. 52 (1), 23-30 (1969).
5. Rexroad, P. R., and Krause, G. F., J. Assoc. Official Anal. Chem. 53 (3), 450-456 (1970).
6. Johnson, F. J., Woodis, T. C., Jr., and Cummings, J. M., Jr., J. Assoc. Official Anal. Chem. 57 (1), 10-13 (1974).
7. Johnson, F. J., and Miller, D. R., J. Assoc. Official Anal. Chem. 57 (1), 8-9 (1974).
8. Woodis, T. C., Jr., and Cummings, J. M., Jr., J. Assoc. Official Anal. Chem. 56 (2), 373-374 (1973).
9. Gehrke, C. W., Killingley, J. S., and Wall, L. L., Sr., Advances in Automated Analysis, Vol. 7, 33-49 (1973). (1972 Technicon International Congress.)
10. Merz, W., Amer. Lab. 5, 25-35 (1973).
11. Perrin, C. H., J. Assoc. Official Anal. Chem. 41 (4), 758-763 (1958).
12. Duncan, R. D., and Brabson, J. A., J. Assoc. Official Anal. Chem. 49 (6), 1201-1207 (1966).

13. Brabson, J. A., Dunn, R. L., Epps, E. A., Jr., Hoffman, W. M., and Jacob, K. D., J. Assoc. Official Anal. Chem. 41 (3) 517-524 (1958).
14. Ferretti, R. J., and Hoffman, W. M., J. Assoc. Official Anal. Chem. 45 (4), 993-996 (1962).
15. Gehrke, C. W., Baumgartner, J. H., and Ussary, J. P., J. Assoc. Official Anal. Chem., 49 (6), 1213-1218 (1966).
16. Hambleton, L. G., J. Assoc. Official Anal. Chem., 56 (5), 1078-1083 (1973).
17. Wall, L. L., and Gehrke, C. W., J. Assoc. Official Anal. Chem. (in press, 1974).
18. Johnson, F. J., J. Assoc. Official Anal. Chem. 55 (5) 979-983 (1972).
19. Johnson, F. J., J. Assoc. Official Anal. Chem. 56 (5), 1084-1086 (1973).
20. Johnson, F. J., "Phosphorus in Fertilizers and Feedstuffs," Analytical Chemistry of Phosphorus Compounds, Ed., M. Halmann, John Wiley and Sons, 1972.
21. Woodis, T. C., Jr., Trimm, J. R., and Duncan, R. D., Anal. Chim. Acta 65, 469-473 (1973).
22. Schall, E. D., Anal. Chem. 29 (7), 1044-1046 (1957).
23. Official Method of Analysis of Fertilizers, September 1972. The National Institute of Agricultural Sciences, Tokyo, Japan.

24. Melton, J. R., Hoover, W. L., and Howard, P. A., J. Assoc. Official Anal. Chem. 56 (2), 375-377 (1973).
25. Ussary, J. P., and Gehrke, C. W., J. Assoc. Official Anal. Chem. 48 (6), 1095-1100 (1965).
26. Hambleton, L. G., J. Assoc. Official Anal. Chem. 53 (3), 456-460 (1970).
27. Hambleton, L. G., J. Assoc. Official Anal. Chem. 54 (3), 646-650 (1971).
28. McBride, C. H., J. Assoc. Official Anal. Chem. 51 (4), 847-851 (1968).
29. Archer, E. E., White, D. C., and Mackison, R., Analyst 96, 879-880 (1971).
30. Woodis, T. C., Jr., Johnson, F. J., and Cummings, J. M., Jr., J. Assoc. Official Anal. Chem. 53 (5), 928-930 (1970).
31. Panteleeva, E. P., and Krupina, I. N., Zh. Anal. Khim. 25 (10) 1989-1994 (1970).
32. Magyar, B., and Santos, F. S., Helv. Chim. Acta 52 (3), 820-827 (1969).
33. Skinner, J. M., Proc. Soc. Anal. Chem. 6 (3), 131-154 (1969).
34. Teicher, K., Landwirt. Forsch. Sonderh. 23 (11), 177-181 (1969).
35. Hammer, H. E., and Page, N. R., At. Absorption Newsletter 6 (2), 33-34 (1967).
36. Weger, S. J., Hossner, L. R., and Ferrara, L. W., J. Agr. Food Chem. 17 (6), 1276-1278 (1969).
37. Pickett, E. E., Pau, J.C.M., and Koirtzohann, S. R., J. Assoc. Anal. Chem. 54 (4), 796-800 (1971).

38. Hofer, A., Brosche, E., and Heidinger, R., Fresenius' Z. Anal. Chem. 253 (2), 117-119 (1971).
39. Koirtyohann, S. R., and Hamilton, M., J. Assoc. Official Anal. Chem. 54 (4), 787-789 (1971).
40. Hatch, W. R., and Ott, W. L., Anal. Chem. 40 (14), 2085-2087 (1968).
41. Johnson, F. J., Woodis, T. C., Jr., and Cummings, J. M., Jr., At. Absorption Newsletter 11 (6), 118-119 (1972).
42. Levesque, M., and Vendette, F. D., Can. J. Soil Sci. 51 (1), 85-93 (1971).
43. Francois, C. A., Anal. Chem. 30 (1), 50-54 (1958).
44. Willard, H. H., and Winter, O. B., Ind. Eng. Chem., Anal. Ed. 5, 7-10 (1933).
45. Duff, E. J., and Stuart, J. L., Anal. Chim. Acta 52 (1), 155-157 (1970).
46. Yamazoe, F., Nippon Dojo-Hiryogaku Zasshi 42 (1), 44 (1971).
47. Hanson, W. C., and Lloyd, D. J., Chem. Ind. (London) 1, 41-42 (1972).
48. Makarevich, V. M., and Koyander, A. E., Agrokhimya 1, 139-143 (1970).
49. Corominas, L. F., J. Assoc. Official Anal. Chem. (in press, 1974).
50. Duff, E. J., and Stuart, J. L., Anal. Chim. Acta. 57 (1), 233-235 (1971).
51. Bikmatova, G. S., Zakharchuk, N. F., and Yudelevich, I. G., Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Khim. Nauk 1, 154-157 (1970).

52. Duncan, R. D., and Brabson, J. A., J. Assoc. Official Anal. Chem. 52
(6), 1127-1131 (1969).
53. Duncan, R. D., J. Assoc. Official Anal. Chem. 54 (4), 988 (1971).
54. Duncan, R. D., J. Assoc. Official Anal. Chem. 54 (4), 989-990 (1971).
55. Duncan, R. D., J. Assoc. Official Anal. Chem. 55 (4), 699-701 (1972).

TABLE 1

Total Nitrogen Contents of Organic Materials

Material	N content, %, determined by indicated method			
	AOAC CNM		Modified Raney	
	Av. ^a	Range	Av. ^a	Range
Cow manure	0.57	0.03	0.58	0.00
Milorganite	5.49 ^b	0.06	5.55	0.03
Hynite tankage	10.42	0.10	10.44	0.02
Castor pomace	5.36	0.05	5.27	0.10
Cottonseed meal	6.14	0.25	6.15	0.15
Feather meal	13.44	0.07	13.42	0.08
Gelatin	15.08	0.11	14.97	0.29
Blood meal	12.41	0.08	12.28	0.10

^a Average of 3 determinations.

^b Average of 6 determinations.

(Johnson, Woodis, and Cummings, Reference 6)

TABLE 2

Total Nitrogen Contents of Selected Fertilizers

Material	N content, %, determined by indicated method			
	AOAC CNM		Modified Raney	
	Av. ^a	Range	Av. ^a	Range
Ammonium sulfate	20.91	0.16	20.93	0.06
Ammonium nitrate	34.14	0.07	34.12	0.12
Urea	46.34	0.20	46.43	0.01
Uran solution	32.42 ^b	0.22	32.48	0.06
Nitroform	38.85	0.11	38.95	0.08
Uramite	36.70	0.03	36.98	0.35
IBDU	31.28	0.37	31.63	0.09
DAP	17.77	0.13	17.88	0.03
13-13-13	13.53	0.07	13.55	0.03
17.6-17.6-17.6	17.32	0.13	17.46	0.04

^a Average of 3 determinations.

^b Average of 6 determinations.

(Johnson, Woodis, and Cummings, Reference 6)

TABLE 3

Analysis of 0.35 g KNO₃

	<u>N content, %, found by indicated method</u>		
	<u>Raney</u>	<u>Devarda</u>	<u>Chromous solution</u>
	13.79	13.78	13.79
	13.77	13.79	13.79
	13.83	13.83	13.77
	13.84	13.77	13.77
	13.77	13.75	13.77
	13.82	13.76	13.77
	13.82	13.76	13.77
		13.76	
Average	13.806	13.775	13.776
Range	0.07	0.08	0.02
Std. deviation	0.028	0.026	0.010

(Johnson and Miller, Reference 7)

TABLE 4

Application of Electrode Method to Fertilizers Containing Urea

Material	Urea in aliquot, g	Electrode method			Reduced pressure distillation
		N, % ^a	Range	Std dev.	N, % ^b
UAP	0.150	5.08	0.24	0.08	5.04
UAN	0.125	7.03	0.20	0.06	7.07
UAPP	0.210	5.54	0.22	0.08	5.48
UAS	0.325	3.85	0.14	0.05	3.84

^a Average of 9 determinations.

^b Single determinations.

(Woodis and Cummings, Reference 8)

TABLE 5

Fertilizer Analyses^a

<u>Type of fertilizer</u>	<u>% N according to method book</u>	<u>% N determined with Rapid-N</u>
Nitrophoska blue	12.01	12.01
Nitrophoska red	12.89	12.96
Nitrophoska 15:15:15	14.84	14.80
Nitrophoska 20:20:0	19.54	19.58
Nitrophoska 15:15:6:4	14.78	14.71
Ammonium sulfate saltpeter	26.12	26.12
Calcium cyanamide	18.63	18.64
Multiple nutrient fertilizer CDH	20.21	20.26
Lawn fertilizer	20.14	20.21
Floranide	28.36	28.40
Isodur	30.10	30.04
Calcium ammonium saltpeter	22.66	22.59

^a Mean value from 10 determinations. Sample weight: 5-30 mg.

(Merz, Reference 10)

TABLE 6

Total P₂O₅ by Gravimetric Quinoline Molybdate Method

<u>Material</u>	<u>% P₂O₅</u>		<u>No. of Detmns</u>	<u>Range</u>	<u>Std. Dev.</u>
	<u>Theory</u>	<u>Found</u>			
Single crystal NH ₄ H ₂ PO ₄	61.701	61.705	10	0.03	0.012
NBS phosphate Rock 56A	32.90 (certificate)	32.915	4	0.03	0.01
KH ₂ PO ₄ (recrystallized)	52.153	52.128	4	0.02	0.01
TSP	47.66 ^a	47.665 47.658	2 2	0.01 0.01	- -
8-20-20 (synthetic)	20.85 (calculated)	20.86	1	-	-

^a Value obtained in collaborative study by differential spectrophotometry.
(Perrin, Reference 11)

TABLE 7

Comparison of Alkalimetric (alk.) and Gravimetric (grav.)
Quimociac Methods in Analysis of Fertilizers

Material	$P_2O_5, \%$							
	Direct Available (DA)		Citrate-Insoluble (CI)		DA + CI		Total	
	Alk.	Grav.	Alk.	Grav.	Alk.	Grav.	Alk.	Grav.
10-6-4	6.38	6.40	0.15	0.14	6.53	6.54	6.54	6.54
6-12-12	10.73	10.71	2.26	2.27	12.99	12.98	13.03	13.01
5-20-20	19.15	19.12	0.67	0.67	19.82	19.79	19.95	19.95
18-46-0	44.87	44.91	0.49	0.49	45.36	45.40	45.59	45.59
KH_2PO_4	52.15	52.09	nil	nil	52.15	52.09	52.13	52.18
APP	56.73	56.76	a	a	-	-	59.18	59.30

^a Citrate-insoluble residue cannot be filtered quantitatively.

(Duncan and Brabson, Reference 12)

TABLE 8

Statistics for the Collaborative Results for the Determination of P₂O₅ in Fertilizers by the Automated Spectrophotometric Method (ASM) and the Gravimetric Quinolinium Molybdophosphate Method (GQM)^a

<u>Pair</u>	<u>Av. found, mg</u>		<u>Sr, precision</u>		<u>Sb, systematic</u>		<u>Sd, total</u>	
	<u>GQM</u>	<u>ASM</u>	<u>GQM</u>	<u>ASM</u>	<u>GQM</u>	<u>ASM</u>	<u>GQM</u>	<u>ASM</u>
1	49.23	49.60	0.145	0.420	0.195	0.615	0.312	0.965
2	59.22	59.38	0.144	0.290	0.132	0.962	0.236	1.392
3	68.23	68.43	0.080	0.215	0.124	0.943	0.193	1.351
4	48.85	48.95	0.100	0.255	0.344	0.553	0.496	0.823
5	58.14	58.39	0.104	0.361	0.262	0.686	0.385	1.034
6	65.93	66.38	0.065	0.185	0.195	0.951	0.283	1.357

^a Results of a single determination on each pair by each collaborator.

(Johnson, Reference 19)

TABLE 9

Chromatographic Analyses of Ammonium Polyphosphates
with Ebel's Solvent and the New Solvent at 17°

Material	Solvent	Distribution (%) of phosphate				
		Ortho	Pyro	Tri	Tetra	Other
$(\text{NH}_4)_3\text{HP}_2\text{O}_7$	Ebel's	0.5	99.0	-	-	0.4
	New	0.2	99.6	-	-	0.2
$\text{Na}_5\text{P}_3\text{O}_{10}\cdot 6\text{H}_2\text{O}$	Ebel's	1.9	2.3	94.0	-	1.8
	New	0.8	0.5	98.4	-	0.3
$(\text{NH}_4)_6\text{P}_4\text{O}_{13}\cdot \text{nH}_2\text{O}$	Ebel's	1.2	2.6	3.8	92.2	0.3
	New	0.6	1.4	0.3	97.7	0.0
APP ^a	Ebel's	20.9	78.3	-	-	0.8
	New	20.3	79.4	-	-	0.4
APP ^a	Ebel's	13.2	16.2	70.6	-	0.0
	New	12.9	15.3	71.8	-	0.0
APP ^a	Ebel's	8.7	10.4	80.7	-	0.2
	New	8.1	9.3	82.5	-	0.0

^a The three ammonium polyphosphates were prepared in the pilot plant by ammoniation of three different electric-furnace polyphosphoric acids.

(Woodis, Trimm, and Duncan, Reference 21)

TABLE 10

Comparison of Volumetric (AOAC 2.090-2.092)
and Gravimetric Methods for Determining K₂O in Fertilizers

Magruder sample	Guarantee, %	K ₂ O, %		Grav. ^c
		AOAC		
		Grand av. ^a	Authors' lab. ^b	
6806	10	10.02	10.07	9.88
6807	24	24.27	24.24	24.26
6809	8	8.75	8.86	8.84
6903	16	15.07	15.09	15.06
7012	18	18.15	18.30	18.44
7105	20	19.99	19.92	20.20
7106	12	12.98	12.97	13.16

^a Means are based on a minimum of 73 analyses by Magruder collaborators.

^b Means are based on 4 analyses.

^c Means are based on 10 analyses in authors' laboratory.

(Melton, Hoover, and Howard, Reference 24)

TABLE 11

Statistics for Collaborative Results for Automated and Official STPB
Methods for K₂O in Fertilizers^a

<u>Pair</u>	<u>Av. Found, %</u>			<u>Sr Precision</u>			<u>S_b Systematic</u>			<u>S_d</u>		
	<u>Oxa- late</u>	<u>Cit- rate</u>	<u>STPB</u>	<u>Oxa- late</u>	<u>Cit- rate</u>	<u>STPB</u>	<u>Oxa- late</u>	<u>Cit- rate</u>	<u>STPB</u>	<u>Oxa- late</u>	<u>Cit- rate</u>	<u>STPB</u>
1	25.24	25.17	25.16	0.18	0.13	0.28	0.11	0.21	-S _b	0.24	0.32	0.19
2	14.89	14.88	14.81	0.06	0.10	0.13	0.08	0.06	0.09	0.10	0.13	0.18
3	8.01	7.95	7.96	0.06	0.14	0.11	0.07	0.19	0.14	0.12	0.30	0.22
4	42.67	42.47	42.54	0.41	0.40	0.12	0.13	-S _b	0.24	0.45	0.22	0.36
5	61.57	61.25	61.42	0.21	0.27	0.09	0.21	0.28	0.13	0.36	0.47	0.21
KNO ₃ std ^b	46.68	46.55	46.60							0.23	0.31	0.22

^a Results of a single determination on each pair by each collaborator.

^b 46.59% K₂O.

(Hambleton, Reference 27)

TABLE 12

Comparison of EDTA and AAS Methods for Ca and Mg in
Wet-Process Acid

Original sample no.	Ca, %			Mg, %		
	<u>EDTA^a</u>	<u>AAS^a</u>	<u>AAS^b</u>	<u>EDTA^a</u>	<u>AAS^a</u>	<u>AAS^b</u>
54469	0.022	0.016	0.021	0.62	0.59	0.60
55080	0.009	0.010	0.016	0.32	0.30	0.34
55084	0.014	0.016	0.028	0.64	0.58	0.60
55640	0.22	0.20	0.19	0.40	0.38	0.39
55641	0.15	0.16	0.16	0.37	0.32	0.33
55642	0.11	0.09	0.10	0.41	0.39	0.39
55644	0.10	0.11	0.10	0.38	0.34	0.34
55646	1.24	1.19	1.20	0.30	0.31	0.30
55647	0.63	0.60	0.59	0.33	0.30	0.31
55648	3.12	3.10	3.10	0.28	0.27	0.28
55756	0.09	0.09	0.06	0.42	0.36	0.38
55760	0.44	0.44	0.41	0.32	0.29	0.29
55889	0.82	0.83	0.81	0.32	0.33	0.32

^a After removal of phosphate and cations with ion-exchange resin
^b Read directly after proper dilution.

(Unpublished data from TVA)

TABLE 13

Analysis of Selected Metal Sulfates

Compound	% SO ₄ , by indicated method				
	Alkali- metric ^a	Chelometric Lead		BaSO ₄ Pptn	
		Less Cations ^b	On Acid Soln ^c	On Acid Soln ^c	Conver- sions
Al ₂ (SO ₄) ₃ K ₂ SO ₄ ·24H ₂ O	40.11	40.04	39.94	40.14	40.73
CuSO ₄ ·5H ₂ O	38.09	38.16	38.01	38.39	38.58
FeSO ₄ ·7H ₂ O	35.99	35.68	35.68	36.21	35.50
Fe ₂ (SO ₄) ₃ (NH ₄) ₂ SO ₄ ·24H ₂ O	40.11	40.16	40.03	40.18	40.15
MgSO ₄ ·7H ₂ O	41.65	41.61	41.35	41.49	41.92
MnSO ₄ ·H ₂ O	56.28	56.17	56.17	55.21	56.62
NiSO ₄ ·6H ₂ O	36.25	36.43	36.17	36.68	36.72
ZnSO ₄ ·7H ₂ O	33.82	33.71	33.76	33.96	34.58

^a Alkalimetric titration of acid formed by removal of cations with Amberlite IR-120-H cation resin; selected referee method.

^b After removal of cations with Amberlite IR-4B anion exchange resin.

^c After removal of cations with Amberlite IR-120-H cation resin.

(Woodis, Johnson, and Cummings, Reference 30)

TABLE 14

Determination of Selected Toxic Elements in Phosphatic Materials

<u>Material</u>	<u>Concentration, ppm</u>						
	<u>Hg</u>	<u>Cd</u>	<u>V</u>	<u>Cr</u>	<u>Pb</u>	<u>Se</u>	<u>As</u>
Phosphate rock							
North Carolina	0.18	25	47	135	9	3.2	16.7
Central Florida	0.04	7	66	49	7	1.1	7.3
Idaho	0.31	150	1380	790	18	11.9	14.1
North Florida	0.04	6	54	64	12	1.6	5.8
Tennessee	0.02	3	33	13	21	0.6	9.6
Missouri	<0.01	3	17	4	9	0.6	81.2
Phosphoric acid ^a							
North Carolina	-	25	46	731	4	0.4	5.0
Central Florida	-	22	174	537	6	0.1	1.0
Idaho	-	132	150	613	4	0.1	5.4
Gypsum							
North Carolina	<0.01	4.8	4.6	9.2	12.3	2.0	5.3
Central Florida	<0.01	0.7	10.3	3.1	8.3	0.9	3.7
Idaho	0.014	17.9	24.1	29.6	8.6	4.8	23.9

^a Superphosphoric acid, 73-75% P₂O₅.

(Unpublished data from TVA)

TABLE 15

Total and Free Water Contents of Fertilizer Compounds

<u>Compound</u>	<u>Water Content, %</u>			<u>Moles Hydrate Water/ Formula Wt</u>
	<u>Total^a</u>	<u>Free^b</u>	<u>Hydrate, by Diff.</u>	
$\text{Ca}_2\text{NH}_4\text{H}_7(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}$	6.70	Nil	6.70	1.94
$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$	20.26	Nil	20.26	1.94
$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$	7.29	0.08	7.21	1.01
$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$	24.80	0.79	24.01	2.11
$\text{Al}_3\text{KH}_{14}(\text{PO}_4)_8 \cdot 4\text{H}_2\text{O}$	7.61	0.24	7.37	3.95
$\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$	31.04	0.07	30.97	3.00
$\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$	43.17	0.05	43.12	5.87
$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$	19.70	0.16	19.54	2.03

^a By distillation with n-amyl alcohol.

^b By extraction with 1,4-dioxane.

(Duncan and Brabson, Reference 52)