The above formulas apply to straight fertilizers. The same Equations 9, 10, 11, and 12 apply to the component risks for mixed fertilizers when the sampling plan is used to judge a manufacturer's performance.

Specimen Plan for Judging Performance of Manufacturer. How many samples should be taken from each of six batches (spread over 6 months, say) of a straight fertilizer and what should the specification limit be for a sampling plan based on the following parameters?

$$\alpha = 1\% \qquad \beta = 1\%$$

U_0 = long term reputed content, or guaranteed analysis
U_2 = 92% of reputed content
σ_1 = 3% of reputed content
σ_2 = 4% of reputed content

Because $\alpha = \beta = 1\% = 0.01$, from tables of the cumulative normal distribution, $t_\alpha = t_\beta = 2.326$. Thus from Equation 16, since $m = 6$,

$$n = (0.04U_0)^2(4.652)^2/\{6(U_0 - 0.92U_0)^2 - (0.03U_0)^2(4.652)^2\}$$

$$= (0.04)^2(4.652)^2/\{6(1 - 0.92)^2 - (0.03)^2(4.652)^2\}$$
$$= 1.83$$

Rounding off to the nearest whole number, $n = 2$. From Equation 18,

$$C = U_0 - (2.326)\{(0.03U_0)^2/6 + (0.04U_0)^2/6(1.83)\}^{1/2}$$
$$= U_0[1 - (2.326)\{(0.03)^2/6 + (0.04)^2/6(1.83)\}^{1/2}]$$
$$= U_0[1 - 0.0400]$$

i.e.,

$$C = 0.96U_0 \,(= 96\% \text{ of } U_0)$$

The specimen sampling plan would be: "Take two random samples from each of six batches, the selected batches being sampled, over a period of time, as they are produced, and analyze the 12 samples (or a smaller number of good composites); if the mean of the 12 analyses (or the mean of the composites) is less than 96% of the long-term reputed content, the manufacturer is producing material which is not acceptable."

The operating characteristic curve for the specimen sampling plan can be constructed from the formula

$$t = (U - C)/(\sigma_1^2/m + \sigma_2^2/mn)^{1/2}$$

which is obtained from Equation 14 by regarding U as a variable and expressing it as a percentage of the long-term reputed content.

ION ASSAYS

Simultaneous Determination of Phosphate and Sulfate Ions in the Presence of Metal Contaminations

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A method is presented for determining phosphate and sulfate ions simultaneously in the presence of calcium, magnesium, aluminum, iron, and fluoride ions as contaminants. The method is suitable for the rapid and simple determination of phosphate and sulfate ion content of phosphorus fertilizers.

A SIMPLE VOLUMETRIC METHOD (5), presented for the determination of phosphate and sulfate ions in the presence of each other, is suitable for the investigation of alkali salts. It is based on the following principle: The dissolved sample is adjusted with an ammonium hydroxide–ammonium chloride buffer to pH 10, ethyl alcohol is added, and the mixture is titrated with a standard solution of magnesium chloride and Eriochrome Black T as indicator. During the course of titration, crystalline magnesium ammonium phosphate is precipitated (2). At the equivalence point the excess magnesium ions react with the indicator to produce a color change from blue to purple-violet. Then the original blue color of the reaction mixture is recovered by adding a few drops of EDTA [(ethylenedinitrilo)tetraacetic acid, complexone III] and the sulfate ions are titrated with standard barium chloride solution

(4). During this titration barium sulfate precipitates and, after the equivalence point is reached, magnesium ions are liberated from their complexonate bonds by the excess barium ions; this is indicated again by a color change from blue to purple-violet as in the first titration.

In a previous communication (4) an analogous measurement of arsenate ions with a standard solution of magnesium sulfate was suggested and was also applied to the determination of calcium arsenate (6). Essentially the same principle was utilized to mask certain ions which interfered in the investigation of phosphate fertilizers (3), as the earlier method suggested for the simultaneous determination of alkali sulfates and phosphates in the presence of Mg^{+2}, Ca^{+2}, Fe^{+3}, and Al^{+3} (1) was unsatisfactory for this purpose. Therefore, in the presence of these ions, as in the analysis of phosphorus ferti-

lizers, the simultaneous determination of phosphates and sulfates was completed as follows:

Ferric and aluminum ions were masked with DCTA (1,2-diaminocyclohexanetetraacetic acid or complexone IV) in a solution whose pH was buffered between 2 and 3; then EDTA was added and the solution was adjusted to pH 10.0 to 10.5 with ammonium hydroxide, and with a buffer mixture of ammonium chloride and ammonium hydroxide solutions. EDTA formed stable complexes with Ca^{+2} and Mg^{+2} and the complexes of DTCA formed with iron and aluminum between pH 2 and 3 did not decompose either, if the pH of the medium was adjusted to 10 (7, 8). Although Ca^{+2} and Mg^{+2} may be masked with DCTA, this technique was abandoned because of the expense.

After the metal ions were masked, Eriochrome Black T was added as indicator and the solution was titrated

Table I. Simultaneous Titration of Phosphate and Sulfate Ions in Solutions of Known Concentration after Masking Metallic Ions with Complexing Agents

KH₂PO₄, Gram	K₂SO₄, Gram	Added to Sample, Mg.				F⁻	DCTA,ᵃ Ml.	EDTA,ᵃ Ml.	Buffer, Ml.	EtOH in Titration of PO₄⁻³, Ml.	MgCl₂ᵃ Consumed, Ml.		Dev., %	KH₂PO₄ Found, Gram	EtOH in Titration of SO₄⁻², Ml.	BaCl₂ᵃ Consumed, Ml.		K₂SO₄ Found, Gram	Dev., %
		Ca⁺²	Mg⁺²	Al⁺³	Fe⁺³						Actual	Mean				Actual	Mean		
0.06685	0.08713	20	7.2	2.7	5.58	1.9	4	8	2	7	4.88 4.90	4.89	−0.45	0.06655	20	5.00 4.90	4.95	0.08626	−1.00
0.06685	0.08713	20	2.4	0.9	11.17	3.8	3	6	2	7	4.93 4.88	4.91	0.00	0.06682	20	5.00 4.95	4.98	0.08678	−0.40
0.06685	0.08713	20	2.4	0.9	11.17	1.9	3	6	2	7	4.88 4.90	4.89	−0.45	0.06655	20	5.00 5.00	5.00	0.08714	+0.12
0.06685	0.1730	20	7.2	1.8	11.17	1.9	5	6	3	10	4.85 4.90	4.88	−0.68	0.06640	25	10.00 9.90	9.95	0.1734	+0.23
0.1351	0.08713	20	7.2	1.8	11.17	1.9	5	6	3	10	9.90 9.85	9.88	−0.44	0.1345	25	5.00 5.00	5.00	0.08714	+0.12

ᵃ 0.1M solution.

with a standard solution of magnesium chloride until the transition color appeared, indicating the complete absence of free EDTA in the medium. After addition of ethyl alcohol, the phosphate ions were titrated with a standard solution of magnesium chloride, and the sulfate ions with a standard solution of barium chloride.

Calcium, magnesium, iron, and aluminum ions (as the chlorides) and sodium fluoride were added in amounts given in Table I to solutions of alkali phosphate and sulfate of known concentration. The results show that the accuracy of the measurements is satisfactory.

In the study of phosphorus fertilizers the sample was dissolved in hydrochloric acid, and phosphate and sulfate ions were determined in the solution by the suggested method. The values obtained were compared with gravimetric results (Table II).

Experimental

Reagents. A $0.1M$ standard solution of MgCl₂, prepared by dissolving magnesium oxide in hydrochloric acid. The solution may be standardized by complexometry.

$0.1M$ standard solution of BaCl₂.

Buffer solution prepared by dissolving 50 grams of ammonium chloride and 400 ml. of concentrated ammonium hydroxide in 1000 ml. of water.

Indicator, Eriochrome Black T triturated with potassium chloride in a ratio of 1 to 100. Both substances should be finely powdered.

Procedure. About 10 grams of the carefully homogenized sample of superphosphate fertilizer were weighed and dissolved by boiling with about 250 to 300 ml. of 15% hydrochloric acid. After filtration, the solution was transferred to a 500-ml. measuring flask, made to volume, and 10-ml. aliquots of this stock solution were examined as follows. The solution was neutralized in the presence of methyl orange with concentrated ammonium hydroxide, then with 10% ammonium hydroxide until a slight turbidity appeared. Care must be taken that the solution remains definitely red. Then 3 to 5 ml. of $0.1M$ DCTA solution were added (according to the requirements), the mixture was boiled, about 9 to 10 ml. of $0.1M$ EDTA solution were added, and the solution was cooled. About 0.015 to 0.020 gram of Eriochrome Black T indicator was dissolved in the medium, then as much concentrated ammonium hydroxide was added dropwise (about 4 to 6 drops) as was needed to obtain a greenish blue tint. Next, 3 ml. of buffer solution were added, and the excess EDTA and DCTA were eliminated by adding $0.1M$ standard solution of magnesium chloride. The proper starting point for the

subsequent titration was indicated by the appearance of the transition color. After this point was reached, about 5 ml. of ethyl alcohol were added and titration of phosphate ions with the standard $0.1M$ solution of magnesium chloride was started, using the same buret from which the magnesium chloride solution was added to attain the proper starting point. The first portion of the standard solution (50 to 75% of the expected total) was added at once, and then the medium was shaken until precipitation started (always within a minute) and the liquid turned greenish blue. Further precipitation of the magnesium ammonium phosphate during titration occurred immediately and titration was continued at the conventional rate until a stable purple-violet color appeared. The end point was easily observable by the color change.

Before titration of the sulfate ions, the original blue tint of the medium was recovered by adding a few drops of a $0.1M$ EDTA solution. In the presence of minute amounts of EDTA the color transition takes place before the equivalence point; therefore, small measured excesses (0.2 ml.) of EDTA solution were added and this volume was subtracted from the total amount of standard solution used. Then enough ethyl alcohol was added to obtain a solution of about 40% with respect to ethyl alcohol at the equivalence point. Sulfate ions were then titrated with $0.1M$ barium chloride solution under continuous shaking. The last drops of standard solution were added slowly until the purple-violet color of the indicator appeared.

Discussion

The presence of ammonium chloride proved to be favorable for the formation of the magnesium ammonium phosphate precipitate. Therefore, in all experiments summarized in Table I, 1 gram of ammonium chloride was added to the titrated solutions.

Addition of ammonium chloride is, however, not necessary if phosphorus fertilizers are analyzed, as they must be dissolved in hydrochloric acid and ammonium chloride is formed on neutralization with ammonium hydroxide.

Table II shows that, for determination of phosphate ion, the suggested method supplies equal results to those of gravimetric procedures, and the results attained for the sulfate ions exceed by 1% the gravimetrically determined value of the same.

Acknowledgment

Table II. Phosphate and Sulfate Ions Found in Phosphorus Fertilizers by Suggested Method and by Gravimetry

Added to 10 Ml. of Superphosphate Stock Soln.			EtOH Added in Titration of PO$_4^{-3}$, Ml.	MgC$_2$[a] Consumed Ml.	P$_2$O$_5$, %		EtOH Added in Titration of SO$_4^{-2}$, Ml.	BaCl$_2$[a] Consumed, Ml.	SO$_4^{-2}$, %		Dev. from Gravimetric Values, %	
DCTA,[a] ml.	EDTA,[a] ml.	Buffer, ml.			Authors' method	Gravimetry			Authors, method	Gravimetry	PO$_4^{-3}$	SO$_4^{-2}$
4	9	3	5	6.45 ⎫ 6.40 ⎬6.43 6.43 ⎭	22.96	22.96	20	7.20 ⎫ 7.30 ⎪ 7.40 ⎬7.33 7.40 ⎪ 7.45 ⎭	35.43	34.98	0.00	1.29

[a] 0.1 M solution.

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PLANT TISSUE ANALYSIS

X-Ray Fluorescence Determination of Zinc in Plant Tissue

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X-ray emission spectroscopy has been applied to determination of zinc in a variety of plant species. Data are presented to show the lack of consistency in the intensity of the zinc emission maxima as a function of zinc concentration in plant tissue of complex and variable composition. Known amounts of zinc are added to samples and the original concentration is calculated on the basis of the response to the known added zinc.

INTERPRETATION of factors affecting intensity of emission maxima and compensation for them are of primary concern in applying x-ray emission spectroscopy to the quantitative analysis of chemical elements. Compensation for interferences can often be calculated or otherwise easily determined in relatively simple systems of limited elemental components. Evaluation and compensation for interferences in complex systems such as soils and plant tissue present a much more difficult problem.

As reviewed by Liebhafsky (9), variations in the intensity of fluorescent x-ray maxima of elements result from absorption of excitation energy and of secondary emission energy by the sample and enhancement of emission maxima of an element as a result of excitation by higher energy secondary radiation emanating from other elements in the sample. Besides these factors which affect intensity of emission maxima directly, variable matrix compositions contribute to variations in background radiation levels. Variable absorption and enhancement together with variable background levels in samples of different composition require most careful evaluation and compensation in quantitative fluorescence analysis.

Compensation for Interferences. The magnitude of absorption interfer-

ence in relatively simple chemical systems can often be calculated from known absorption coefficients, so that suitable corrections can be made (4). Alternatively, in simple systems, standard curves may be prepared in which elemental emission intensity is plotted against concentration of interfering elements (5). A commonly used technique is the addition of internal standards which are affected in the same manner as the elements being analyzed (3, 5). Suitable correction can be applied to the emission intensity of the unknown on the basis of variation in intensity of known concentration of internal standard.

An interference compensating technique employed by Kemp and Andermann (7), Andermann and Kemp (1), and Brandt and Lazar (2) utilizes scattered radiation as an internal standard in emission intensity measurements. In theory, scattered radiation of specific wave length can be selected which is affected by absorption in nearly the same way as the emitted radiation of an element being analyzed. A ratio of an element's emission intensity to intensity of the scattered radiation at the selected wave length will be constant so long as the interferences result only from instrument variability and absorption of secondary emission energy. The ratio technique can be valid only

if interferences affect emission and scatter intensity proportionately—not in situations where scatter intensity varies independently of elemental emission intensity, or where there is variable absorption of primary excitation energy.

It would appear that any variable affecting the intensity of an element's emission maxima in a sample could conveniently be measured and compensated for by adding a known quantity of the element concerned and relating the increase in intensity obtained by the addition to that originally present. Such a technique has been applied in analysis of inorganic mineral samples (3, 10). The present investigation is concerned with instrumentation and a comparison of methods of evaluating concentration levels of zinc in tissue of various plant species. The method of analysis described combines precision and accuracy with speed suitable for routine analyses on a large scale.

Experimental

Instrumentation. A spectrograph (General Electric XRD-5) equipped with a tungsten target x-ray tube (Machlett AEG-50), lithium fluoride analyzing crystal, 0.005-inch Solar slit, and krypton-filled proportional counter detector was used. The optimum voltage