

Table I. Recovery of Nitrates Added to Solutions

Added, $\mu\text{g.}$	Total		Recovery, %
	NO_3 Found, $\mu\text{g.}$	NO_3 Recovered, $\mu\text{g.}$	
BLOOD			
0	46
50	90	44	88
100	144	98	98
250	283	237	95
500	514	468	94
BLOOD			
0	159
50	206	47	94
100	257	98	98
250	386	227	91
500	642	483	97
MILK			
0	4
50	56	52	104
100	104	100	100
URINE			
0	12
50	61	49	98
100	116	104	104
RUMEN LIQUOR			
0	2
50	48	46	92
100	100	98	98

expected) of 0.4% NaOH into the funnel, add the CCl_4 extract, shake vigorously for about 30 seconds, and allow the layers to separate. Discard the CCl_4 layer and filter the yellow sodium hydroxide extract through a slow paper (S & S No. 605 or equivalent). Measure the transmittance of the filtered solution at 420 $\text{m}\mu$ vs. distilled water and compare the results to calibration curves established by carrying zero to 200 $\mu\text{g.}$ of NO_3 through the procedure. A series of curves covering a large range of NO_3 concentration may be established by varying the final volume of added NaOH from 10 to 50 ml.

FERTILIZER PROCESS CONTROL

Analytical Procedures for Nitrogen Fertilizers Containing Phosphates and Sulfates

NEW PROCESSES for producing granular nitrogen fertilizers have recently been developed at TVA. These fertilizers include ammonium nitrate, ammonium phosphate nitrate, and ammonium nitrate sulfate. Although analytical methods were available for deter-

Table II. Comparative Analyses of Three Blood Samples

Sample No.	$\mu\text{g. per ml. NO}_3$ Found	
	Micro-biological method	Xylenol method
273	77	70
274	24	25
284	9	6

The above method is a modification of a procedure developed by Morris for the determination of water-soluble nitrate in plant tissue. Several solvents may be substituted for carbon tetrachloride for the extraction of the nitrated xylenol, including chloroform, toluene, benzene, Skelly Sol-B, xylene, and petroleum ether. Carbon tetrachloride was chosen because it showed less tendency to form emulsions than the other solvents and because it gave a lower blank value.

With the exception of the original aliquot and the final NaOH, the solutions added may be measured with a graduated cylinder. The aqueous solution after the final extraction with NaOH must be alkaline. If no yellow color appears at this point, the solution should be tested with pH paper before drawing off the CCl_4 . If the solution is not alkaline, solid NaOH should be added and the solution shaken again.

Originally, two 15-ml. CCl_4 extractions were used; however, later tests showed a single 25-ml. extraction was equally effective. The yellow color of the sodium salt of nitro-xylenol is quite stable; no change occurs in the transmittance of the yellow solution over several days.

As recommended by Holler and Huck (4), 3,4-xylenol was used rather than the less reliable *m*-xylenol. Tests showed that the final sulfuric acid concentration in the nitration step could be varied be-

tween 54 and 80%. Above 80% there appeared to be some loss of nitrate. For best results, the temperature of nitration should be kept from 40° to 50° C. Lower temperatures slowed the reaction considerably. Above 60° C. some loss of nitrate occurred. A reaction time of 20 minutes was found sufficient when the temperature remained between 40° and 50° C. The concentration of NaOH used to extract the nitrated xylenol is immaterial so long as an excess is present to neutralize any acid carried over in the CCl_4 extract.

Recoveries of nitrates added to the solutions tested are listed in Table I. In addition, three samples of blood were analyzed by this method while subsamples were frozen and sent to the University of Missouri for analysis by the microbiological method of Garner and coworkers (2). Comparison of results obtained by the two procedures is shown in Table II.

The precision of the method was tested by repeated analyses of several samples. The average coefficient of variation was found to be 7.8%.

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sulfuric—is added to control the degree of granulation and to give a product of the desired chemical composition. In addition, the moisture content of the product must be kept at 0.5% or less.

Conventional methods of determining moisture, phosphate, and sulfate in nitro-

Nitrogen fertilizers produced at TVA by mixing ammonium nitrate crystals with either phosphoric or sulfuric acid and then ammoniating the mixture require rapid determinations of moisture, phosphate, and sulfate for control of the processes. Moisture is determined by titrating the mixture with Karl Fischer reagent. Sulfate in low concentrations (4% or less) is determined by adding an excess of barium chloride, precipitating the sulfate as barium sulfate, and titrating the excess barium ions (Ba^{+2}) with EDTA in the presence of Eriochrome Black T indicator. Sulfate in higher concentrations (about 15%) is determined by titrating the mixture with lead nitrate in a water-acetone solution that contains dithizone as an indicator. Phosphate is determined by adding an excess of magnesium chloride, precipitating the phosphate as magnesium ammonium phosphate, and titrating the excess magnesium ions (Mg^{+2}) with EDTA in the presence of Eriochrome Black T indicator. These methods give accurate analyses and permit more rapid control of the fertilizer production process than is possible with more conventional methods of analysis.

gen fertilizers require several hours. And such analyses are of little value to the plant operators because the material represented by the sample has usually been processed before the analytical results are available. Therefore, analytical methods were investigated to find ones that would facilitate control of the production processes.

Moisture

The moisture content of such fertilizers is conventionally determined by an oven-drying, vacuum-desiccation, or air flow drying method. All of these methods have disadvantages because of the time involved. Furthermore, with the oven-drying method ammonium phosphate salts lose ammonia when heated above 60°C .

The authors found that the moisture content of any of the three nitrogen fertilizers made by TVA could be determined in about 10 minutes with the Karl Fischer method. This method consists of titrating the moisture in the sample (dispersed in dehydrated methanol) with the well known Karl Fischer reagent. The titration end point is detected electrometrically with a Serfass Electron Ray titrating unit which uses a cathode ray tube as the indicating device. The direct "dead-stop" technique is used. The end point is easily detected even in colored or turbid solutions.

Sulfate

Granulated ammonium nitrate contains about 3.6% sulfate (SO_4) in the form of ammonium sulfate. Several analytical methods are available for analyzing this material. Those methods considered involved precipitation of the sulfate with an excess of barium chloride and subsequent titration with EDTA to determine either the barium content of the precipitate or the amount of unreacted barium in the solution.

Several investigators (1, 3, 5-8, 10, 12,

13, 17, 20) determined the excess barium in the unfiltered solution (still containing the sulfate precipitate) by titration with EDTA. In some cases, magnesium chloride or zinc chloride was used to make the end point more definite.

Good accuracy was reported for all of these methods. Because of the time required, the method selected was the direct titration of the excess barium in the unfiltered solution. The adaptation of this method to the analysis of sulfate in nitrogen fertilizers involved the following steps. Standard barium chloride was added to a slightly acid solution of the sample; the amount used was in excess of that required to precipitate the sulfate. After the sample had been stirred for 5 minutes on a magnetic stirrer to allow the barium sulfate to precipitate, the excess barium was titrated with disodium ethylenediaminetetraacetate (EDTA) using Eriochrome Black T as an indicator. The pH of the solution was about 9. The titration had to be carried out rapidly and continuously to prevent dissolution of the precipitate.

In the preparation of ammonium nitrate sulfate, enough sulfuric acid is added to the wet ammonium nitrate crystals so that the resulting fertilizer will contain about 5% sulfur present as ammonium sulfate (22% ammonium sulfate). The EDTA method described above was not applicable for the determination of sulfate in ammonium nitrate sulfate because its use was limited to samples containing 7 to 15 mg. of sulfate and the reduced sample weight or the diluting process necessary in preparing such samples led to inaccuracies. Therefore, a different method was needed in this case.

Recently, a number of methods using lead nitrate to precipitate the sulfate has been reported to be rapid, accurate, and applicable to wide variations in the concentrations of sulfate. Generally, the precipitation is carried out in a slightly acid medium containing an organic solution such as alcohol or acetone to lower

the solubility of the lead sulfate precipitate. Archer (2), Nechiporenko (14), Puschel *et al.* (15), Ryazanov (16), Soep and Demoen (18), and White (27) titrated the sulfate directly with lead nitrate, using dithizone indicator.

The direct titration method appeared to be simple, rapid, and accurate. Therefore, it was adapted for analyzing nitrogen fertilizers containing about 5% sulfur as sulfate. In this method, the sulfate was quantitatively precipitated as lead sulfate by the addition of a standard lead nitrate solution to a solution containing the sample. The selection of a solvent for the sample posed a problem, however, because both lead sulfate and ammonium sulfate (one of the sample constituents) are soluble in water, but practically insoluble in most organic solvents. During the analysis, the sample must remain in solution, but the precipitated lead sulfate must not be dissolved. A mixture of one part of water and three parts of acetone was found to be a suitable solvent for this purpose since it permits rapid reaction between the sulfate ions and the lead nitrate solution and does not interfere with the quantitative precipitation of the lead sulfate. Dithizone (diphenyl thiocarbazone) was used as an indicator. When all the sulfate ions have been precipitated, the dithizone reacts with the excess lead nitrate solution to give a distinct green-to-red color change.

Phosphate

In the determination of the phosphate content of ammonium phosphate nitrate, several methods had been reported which involve the use of EDTA and magnesium. The magnesium content of the precipitate has been determined by titrating it directly with EDTA solution (4, 9, 11). Wakamatsu (19) precipitated the phosphate with an excess of magnesium chloride and titrated the excess magnesium in the unfiltered solution with EDTA.

The method used involves precipitation of the phosphate as magnesium ammonium phosphate ($MgNH_4PO_4 \cdot 6H_2O$) and titration of excess magnesium with EDTA. In this method, the pH of a diluted sample is adjusted to 9 with a buffer, and a magnesium chloride solution is added. The solution is stirred for 5 minutes with a magnetic stirrer. Then the excess magnesium is rapidly titrated with EDTA to the first color change of Eriochrome Black T indicator. A delay in titration near the end point results in some dissolution of the precipitate and subsequent titration of the released magnesium.

Karl Fischer Procedure for Moisture

Apparatus. Serfass Electron Ray titration unit.

Magnetic stirrer.

Titration flask (250-ml.) with two platinum electrodes.

Buret, reservoirs, and assembly for maintaining sealed system to eliminate moisture absorption from the atmosphere.

Reagents. Karl Fischer solution and Karl Fischer diluent.

Sample Titration. A 10-gram sample containing between 60 and 250 mg. of water is added to the 250-ml. flask containing desiccated methanol (the water content of the methanol is removed by titrating it immediately prior to adding the sample). The flask is connected with an airtight joint to the buret, and its contents are titrated while they are being stirred with the magnetic stirrer. The end point is detected with the electron ray tube which indicates when all the water has been titrated.

Barium Chloride-EDTA Procedure for Sulfate

Reagents. EDTA SOLUTION. Dissolve 2.8 grams of reagent grade EDTA, 0.26 gram of $MgCl_2 \cdot 6H_2O$, 0.191 gram of $CaCl_2$, and 0.37 gram of NaOH in distilled water and dilute to 1 liter. Standardize against a standard barium chloride solution and a magnesium chloride solution to determine its equivalent in milliliters per milliliter for each of these solutions.

BARIUM CHLORIDE SOLUTION. Dissolve 2.6 grams of reagent grade $BaCl_2$ in distilled water and dilute to 1 liter. Standardize against 0.1N H_2SO_4 .

MAGNESIUM CHLORIDE SOLUTION. Dissolve 1.433 grams of reagent grade $MgCl_2 \cdot 6H_2O$ in distilled water and dilute to 1 liter.

BUFFER SOLUTION. Dissolve 90 grams of reagent grade NH_4Cl in 560 ml. of reagent concentrated ammonium hydroxide. Dilute to 950 ml. with distilled water, then add 0.83 gram of EDTA and 0.5 gram of reagent grade $MgSO_4 \cdot 7H_2O$. Mix well and test the magnesium-EDTA ratio by adding 2 ml. of the solution to 50 ml. of distilled

water in a few drops of Eriochrome Black T indicator. One drop of either EDTA or standard $CaCO_3$ solution (0.855 mg. of $CaCO_3$ per ml.) should give the color change. Adjust as required.

ACIDIFIED METHANOL SOLUTION. Dissolve 0.5 ml. of reagent grade concentrated HCl in 1 liter of reagent grade methanol.

ERIOCHROME BLACK T INDICATOR. Add 0.5 gram of pulverized reagent grade anhydrous Na_2CO_3 to 10 grams of Eriochrome Black T powder; screen several times through a 20-mesh sieve. Dissolve 0.45 gram of the mixture in 60 ml. of acidified methanol solution.

STANDARD CALCIUM CARBONATE SOLUTION. Dissolve 0.855 gram of reagent grade $CaCO_3$ in 10 ml. of dilute HCl (1:3). Dilute to 200 ml. with distilled water and boil a few minutes to expel the CO_2 . Dilute to 1 liter.

Procedure. SAMPLE DISSOLUTION. Dissolve a 10-gram sample in distilled water and dilute to 1 liter.

PRECIPITATION AND TITRATION. Transfer a 25-ml. aliquot to a 400-ml. beaker and dilute to about 200 ml. Add 5 drops of 0.1N HCl and exactly 20 ml. of standard barium chloride solution. Stir on a magnetic stirrer for 5 minutes and then add exactly 10 ml. of magnesium chloride solution followed by 1 ml. of buffer solution and 13 drops of Eriochrome Black T indicator. Continue stirring and titrate rapidly and continuously with EDTA to a sky-blue color.

CALCULATION. The sulfate content is calculated as the amount of barium used to precipitate the sulfate, taking the barium used as the difference between the amount added and that titrated with the EDTA.

Lead Nitrate Procedure for Sulfate

Reagents. STANDARD LEAD NITRATE SOLUTION. Dissolve 8.28 grams of reagent $Pb(NO_3)_2$ in distilled water and dilute to 1 liter. Standardize against standard ammonium sulfate solution.

STANDARD AMMONIUM SULFATE SOLUTION. Dissolve 3 grams of standard $(NH_4)_2SO_4$ in distilled water and dilute to 1 liter.

BROMPHENOL BLUE INDICATOR. Dissolve 0.1 gram of bromphenol blue powder in 95% ethanol and dilute to 100 ml. with ethanol.

DITHIZONE INDICATOR. Dissolve 0.1 gram of dithizone in acetone and dilute to 100 ml. with acetone. This solution must be prepared each day.

Procedure. SAMPLE DISSOLUTION. Dissolve a 15-gram sample in distilled water and dilute to 1 liter.

TITRATION. Transfer a 25-ml. aliquot to a 250-ml. beaker, and while stirring with a magnetic stirrer, add 6 drops of bromphenol blue indicator. Adjust to

pale green with 0.3N HNO_3 or 0.02N NH_4OH . Add 1 ml. of 20% acetic acid, 75 ml. of acetone, and 1 ml. of 0.1% dithizone. Continue stirring and titrate to first purple color with standard lead nitrate solution.

Magnesium Chloride-EDTA Procedure for Phosphate

Reagents. EDTA SOLUTION. Dissolve 3.2 grams of reagent grade EDTA, 0.5 gram of sodium propionate, and 0.3 gram of NaOH in distilled water and dilute to 1 liter. Standardize against standard calcium carbonate solution.

STANDARD MAGNESIUM CHLORIDE SOLUTION. Dissolve 1.433 grams of $MgCl_2 \cdot 6H_2O$ in distilled water and dilute to 1 liter. Standardize against the EDTA solution given above.

ERIOCHROME BLACK T INDICATOR. Prepare this solution in the same manner as that used in the barium chloride-EDTA procedure above.

Procedure. SAMPLE DISSOLUTION. Dissolve 10 grams of sample in distilled water and dilute to 2 liters.

PRECIPITATION AND TITRATION. Transfer a 25-ml. aliquot to a 400-ml. beaker and dilute to about 200 ml. Add 5 drops of 1:1 HCl and exactly 50 ml. of standard magnesium chloride solution. Then add 10 ml. of 1:1 NH_4OH and stir 5 minutes on a magnetic stirrer. Add 10 drops of Eriochrome Black T indicator. Continue stirring rapidly and titrate to first blue color flash with EDTA solution. The pink color will reappear because of the precipitate dissolution.

Discussion of Results

Samples of ammonium nitrate, ammonium nitrate sulfate, and ammonium phosphate nitrate were analyzed for their moisture contents by vacuum-desiccation, oven-drying, air flow, and Karl Fischer methods. The results obtained by the Karl Fischer method on ammonium nitrate and ammonium nitrate sulfate were in reasonable agreement with those obtained by the air flow and the oven-drying methods after the samples had been dried for 2 to 8 hours. In both drying methods, the samples continued to show a slight further loss in weight as the drying time was increased. Vacuum desiccation did not remove all of the free moisture from the granules within 24 hours. Instead, the samples showed weight losses that slowly but steadily increased during the drying period.

Analyses of ammonium phosphate nitrate samples by the four methods show that the oven-drying and the air flow methods are not suited to this material because they give a continuing excessive weight loss (which is attributed to decomposition of ammonium phosphate

Table I. Analyses of Ammonium Nitrate Granules Containing a Known Quantity of Sulfate by EDTA-Titration and Gravimetric^a Methods

Sample No.	% SO ₄ Added	% SO ₄ Determined by:	
		EDTA titration	Gravimetric method
1	3.6	3.6	3.6
2	3.6	3.6	3.7
3	3.6	3.7	3.7
4	3.6	3.7	3.6
5	3.6	3.6	3.7
6	3.6	3.6	3.7
Av.		3.63	3.67

^a Gravimetric barium sulfate method.

Table IV. Analyses of Ammonium Nitrate Solutions Containing Added Ammonium Sulfate and Ammonium Phosphate by Lead Nitrate Titration

Sample No.	P ₂ O ₅ Added, %	SO ₄ , %	
		Added	Determined ^a
1-3	0.2	3.6	3.6
4-7	0.0	14.5	14.5
8-10	0.1	14.5	14.5
11-13	0.2	14.5	14.5
14-16	0.3	14.5	14.5
17-19	0.5	14.5	14.5
20-22	0.7	14.5	14.5

^a The ml. of Pb(NO₃)₂ equivalent to the P₂O₅ in the aliquot titrated was subtracted from the titer before the percentage sulfate recovered was calculated.

salts). Vacuum desiccation gave results similar to those found in the analyses of the other two fertilizers. (Pulverization of a sample before it is weighed will cause the sample to lose much of its moisture to the air and give entirely erroneous results.) However, the moisture contents indicated by the Karl Fischer analyses appeared to be quite reasonable.

The barium chloride-EDTA method of determining the sulfate content of ammonium nitrate was tested by analyzing samples to which ammonium sulfate had been added and which were known to contain 3.6% sulfate (SO₄). A comparison of the results obtained by this method with those obtained by a gravimetric method in which the sulfate is precipitated as barium sulfate showed that the methods are equally precise and that both are essentially quantitative (Table I). When the two methods were used to analyze plant products, the standard deviation of the difference between analyses was 0.25% sulfate, and the results were considered sufficiently precise for plant control (Table II). However, the use of this EDTA method is restricted to samples containing 7 to 15 mg. of sulfate in the portion titrated.

The lead nitrate method of determining sulfate in ammonium nitrate

Table II. Analyses of Plant Samples of Ammonium Nitrate Granules by EDTA-Titration and Gravimetric^a Methods

	% SO ₄ Determined by:	
	EDTA titration	Gravimetric method
Range of 14 samples	3.3-4.2	3.3-4.4
Av.	3.72	3.76

^a Gravimetric barium sulfate method.

Table V. Analyses of Ammonium Phosphate Nitrate by EDTA-Titration and Volumetric Ammonium Phosphomolybdate Methods

Sample No.	% P ₂ O ₅ , Determined by:	
	EDTA titration	Molybdate method
1	11.2	11.1
2	11.2	11.2
3	9.1	8.9
4	11.4	10.8
5	9.2	9.2
6	9.8	9.7
7	10.0	9.8
8	9.6	9.8

sulfate was tested by analyzing samples containing known concentrations of sulfate, prepared from mixtures of ammonium nitrate and ammonium sulfate. These analyses were compared with those obtained by use of the gravimetric barium sulfate precipitation method (Table III). This comparison showed that the lead nitrate method is slightly more accurate and precise than the gravimetric method. When the two methods were used to analyze plant samples, the standard deviation of the differences in analyses was 0.24% sulfate. The presence of phosphate in the fertilizer (as the result of previous use of the plant to produce ammonium phosphate nitrate) affects the sulfate analyses because the phosphate also reacts with the lead nitrate. But, as shown in Table IV, a correction can be made for the phosphate (up to 0.7% P₂O₅) since the reaction between the phosphate and the lead nitrate is a quantitative one.

The EDTA method of determining the phosphate content of ammonium phosphate nitrate was tested on samples of known composition. The phosphate content ranged from 2 to 18 mg. of P₂O₅ in the portion titrated. Recovery of the phosphate was good, the standard error being 0.1% P₂O₅. Table V gives a comparison of the results obtained by this method and those obtained by the A.O.A.C. volumetric molybdate method on plant samples. This comparison shows that one method is as accurate as the other and that good, rapid analyses can be made by use of the EDTA method.

Table III. Analyses of Mixtures of Ammonium Nitrate and Ammonium Sulfate by Lead Nitrate-Titration and Gravimetric^a Methods

Sample No.	% SO ₄ Added	% SO ₄ Determined by:	
		Lead nitrate titration	Gravimetric method
1	3.6	3.6	3.8
2	3.6	3.6	3.8
3	14.5	14.5	14.9
4	14.5	15.0	15.0

^a Gravimetric barium sulfate method.

These procedures have been developed for the analysis of fertilizers consisting of relatively pure salts. Although they may be useful in the analysis of other materials, such as some mixed fertilizers, the possibility of interfering factors not encountered in the work reported here should be investigated before the procedures are used on new materials.

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