Figure 2. Influence of composition on reactivity of zinc frits

1. 62% (K₂O + SiO₂).30% ZnO.8% Na₂O
2. 64% (K₂O + SiO₂).30% ZnO.6% Na₂O
3. 62% (Na₂O + SiO₂).30% ZnO.8% Al₂O₃
4. 70% (Na₂O + SiO₂).30% ZnO
5. 70% (K₂O + SiO₂).30% ZnO

mixing during the molten stage is important in making a glass for agricultural purposes. Homogeneity of the glass at a given level of reactivity has not been shown, in itself, to affect vegetative results. However, the procedure for making a frit is simpler, since the melt is not stirred or otherwise mixed. The preparation of frits is also preferred because their reactivity is less affected by differences in composition.

Influence of Chemical Composition

The molar compositions of suitable sodium-zinc glasses are given in Table I. To define the type of material, zinc in the glass is arbitrarily assigned the composition of Zn_2SiO_4, the only known silicate of zinc (5). The ratio of the matrix silica (excess of that in the form of Zn_2SiO_4) to sodium oxide content varied from 1.9 to 2.2 with homogeneous glasses and from 1.9 to 3.1 with the frits. Hence, these materials may be characterized as solutions consisting of $2ZnO.SiO_2$ and $Na_2O.nSiO_2$, where n has the value of about 2 to 3.

The release of zinc from frits containing potassium or aluminum is compared with that from the sodium frit in Figure 2. The frits were clear glass, except in a few cases at low reactivity, as depicted by broken line segments of the curves. Within the useful range of reactivity, the curves are nearly parallel. Thus, the sensitivity of zinc release to differences in composition was much the same for each type of frit.

The molar ratio of the acid and basic constituents largely determined reactivity of the frits, as shown by the data in Table II. At a given level of reactivity, the ratio of "acidic" oxides (SiO_2 and Al_2O_3) to basic oxides (Na_2O, K_2O, and ZnO) was sensibly constant. Potassium oxide merely replaced sodium oxide, and alumina replaced silica with little or no effect on the release of zinc.

Acknowledgment

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FERTILIZER ANALYSIS

Quantitative Analysis of Mixed Fertilizers by X-Ray Diffraction

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An x-ray diffraction method is described by which the compounds in mixed fertilizers are identified and their amounts determined quantitatively. Spinel ($MgAl_2O_4$) serves as an internal standard. The method is sufficiently accurate to yield practical information on the mineralogical composition of mixed fertilizers, and results are reported of the analyses of typical fertilizers.

KNOWLEDGE of the mineralogical composition of a mixed fertilizer is a great help toward understanding the reactions involved in its manufacture, its caking during storage, and its behavior in the soil. Chemical analysis yields little information on the actual compounds in a complex mixed fertilizer, and petrographic examination is hampered, considerably more than are x-ray methods, by the colloidal and gelatinous materials present in many mixed fertilizers.

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Development of Method

Ando and Matsuno (1, 2) adapted the quantitative x-ray diffraction method of analysis (3, 4) to fertilizers. Spinel ($MgAl_2O_4$) served as an internal standard; its diffraction peaks are relatively free of interference from those of many of the compounds in mixed fertilizers, the intensity of its principal peak is virtually unaffected by the grinding required in preparing samples for examination, it has a moderate x-ray absorption coefficient, and it is inert to the common fertilizer components.

The procedure based on spinel was developed further and applied to the analysis of different types of fertilizers. Calibration curves were made for some 20 compounds and several solid solutions often present in mixed fertilizers. Interferences of diffraction peaks of the compounds with those of spinel were identified, and corrections were made. The method yields dependable information on the mineralogical composition of mixed fertilizers, and the results are in reasonable agreement with those of chemical analyses.

Table I. Precipitated Apatite

	Precipitation			Product					
No.	Temp., °C.	Time,[a] min.	pH	Relative peak height[b]	Ca	P	F	CaO	P₂O₅
A	75	7	7.8	1.00	37.2	18.4	0.0	52.1	42.2
B	65	2	7.8	0.85	36.5	18.2	0.4	51.0	41.8
C	50	0.25	8.2	0.68	35.4	18.5	0.0	49.6	42.4

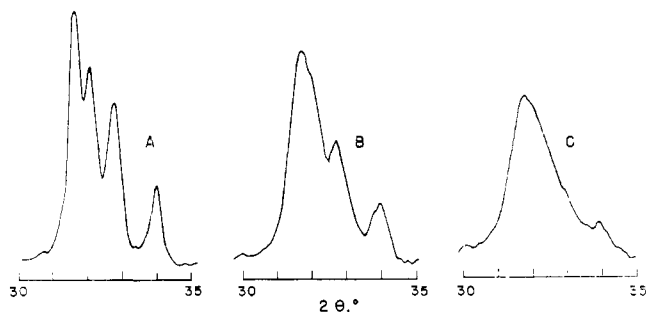[a] Time of addition of reagents. [b] $2\theta = 31.8°$.

Figure 1. X-ray diffraction patterns of precipitated apatites

Reference Compounds. Reagent grades of common fertilizer salts, such as ammonium and potassium phosphates, chlorides, sulfates, and nitrates, were used directly from stock bottles as reference compounds when their diffraction patterns showed impurities to be inconsequential. Preparation of the less common salts is described.

SPINEL, $MgAl_2O_4$. An equimolar mixture of magnesia and alumina (reagent grades) was moistened, pelletized, and calcined for 30 minutes at 1600° to 1670° C. The product was ground to −200 mesh.

SYNGENITE, $(NH_4,K)_2SO_4.CaSO_4.H_2O$. Mixtures of ammonium, potassium, and calcium sulfates were repeatedly moistened, ground, and dried at 80° C. until homogeneous. Better results were obtained when 3% of the ammonium sulfate was replaced by its weight of diammonium phosphate; the product then consisted of crystals with a habit more like that of syngenite in mixed fertilizers.

$3NH_4NO_3.(NH_4)_2SO_4$. Salt was crystallized by slow cooling of a boiling saturated solution of NH_4NO_3 and $(NH_4)_2SO_4$ in mole ratio 6 to 1 (9).

$2NH_4NO_3.(NH_4)_2SO_4$ AND $NH_4NO_3.2KNO_3$. Stoichiometric mixtures of the component salts were repeatedly moistened, ground, and dried at 70° C. until the x-ray diffraction pattern of the product showed no peaks of the component salts.

ANHYDRITE, $CaSO_4$. Calcium carbonate was treated with a slight excess of concentrated sulfuric acid. The mixture was heated at 160° C. to volatilize the excess acid. The resultant crystal particle size was −10 micron.

PLASTER OF PARIS, $CaSO_4.0.5H_2O$. A mixture of 8 grams of $CaCO_3$, 30 grams of 65% H_3PO_4, and 10 grams of concentrated H_2SO_4 was heated at 90° C. The mixture was filtered, and the product was washed with acetone and air-dried. The crystal particle size was −10 micron.

MONOCALCIUM PHOSPHATE MONOHYDRATE, $Ca(H_2PO_4)_2.H_2O$. Calcium carbonate was treated with twice the stoichiometric amount of 65% phosphoric acid. The mixture was filtered, and the product was washed with acetone and air-dried. The crystal particle size was −10 micron.

ANHYDROUS DICALCIUM PHOSPHATE, $CaHPO_4$. A suspension of the dihydrate, $CaHPO_4.2H_2O$, in boiling water was filtered, and the product was washed with acetone and air-dried. The crystal particle size was −25 micron.

APATITE, $Ca_5(PO_4)_3(OH,F)$. Crystalline apatites prepared by conventional methods (7) were unsatisfactory as reference materials because they gave much sharper peaks than the apatitic material in fertilizers. Suitable reference apatitic materials were prepared by rapidly mixing in 1 liter of water 100 ml. each of an $0.85M$ solution of $Ca(NO_3)_2$ and a $0.57M$ solution of $(NH_4)_2HPO_4$. Fluorine was incorporated by adding small amounts (1 to 20 ml.) of a $1.9M$ solution of NH_4F.

The compositions of three such preparations are shown in Table I and their x-ray diffraction patterns are shown in Figure 1. The crystal size of the precipitates decreased and their peaks decreased in height and increased in width as the temperature of preparation was lowered and as the rate of combining the reagents was increased. The compositions of the precipitates were never quite that of $Ca_5(PO_4)_3(OH,F)$—the ratio of calcium to phosphorus was always low—and as the crystal size decreased the composition shifted even farther toward a less basic calcium phosphate. The x-ray diffraction patterns of the precipitates resembled closely those of the apatitic materials in fertilizers, however, and the precipitates, which had an apatite-like structure, were called apatites for convenience.

SOLID SOLUTIONS. Mixtures of the component salts [$(NH_4)_2SO_4$ and K_2SO_4, NH_4Cl and KCl, $NH_4H_2PO_4$ and KH_2PO_4, NH_4NO_3 and KNO_3] were repeatedly moistened, ground, and dried at 70° C. until the x-ray diffraction pattern of the product showed no peaks of the component salts.

Procedure. The diffraction patterns were obtained with nickel-filtered copper radiation from a North American Phillips Geiger counter diffractometer operating at 35 kv. and 15 ma. The optical system contained a 1° divergence slit and a 0.005-inch receiving slit.

The samples (about 250 mg.) were packed into a holder with a rectangular chamber 10 by 20 mm. and 1 mm. deep. The chart speed was 0.5 inch per minute, the scanning rate 1° per minute (all angles referring to diffraction patterns are Bragg angles, 2θ). In most of the work, the scale factor was 8, the time constant 4 seconds.

Diffraction patterns of three double salts and five solid solutions are listed in Table II. Diffraction angles and relative intensities of the compounds and solid solutions often present in mixed fertilizers must be determined in calibrating the method and allowing for interferences.

PREPARATION OF SAMPLES. Each reference compound was tested to determine the extent of grinding required and the largest crystal size that would yield reproducible diffraction peak heights. Thus, equal weights (100 to 200 mg. each) of monoammonium phosphate and spinel were mixed by light grinding in a 56-mm. agate mortar. After each minute of grinding, the sample was scraped from the surface of the mortar with a spatula and the grinding was continued. After each 2 minutes of grinding the pattern of the sample was run and the heights of the monoammonium phosphate peak at 16.6° and of the spinel peak at 36.8° were measured.

In 10 minutes of grinding the ratio of the heights of the two peaks became constant; microscopic examination of the sample showed that the maximum particle size was 30 microns. Less than 10 minutes of grinding was sufficient for most of the reference compounds, and a particle size of 30 microns or less was satisfactory for all the compounds.

The effect of crystal size on the ratio of the peak height of the sample to that of the internal standard (spinel) was studied with two samples of ammonium syngenite. One, without added phosphate, had an initial crystal size of about 100 microns; the other, with a small addition of phosphate, had an initial crystal size of −10 micron. The sample with the smaller crystals (more like the syngenite found in mixed fertilizers) yielded constant peak-height

Table II. Powder Diffraction Patterns

2θ	I/I₁
3NH₄NO₃·(NH₄)₂SO₄	
11.5	7
16.4	18
17.2	16
17.7	12
18.5	47
18.8	16
19.4	27
21.4	24
22.2	16
22.7	7
23.3	14
24.0	8
24.5	6
26.1	8
27.2	60
28.0	100
28.7	49
29.6	8
30.0	24
30.7	44
32.1	9
32.4	8
33.2	9
36.1	34
37.6	8
38.3	9
39.5	5
40.9	18
2NH₄NO₃·(NH₄)₂SO₄	
8.8	9
11.7	9
13.1	6
16.2	10
17.8	52
18.8	55
19.4	9
21.1	9
22.2	7
23.5	19
26.9	98
27.1	100
27.9	68

2θ	I/I₁
2NH₄NO₃·(NH₄)₂SO₄	
30.4	44
31.2	27
34.6	10
36.1	34
37.2	14
37.7	12
39.7	10
42.4	20
NH₄NO₃·2KNO₃	
20.8	5
24.2	2
26.9	100
29.4	40
32.1	21
38.6	25
42.4	15
Spinel, MgAl₂O₄	
18.9	40
31.2	37
36.8	100
44.7	55
NH₄KSO₄·CaSO₄·H₂O^a	
9.0	100
15.3	60
18.1	18
19.0	25
19.5	18
20.7	17
22.0	13
22.5	13
24.8	40
26.5	27
27.4	40
27.8	43
29.1	25
30.1	17
30.5	19
31.0	55
31.4	28
31.6	15
32.4	31
35.2	13

2θ	I/I₁
NH₄KSO₄·CaSO₄·H₂O^a	
36.5	7
37.7	13
38.6	9
40.6	5
(NH₄,K)H₂PO₄^a	
16.85	40
21.4	6
23.65	100
29.3	26
29.7	44
33.8	29
34.3	6
38.1	16
NH₄KSO₄^a	
17.2	14
20.7	100
23.0	22
28.9	62
30.2	87
34.9	23
35.9	14
39.5	12
40.1	11
42.0	21
NH₄Cl + 4KCl^b	
28.1	100
40.1	28
49.7	7
95NH₄NO₃ + 5KNO₃^b	
16.9	17
19.5	16
22.7	63
26.2	60
27.4	100
27.7	84
30.4	17
31.5	34
34.1	72
35.1	5
37.2	45
38.7	19
39.6	15
39.8	22

^a Equal weights of NH₄ and K salts.
^b Solid solution; proportions on weight basis.

Table III. Calibration of Peaks of Fertilizer Compounds

(Each compound present as 25% of a mixture with an inert diluent; 200 mg. of mixture mixed with 50 mg. of spinel)

Compound	2θ°	I/Iₛ^a	Compound	2θ°	I/Iₛ^a
(NH₄)₂SO₄·CaSO₄·H₂O	8.8	0.83	2NH₄NO₃·(NH₄)₂SO₄	27.1	0.47
NH₄KSO₄·CaSO₄·H₂O^b	9.0	0.39	NH₄NO₃(III)^c	27.4	0.45^d
CaSO₄·2H₂O	11.6	1.31	2NH₄NO₃·(NH₄)₂SO₄	27.9	0.38
CaSO₄·0.5H₂O	14.7	0.76	3NH₄NO₃·(NH₄)₂SO₄	28.0	0.50
(NH₄)₂SO₄·CaSO₄·H₂O	15.2	0.37	NH₄Cl-KCl^e	28.1	2.46
NH₄KSO₄·CaSO₄·H₂O^b	15.3	0.25	NH₄Cl-KCl^e	28.1	3.20^f
(NH₄)₂HPO₄	15.8	0.42^g	KCl	28.3	3.30
NH₄H₂PO₄	16.6	1.25	NH₄NO₃(IV)	28.8	0.78
2NH₄NO₃·(NH₄)₂SO₄	17.8	0.19	CaHPO₄	30.2	0.49
(NH₄)₂SO₄	20.4	0.95	Apatite B^h	31.8	0.32
NH₄NO₃(IV)	22.3	0.47	Apatite C^h	31.8	0.26
KNO₃	23.5	0.73	NH₄Cl	32.6	2.90
NH₄H₂PO₄	23.6	0.86	NH₄NO₃(IV)	32.7	0.64
Ca(H₂PO₄)₂·H₂O	24.0	0.46	NH₄NO₃(IV)	39.7	0.32
CaSO₄	25.4	1.83	KNO₃	33.8	0.50
NH₄NO₃·2KNO₃	26.9	1.25			

^a Ratio of height of indicated peak to 36.8° peak of spinel.
^b Solid solution; equal weights of NH₄ and K salts.
^c 95% NH₄NO₃ (III) + 5% KNO₃.
^d After subtraction of 22% of 27.4° peak from 36.8° peak.
^e Solid solution: 20% NH₄Cl, 80% KCl.
^f Ratio of peak areas.
^g After subtraction of 11% of 15.8° peak from 36.8° peak.
^h Described in Table I.

ratios with no more than 5 minutes of grinding, but the coarser, phosphate-free syngenite required more than 15 minutes of grinding.

CALIBRATION CURVES. To prepare calibration curves, 50 mg. of spinel and 200 mg. of a mixture of the reference compound with a powdered diluent (borosilicate glass or calcite) were ground together in an agate mortar for 10 minutes. The ratio of the height of the selected peak of the reference compound to that of the 36.8° peak of spinel was determined for several known concentrations of the reference.

With some reference compounds, such as solid solutions of ammonium and potassium chlorides, peak areas were more reliable than peak heights. For patterns of these materials, the scanning rate was decreased to 0.25° per minute, but the chart speed was still 0.5 inch per minute. The chart paper was uniform, and satisfactory measurements of peak areas were obtained by cutting out and weighing the areas.

When free of interference from other compounds, all the calibration curves were straight lines through the origin when the ratio of peak heights (or peak areas) was plotted against concentration of the reference compound as weight per cent of the sample. The calibration curves are summarized in Table III as the ratio of the height (or area) of the selected peak to that of the standard peak (36.8°) of spinel for mixtures containing 25% of the reference compound.

The diffraction pattern of diammonium phosphate contains a large peak at 15.8° and a small peak with about 11% of the intensity at 36.8°. Interference of the 36.8° peak of diammonium phosphate with the same peak of spinel is corrected for by subtracting 11% of the 15.8° peak from the 36.8° peak. Although no peak of diammonium phosphate interferes with the 18.9° peak of spinel, peaks of many other fertilizer salts do, so that this peak of spinel is inconvenient for use as the standard.

Ammonium nitrate, form III, when present as a solid solution of 95% NH₄NO₃ and 5% KNO₃, also interferes with the 36.8° peak of spinel and is corrected for by subtracting 22% of the 27.4° peak of the ammonium nitrate from the spinel peak.

Solid solutions of ammonium and potassium salts of the same anion are common constituents of mixed fertilizers. The position and intensity of the characteristic peak of each solid solution change continuously with change in the ratio of the cations. It was necessary to prepare several compositions in each series of solid solutions and to determine the position and intensity of the selected principal peak for each. Calibration curves were then prepared for samples containing 25% of each composition, with the 36.8° peak of spinel as the
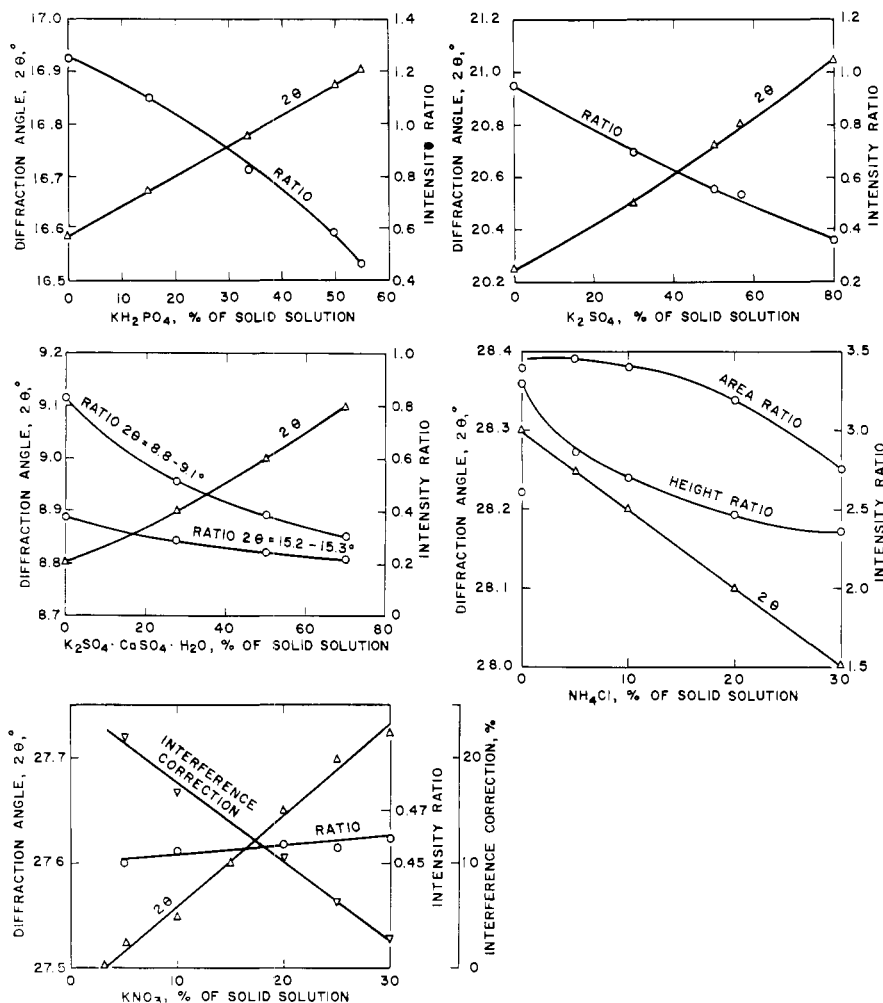
Figure 2. Calibration curves of solid solutions

Each solid solution comprises 25% of sample; 200 mg. of sample mixed with 50 mg. of spinel. Intensity ratio is that of salt peak–spinel peak at $2\theta = 36.8°$

Upper left. $NH_4H_2PO_4$–KH_2PO_4
Upper right. $(NH_4)_2SO_4$–K_2SO_4
Center left. $(NH_4)_2SO_4 \cdot CaSO_4 \cdot H_2O$–$K_2SO_4 \cdot CaSO_4 \cdot H_2O$
Center right. NH_4Cl–KCl
Lower left. NH_4NO_3–KNO_3

diffraction pattern of this final mixture was recorded.

Apatite and dicalcium phosphate usually were determined on the water-insoluble fraction of the fertilizer. This fraction was obtained by rapid washing of a 4-gram portion of the −100-mesh fertilizer on a fritted-glass filter with 500 ml. of water. The residue was washed with acetone, dried at 50° C., and weighed; 200 mg. of the dried residue was then mixed with 50 mg. of spinel, and the mixture was ground in the agate mortar for 10 minutes. The apatite and dicalcium phosphate contents were determined in the usual manner and calculated on the basis of the original sample.

Discussion. The peak used for the determination of each compound (Table III) was chosen on the basis of its relative intensity, the reproducibility of its height, and its freedom from interference by peaks of other compounds. When interference was unavoidable, corrections were made. For example, ammonium sulfate interferes with the 16.6° peak of monoammonium phosphate. When both these compounds are present, 32% of the 20.4° peak of ammonium sulfate is subtracted from the 16.6° peak to obtain the corrected peak height for monoammonium phosphate. Alternatively, the 23.4° peak of monoammonium phosphate can be used for the determination.

Peaks of many common fertilizer salts interfere with the peaks of apatite, and it is convenient to avoid much of this interference by determining apatite on the water-insoluble fraction of the fertilizer. Even then, however, anhydrite interferes, and 5% of the 25.4° peak of anhydrite is to be subtracted from the 31.7° to 31.9° peak of apatite. Other interferences are shown in Table

standard. The results of these calibrations for five common solid solutions are shown in Figure 2.

When the peak of a solid solution of $NH_4H_2PO_4$ and KH_2PO_4 is at 16.67°, for example, the solid solution contains 15% KH_2PO_4; for a mixture containing 25% of this solid solution, the intensity of the 16.67° peak is 1.10 that of the 36.8° peak of spinel.

Solid solutions of ammonium and potassium syngenites have two usable peaks. The position of one peak moves from 8.85° to 9.12° as the potassium syngenite increases from 0 to 70% of the solid solution, whereas that of the other peak moves only from 15.2° to 15.3° in the same concentration range. The relative intensity of the peak at about 9°, however, changes more rapidly with change in composition than that of the peak at 15.2°.

Solid solutions of ammonium and potassium nitrate interfere with the

36.8° peak of spinel, and the interference changes with change in composition of the solid solution. Thus, if the peak of the solid solution is at 27.6°, the solid solution contains 15% KNO_3, and 13% of the 27.6 peak is to be subtracted from the 36.8° peak of spinel. With this correction, the intensity ratio of the sample containing 25% of the solid solution is 0.455.

Interference is minimized by slow scanning of the sample spectrum, and for best results slow scanning and use of peak areas rather than peak heights are recommended.

ANALYSIS OF FERTILIZER SAMPLES. A 50-gram sample of fertilizer, obtained by repeated quartering, was ground to −35-mesh, and a 5-gram portion of this material was then ground to −100-mesh. A mixture of 200 mg. of ground fertilizer and 50 mg. of spinel then was ground for 10 minutes in an agate mortar, as in the preparation of the reference compounds, and the x-ray
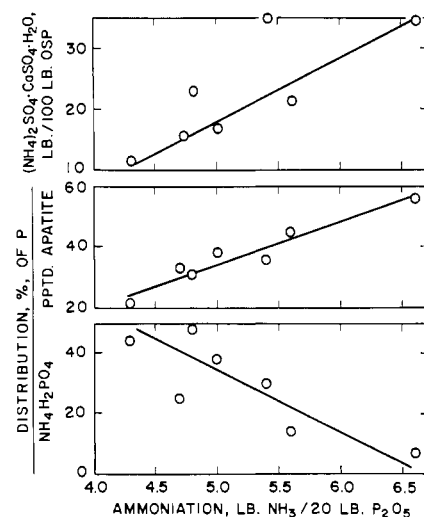

Figure 3. Effect of degree of ammoniation on composition of ammoniated superphosphate fertilizers

Table IV. Fertilizers Based on Ammoniated Superphosphate

Sample	All P₂O₅ from Ordinary Superphosphate									P_2O_5 from OSP and CSP	
	OSP-1	OSP-2	OSP-3	OSP-4	OSP-5	OSP-6	OSP-7	OSP-8	OSP-9	SP-1	SP-2
Grade											
N–P–K	3–5–10	4–5–10	4–5–10	6–5–10	10–4–8	10–4–8	6–3–7	5–4–12	8–7–0	5–9–17	15–6–12
$N–P_2O_5–K_2O$	3–12–12	4–14–12	4–12–12	6–12–12	10–10–10	10–10–10	6–8–8	5–10–15	8–16–0	5–20–20	15–15–15
Formulation, lb./ton											
NH_3, anhydrous	77	105	...	60	...	25	...	87	...	127	...
Nitrogen solution	...	...	183[a]	165[b]	484[b]	364[c]	183[a]	69[c]	365[c]	...	534[c]
$(NH_4)_2SO_4$	...	...	...	...	...	95	190	...	...	...	...
$(NH_4)_2HPO_4$	...	...	...	...	...	...	...	...	...	...	404
Ordinary superphosphate	1244	1260	1210	1183	1037	1030	810	1034	1735	478	222
Concd. superphosphate	...	...	...	...	...	...	...	...	...	654	80
H_2SO_4, 66° Be.	75	147	...	100	150	175	...	163	50	113	329
KCl	400	410	394	397	334	334	263	500	...	688	496
Dolomitic limestone	...	60	213	...	...	42	554	200	...	...	...
Other filler	258	...	...	163	104	...	...	...	...	...	...
Ammoniation of OSP[d]	4.4	4.7	5.6	5.0	4.8	5.4	6.6	4.9	4.3	6.1[e]	5.9[e]
Compn., %, by chem. anal.											
N											
Total	3.2	3.8	4.2	5.8	10.0	10.0	5.9	4.8	8.1	4.8	16.0
NH_4	3.2	3.8	3.2	5.0	6.8	8.0	4.4	4.5	5.9	4.7	12.4
Urea	...	...	1.0	0.2	0.6	...	1.5	...	...	...	...
P											
Total	5.0	6.4	5.9	5.6	4.5	4.5	3.8	4.7	7.3	9.8	6.7
AOAC "available"[f]	4.6	5.3	5.5	5.5	4.2	4.5	3.7	4.4	7.1	9.3	6.6
Water-soluble	2.6	2.5	1.4	2.3	2.1	1.8	0.3	1.3	4.1	4.7	5.1
K	10.3	9.1	10.1	9.4	9.3	8.1	7.1	13.1	...	13.8	11.3
Ca	12.4	15.6	15.5	12.9	10.4	10.4	...	13.4	16.6	11.0	3.4
S	8.5	9.4	7.8	9.0	8.4	10.3	7.3	8.8	10.8	5.2	6.3
P_2O_5											
Total	11.3	14.6	13.5	12.8	10.2	10.4	8.7	10.8	16.8	22.4	15.4
AOAC "available"[f]	10.6	12.2	12.5	12.5	9.6	10.3	8.4	10.1	16.2	21.2	15.1
Water-soluble	6.0	5.7	3.1	5.2	4.9	4.2	0.7	2.9	9.3	10.7	11.7
K_2O	12.4	11.0	12.2	11.3	11.2	9.8	8.5	15.8	...	16.6	13.6
CaO	17.4	21.9	21.7	18.0	14.6	14.5	...	18.7	23.3	15.4	4.8
SO_3	21.2	23.4	19.4	22.4	20.9	25.8	18.2	22.0	27.1	13.0	15.7
Compn., %, by x-ray											
NH_4Cl	10	9	9	11	12	12	7	12	...	11	10
NH_4NO_3	...	...	...	...	5	4	...	...	7	...	5
$(NH_4)_2SO_4$	...	...	...	1	3	3	7	...	...	4	8
$(NH_4)_2SO_4.CaSO_4.H_2O$	9	10	13	10	12	18	14	16	10	2	...
$3NH_4NO_3.(NH_4)_2SO_4$	...	...	...	...	...	...	...	...	9	...	10
$2NH_4NO_3.(NH_4)_2SO_4$	...	...	...	...	...	...	...	...	...	...	5
$NH_4NO_3.2KNO_3$	...	...	...	...	6	3	...	...	...	...	...
$NH_4H_2PO_4$	4	6	3	8	8	5	1	2	12	11	7
$(NH_4)_2HPO_4$	...	...	...	...	...	...	...	...	...	...	13
$Ca(H_2PO_4)_2.H_2O$	4	...	...	...	...	...	...	3	...	...	...
$CaHPO_4$	4	3	2	2	3	3	2	3	5	6	3
Apatite	11	17	17	12	9	9	12	13	10	14	5
KCl	8	7	11	4	4	3	6	10	...	19	16
KNO_3	...	...	...	5	1	4	...	...	...	10	7
K_2SO_4	...	...	...	2	5	...	1	...	...	10	...
KH_2PO_4	1	1	...	2	1	...	...	...	...	3	...
$K_2SO_4.CaSO_4.H_2O$	21	23	20	22	18	18	14	24	...	3	...
$CaSO_4$	12	9	5	7	9	5	2	2	28	3	3
$CaSO_4.\frac{1}{2}H_2O$	5	5	3	...	...	...	...	2	4	...	...
Dolomite	...	2	10	...	...	2	20	5	...	...	...
Quartz	3	3	...	7	4	3	3	...	3	4	2
Total	92	95	93	93	100	92	89	92	88	90	94

[a] Solution 425 (27–0–39) contains 10% $(NH_4)_2SO_4$.
[b] Solution 430 (20–68–6).
[c] Solution 440 (24–70–0).
[d] Pounds of neutralizing ammonia per 20 pounds of available P_2O_5 fed as ordinary superphosphate.
[e] Assuming concentrated superphosphate ammoniated to 4.0 pounds per unit of P_2O_5.
[f] Soluble in water and neutral ammonium citrate solution.

Table V. Distribution of Nutrients in Fertilizers Based on Ammoniated Superphosphate

Sample	All P₂O₅ from Ordinary Superphosphate									P₂O₅ from OSP and CSP	
	OSP-1	OSP-2	OSP-3	OSP-4	OSP-5	OSP-6	OSP-7	OSP-8	OSP-9	SP-1	SP-2
Grade											
N–P–K	3-5-10	4-5-10	4-5-10	6-5-10	10-4-8	10-4-8	6-3-7	5-4-12	8-7-0	5-9-17	15-6-12
N–P₂O₅–K₂O	3-12-12	4-12-12	4-12-12	6-12-12	10-10-10	10-10-10	6-8-8	5-10-15	8-16-0	5-20-20	15-15-15
Distribution, %, of NH₄–N[a]											
NH₄Cl	81	63	75	58	46	39	41	69	...	62	21
NH₄NO₃	...	...	...	...	13	9	...	...	20	...	7
(NH₄)₂SO₄	...	...	...	4	9	8	34	...	...	17	14
NH₄H₂PO₄	16	18	13	20	15	8	2	4	25	28	7
(NH₄)₂HPO₄	..	...	...	...	...	...	...	...	...	...	23
(NH₄)₂SO₄.CaSO₄.H₂O	28	26	41	20	18	23	32	36	17	4	...
3NH₄NO₃.(NH₄)₂SO₄	...	...	...	...	...	...	...	...	29	...	15
2NH₄NO₃.(NH₄)₂SO₄	...	...	...	...	...	...	...	...	...	...	8
NH₄NO₃.2KNO₃	...	...	...	...	4	3	...	...	...	...	...
Distribution, %, of P[a]											
NH₄H₂PO₄	22	25	14	38	48	30	7	11	44	30	28
(NH₄)₂HPO₄	...	...	...	...	...	...	...	...	...	...	45
KH₂PO₄	4	3	...	8	5	...	...	...	...	7	...
Ca(H₂PO₄)₂.H₂O	20	...	...	...	...	...	...	16	...	...	...
CaHPO₄	19	11	7	8	16	15	11	15	15	14	10
Apatite											
Precipitated[b]	35	33	45	38	31	36	56	44	21	21	12
Unreacted rock	6	16	8	2	6	1	3	7	4	5	2
Distribution, %, of K[a]											
KCl	41	40	57	22	22	19	45	40	...	72	74
KNO₃	...	...	...	20	4	19	...	...	...	...	24
K₂SO₄	...	...	...	10	24	...	6	...	...	33	...
KH₂PO₄	2	3	...	6	3	...	...	...	...	6	...
K₂SO₄.CaSO₄.H₂O	48	60	47	56	46	53	47	44	...	5	...
NH₄NO₃.2KNO₃	...	...	...	...	18	10	...	...	...	...	...

[a] Based on total amount shown by chemical analysis.
[b] AOAC "available," soluble in neutral ammonium citrate solution.

III, which includes only the stronger peaks of the compounds.

The intensity of a peak in an x-ray diffraction pattern varies with the absorption characteristic of the sample. To determine whether this effect was a significant source of error, a series of samples was prepared with linear absorption coefficients, μ, in the range 80 to 160 cm.$^{-1}$ Each sample contained 20% ammonium sulfate, 20% spinel, and 60% of a mixture of anhydrite and borosilicate glass. Patterns of the samples were run, and the intensities of the 20.4° peak of ammonium sulfate and the 36.8° peak of spinel were measured. The ratio of the intensities of the two peaks remained constant, thus demonstrating the validity of the use of an internal standard in this method of x-ray analysis.

The apatite in mixed fertilizers usually is present in colloidal forms that give diffuse x-ray patterns. In the preparation of reference samples of apatite, attempts were made to precipitate the apatite in forms whose x-ray patterns were like those of the apatite in fertilizers. On this basis, apatite B (Table I, Figure 1) was the reference for fertilizers based on superphosphate; apatite C for nitric phosphates. In calculating the chemical composition from the x-ray analysis, however, the apatite was assumed to

have the stoichiometric composition of $Ca_5(PO_4)_3OH$; fluorine usually was ignored.

Gypsum was an uncommon constituent of the fertilizers and its presence usually indicated that it had been added as a filler. Considerable difficulty was encountered in the preparation of calibration curves for gypsum, as the gypsum dehydrated slowly during the grinding.

Reference samples of monocalcium phosphate monohydrate also were difficult to prepare because the platy crystals tend to orient preferentially during grinding. Resultant errors in the calibration curve are not significant when the fertilizer contains only small amounts of monocalcium phosphate, but further study will be required to adapt the x-ray method of analysis to fertilizers containing large amounts of this compound.

Solid solutions were formed at all compositions in the systems $(NH_4)_2SO_4$–K_2SO_4 and $NH_4H_2PO_4$–KH_2PO_4, but in the system NH_4Cl–KCl potassium chloride–type solid solutions were formed only in compositions containing less than 30% NH_4Cl.

In the system NH_4NO_3–KNO_3, only NH_4NO_3 (III)-type solid solutions were formed in compositions containing less than 30% KNO_3. Compositions containing 30 to 72% KNO_3 were mixtures

of NH_4NO_3 (III)-type solid solutions and the double salt, $NH_4NO_3.2KNO_3$. At the KNO_3 end of the concentration range, as much as 5% of the KNO_3 could be replaced by its equivalent of NH_4NO_3 without changing the potassium nitrate structure, and it was found that the potassium nitrate in mixed fertilizers invariably contained substituted ammonia. Compositions in the range 72 to 95% KNO_3 were mixtures of the ammonia-substituted potassium nitrate and the double salt, $NH_4NO_3.2KNO_3$.

The results of the x-ray analyses show that extensive reactions among the original components take place in the preparation of mixed fertilizers. For example, potassium chloride was the only source of potassium in all the fertilizers examined, but the fertilizers contained several other potassium salts. The extent of these reactions varied with variation in particle size of the starting materials. In incompletely reacted fertilizers, some additional reaction occurred during the grinding of the sample for x-ray analysis. This change, however, can be detected by comparing a pattern of the lightly ground material, without addition of the internal standard, with the pattern of a sample prepared for quantitative analysis.

As a compound such as apatite becomes colloidal, the intensity of its peak

Table VI. Ammonium Phosphate Fertilizers

Sample	AP-1	AP-2	AP-3	AP-4	AP-5
Grade					
N–P–K	11–21–0	16–21–0	18–20–0	16–9–0	14–6–12
N–P_2O_5–K_2O	11–48–0	16–48–0	18–46–0	16–20–0	14–14–14
Formulation, lb./ton					
NH_3, anhydrous	270	388	. . .	169	340
$(NH_4)_2SO_4$	. . .	. . .	. . .	932	. . .
H_3PO_4	2133[a]	2133[a]	. . .	792[b]	881[c]
H_2SO_4, 66° Be.	129	172	. . .	. . .	852
KCl	. . .	. . .	. . .	. . .	468
Filler or conditioner	204[d]	. . .	. . .	225	15
Compn., %, by chem. anal.					
N					
Total	11.2	16.3	18.7	16.9	14.5
NH_4	11.2	16.3	18.7	16.9	14.5
P					
Total	20.8	20.7	21.0	9.2	6.6
AOAC "available"[e]	20.7	20.7	20.9	9.2	6.5
Water-soluble	20.0	19.8	17.9	8.1	6.2
K	. . .	. . .	. . .	. . .	11.0
Ca	2.4	0.0	0.4	<0.1	0.0
S	3.7	2.4	1.0	12.4	12.2
P_2O_5					
Total	47.6	47.5	48.1	21.0	15.1
AOAC "available"[e]	47.5	47.5	47.9	21.0	15.0
Water-soluble	45.7	45.2	41.1	18.5	14.1
K_2O	. . .	. . .	. . .	. . .	13.2
CaO	3.3	0.0	0.6	<0.1	0.0
SO_3	9.2	6.0	2.6	31.0	30.5
Compn., %, by x-ray					
NH_4Cl	. . .	. . .	. . .	. . .	10
$(NH_4)_2SO_4$	4	10	4	52	35
$NH_4H_2PO_4$	67	35	2	11	15
$(NH_4)_2HPO_4$	. . .	44	75	20	8
$(NH_4)_2SO_4.CaSO_4.H_2O$	8	. . .	. . .	. . .	. . .
KCl	. . .	. . .	. . .	. . .	7
K_2SO_4	. . .	. . .	. . .	. . .	20
KH_2PO_4	. . .	. . .	. . .	. . .	2
Quartz	. . .	. . .	. . .	9	. . .
Total	79	89	81	92	97
Distribution, %, of NH_4–N[f]					
NH_4Cl	. . .	. . .	. . .	. . .	18
$(NH_4)_2SO_4$	7	13	4	65	51
$NH_4H_2PO_4$	73	26	1	8	12
$(NH_4)_2HPO_4$	. . .	57	85	25	12
$(NH_4)_2SO_4.CaSO_4.H_2O$	7	. . .	. . .	. . .	. . .
Distribution, %, of P[f]					
$NH_4H_2PO_4$	87	45	2	32	62
$(NH_4)_2HPO_4$	. . .	50	84	51	28
KH_2PO_4	. . .	. . .	. . .	. . .	7
Distribution, %, of K[f]					
KCl	. . .	. . .	. . .	. . .	33
K_2SO_4	. . .	. . .	. . .	. . .	82
KH_2PO_4	. . .	. . .	. . .	. . .	5

[a] Wet-process, 20% P, 45% P_2O_5.
[b] Source and composition unknown.
[c] Wet-process, 14% P, 32% P_2O_5.
[d] Gypsum from wet-process H_3PO_4.
[e] Soluble in water and neutral ammonium citrate solution.
[f] Based on total amount shown by chemical analysis.

decreases, and when the particle size decreases below 0.1 micron the peak broadens. Peaks of solid solutions, such as those of ammonium and potassium chlorides, are broad when the composition is not uniform. With broad peaks, concentrations are determined more accurately from the areas under the peaks than from the heights of the peaks, but interference of other compounds is more serious with peak areas than with peak heights. Use of the peak area is necessary with some constituents, such

as solid solutions of ammonium and potassium chlorides, and would be advantageous with other constituents, notably other solid solutions and apatite.

Analyses of Commercial Fertilizers

Commercial mixed fertilizers from ten producers were examined by the x-ray method. The fertilizers fell into three groups: ammoniated superphosphates, ammonium phosphates and ammonium phosphate sulfates, and nitric phosphates. The chemical analyses

and formulations of the fertilizers are tabulated, but the conditions of manufacture, such as particle size of solid raw materials and temperature, which affect the extent of the reactions of the ingredients, are not known.

Ammoniated Superphosphate Fertilizers. The formulations, chemical analyses, and x-ray analyses of nine fertilizers (OSP-1 through -9), based on ammoniated ordinary superphosphate, are shown in Table IV. Samples OSP-3 and -7 were semigranular; the

Table VII. Nitric Phosphates[a]

Sample	NP-1	NP-2	NP-3
Grade			
N–P–K	20–9–0	20–4–0	14–6–12
N–P$_2$O$_5$–K$_2$O	20–20–0	20–10–0	14–14–14
Compn., %, by chem. anal.			
N			
Total	20.5	20.0	14.0
NH$_4$	11.0	10.7	7.0
P			
Total	9.0	4.4	6.5
AOAC "available"[b]	8.9	4.3	6.4
Water-soluble	3.0	0.7	0.3
K	...	...	11.8
Ca	9.1	10.2	9.3
S	...	4.0	...
P$_2$O$_5$			
Total	20.5	10.0	14.9
AOAC "available"[b]	20.4	9.9	14.6
Water-soluble	6.9	1.5	0.8
K$_2$O	...	...	14.2
CaO	12.7	14.3	13.0
SO$_3$	...	9.9	...
Degree of ammoniation[c]	1.15	1.65	1.10
Compn., %, by x-ray			
NH$_4$Cl	...	...	15
NH$_4$NO$_3$	50	52	5
NH$_4$H$_2$PO$_4$	8	...	...
(NH$_4$)$_2$SO$_4$.CaSO$_4$.H$_2$O	...	9	...
NH$_4$NO$_3$.2KNO$_3$	...	...	42
CaHPO$_4$	30	14	26
Apatite	...	6	1
CaSO$_4$	...	2	...
CaSO$_4$.$^1/_2$H$_2$O	...	3	...
CaSO$_4$.2H$_2$O	...	4	...
Quartz	5	...	3
Total	93	90	92
Distribution, %, of NH$_4$–N[d]			
NH$_4$Cl	...	...	56
NH$_4$NO$_3$	80	85	13
NH$_4$H$_2$PO$_4$	9	...	...
(NH$_4$)$_2$SO$_4$.CaSO$_4$.H$_2$O	...	8	...
NH$_4$NO$_3$.2KNO$_3$	...	...	30
Distribution, %, of P[d]			
NH$_4$H$_2$PO$_4$	24	...	...
CaHPO$_4$	76	73	91
Apatite			
Precipitated[e]	0	24	1
Unreacted rock	0	1	2
Distribution, %, of K[d]			
NH$_4$NO$_3$.2KNO$_3$	...	...	99

[a] Formulations not available.
[b] Soluble in water and neutral ammonium citrate solution.
[c] (CaO − SO$_3$ + NH$_4$ − NO$_3$)/P, where formulas denote number of moles of indicated components. Theoretical ammoniation to give CaSO$_4$, CaHPO$_4$, NH$_4$H$_2$PO$_4$, and NH$_4$NO$_3$ is 1.00.
[d] Based on total amount shown by chemical analysis.
[e] AOAC "available," soluble in neutral ammonium citrate solution.

Table VIII. Chemical Composition of Fertilizers

		Composition, %									
		N									
Sample[a]	Analysis	Total	NH$_3$	P	K	Ca	S	P$_2$O$_5$	K$_2$O	CaO	SO$_3$
OSP-6	X-ray	8.7	7.0	3.7	8.2	11.1	9.4	8.5	9.9	15.5	23.6
10–4–8 (10–10–10)	Chemical	10.0	8.0	4.5	8.1	10.4	10.3	10.4	9.8	14.5	25.8
OSP-9	X-ray	7.6	5.4	6.2	...	16.2	10.5	14.2	...	22.7	26.2
8–7–0 (8–16–0)	Chemical	8.1	5.9	7.3	...	16.6	10.8	16.8	...	23.3	27.1
AP-3	X-ray	17.0	17.0	18.1	...	...	1.0	41.5	...	...	2.4
18–20–0 (18–46–0)	Chemical	18.7	18.7	21.0	...	...	1.0	48.1	...	...	2.6
NP-2	X-ray	19.1	10.0	4.3	...	10.1	3.9	9.8	...	14.2	9.7
20–4–0 (20–10–0)	Chemical	20.0	10.7	4.4	...	10.2	4.0	10.0	...	14.3	9.9

[a] Designation same as in Tables IV through VII.

rest were well granulated. The grades represented by the samples are very popular and account for about 20% of all mixed fertilizers consumed in the United States in 1962 (8). The degree of ammoniation ranged from 4.3 to 6.6 pounds of NH_3 per unit of available P_2O_5 in the ordinary superphosphate; 6 pounds of NH_3 per unit of P_2O_5 usually is considered the maximum that can be used without excessive loss of ammonia (6). All the potassium was supplied as potassium chloride.

The distribution of ammoniacal nitrogen, phosphorus, and potash in the various compounds is shown in Table V. The x-ray analysis showed that ammonium and potassium salts of the same anion often were present as solid solutions, but for convenience the individual salts are reported separately.

Except in OSP-9, which contained no potash, most of the ammoniacal nitrogen was present as ammonium chloride and ammonium syngenite, $(NH_4)_2SO_4$. $CaSO_4.H_2O$. Ammonium chloride, which accounted for 39 to 81% of the total ammoniacal nitrogen, resulted from reactions of potassium chloride. The formation of ammonium syngenite increased with increased degree of ammoniation, as shown in Figure 3. Monoammonium phosphate was present in all samples and ammonium sulfate was present in four samples.

Five fertilizers (OSP-4, -5, -6, -8, and -9) had been made with nitrogen solution containing ammonium nitrate. Ammonium nitrate was present in potash-free OSP-9 as both the single salt and the double salt, $3NH_4NO_3.(NH_4)_2$-SO_4. In the other samples, ammonium nitrate reacted with potassium chloride to form potassium nitrate which appeared either as the single salt or as the double salt, $NH_4NO_3.2KNO_3$.

Several samples (OSP-3, -4, -5, and -7) had been made with nitrogen solutions containing urea. Chemical analysis showed these samples to contain 0.2 to 1.5% urea nitrogen, but urea was not detected by x-ray analysis and was found petrographically only in OSP-7.

Monocalcium phosphate, the principal phosphatic compound in ordinary superphosphate, is converted on ammoniation to monoammonium phosphate, dicalcium phosphate, and apatite. Two of the fertilizers (OSP-1 and -8) contained unreacted monocalcium phosphate, probably as the result of non-uniform ammoniation, since other samples with the same degree of ammoniation contained no monocalcium phosphate. Data from samples OSP-1 and OSP-8 were omitted in correlations of composition with degree of ammoniation.

The predominant water-insoluble phosphate was apatite. Most of the apatite was soluble in neutral ammonium

citrate solution (AOAC "available") and must have been formed in the ammoniation reactions, since its amount increased regularly from 21 to 56% of the total phosphorus as ammoniation was increased from 4.3 to 6.6 pounds of NH_3 per unit of P_2O_5 (Figure 3). This increase in apatite with increasing ammoniation was reported also by Hignett and Brabson (5). The apatite insoluble in neutral ammonium citrate solution (1 to 16% of total P) was shown petrographically to be largely unreacted phosphate rock.

The proportion of phosphorus present as dicalcium phosphate ranged from 7 to 19%, apparently independently of the degree of ammoniation. The proportion of phosphorus present as monoammonium phosphate ranged from 7 to 48% and generally decreased as the degree of ammoniation increased (Figure 3). Small amounts of monopotassium phosphate were present in some of the samples.

Potassium chloride reacted extensively with ammonium salts to form ammonium chloride and potassium nitrate, sulfate, and monobasic phosphate, each of which formed double salts or solid solutions with ammonium salts of the same anion. The most significant conversion of potassium, however, was that to potassium syngenite, $K_2SO_4.CaSO_4.H_2O$, usually as a solid solution with ammonium syngenite. Potassium syngenite is only slightly soluble in water (ammonium syngenite decomposes readily); about half the potassium was converted to this relatively insoluble form in all the fertilizers examined.

Calcium sulfate was present in all the fertilizers. Dolomitic limestone had been used in five formulations, and dolomite was detected in all these samples. No other magnesium compound was detected by either x-ray or petrographic examination. Quartz constituted 3 to 7% of nearly every fertilizer.

Included in Tables IV and V are data on two fertilizers prepared by ammoniation of mixtures of ordinary superphosphate and concentrated superphosphate. In SP-1 about 25% of the phosphorus was supplied as ordinary superphosphate and 75% as concentrated superphosphate. In SP-2 about 15% of the phosphorus was supplied as ordinary superphosphate, 13% as concentrated superphosphate, and 72% as diammonium phosphate. The amount of ammonia fed as anhydrous ammonia (SP-1) or ammonia–ammonium nitrate solution (SP-2) supplied about 6 pounds of NH_3 per unit of P_2O_5 in the ordinary superphosphate, assuming that 4 pounds was fixed per unit of P_2O_5 in the concentrated superphosphate. These degrees of ammoniation are about the maximum obtained in most plants (6).

In both fertilizers about 30% of the

phosphorus was present as monoammonium phosphate. Although 72% of the phosphorus in SP-2 was fed as diammonium phosphate, only 45% of the phosphorus in the product was in that form. The water-insoluble phosphorus was present as dicalcium phosphate and apatite. About 75% of the potassium chloride remained unreacted.

Although both fertilizers prepared with concentrated superphosphate contained considerable sulfate, SP-1 contained little syngenite and SP-2 contained none. It appears probable that the relatively high ratio of phosphate to sulfate in these fertilizers suppressed the formation of syngenite. The formulation of SP-2 included a relatively large amount of ammonium nitrate; about 25% of this salt reacted with potassium chloride to form ammonium chloride, and the rest was present as free ammonium nitrate and the double salts, $2NH_4NO_3.(NH_4)_2SO_4$ and $3NH_4NO_3.(NH_4)_2SO_4$.

Ammonium Phosphates and Ammonium Phosphate Sulfates. Analyses of five fertilizers in which all the phosphorus was supplied as phosphoric acid and all the nitrogen was ammoniacal are shown in Table VI. Information on the formulations is incomplete, but wet-process phosphoric acid probably was the source of phosphorus. Different ratios of nitrogen to phosphorus were obtained by varying the degree of ammoniation of the phosphoric acid and the proportions of sulfuric acid or ammonium sulfate.

Fertilizers AP-1, -2, and -3 contain little sulfate and are of the type known as ammonium phosphate fertilizers. Fertilizers such as AP-4 and -5, which contain large amounts of sulfate, are known as ammonium phosphate sulfates.

In all these fertilizers, nearly all the phosphorus was present as mono- or diammonium phosphate; AP-5 contained a little monopotassium phosphate. Materials such as these that are prepared from wet-process phosphoric acid contain a small amount of a gelatinous mixture of iron and aluminum phosphates that accounts for the rest of the phosphorus but is not detected by x-ray examination.

The small amount of syngenite in AP-1 was formed from the gypsum which was added as a filler.

Nitric Phosphates. Results of analyses of three nitric phosphates are shown in Table VII. The formulations of these fertilizers are not known, but it is apparent that NP-1 and -3 were prepared with nitric and phosphoric acids and NP-2 was prepared with nitric and sulfuric acids.

In the absence of potash (NP-1 and -2), most of the nitrogen was present as ammonium nitrate. In the presence of potash (NP-3), all the potassium chloride was converted to potassium

nitrate which then formed the double salt, $NH_4NO_3 \cdot 2KNO_3$. In contrast to the superphosphate-based fertilizers, most of the water-insoluble phosphate in the nitric phosphates was dicalcium phosphate; the apatite in NP-2, which accounted for 24% of the total phosphorus, was nearly all in the precipitated form and resulted from the high degree of ammoniation. The only water-soluble phosphate, found only in NP-1, was monoammonium phosphate.

The high degree of ammoniation of NP-2 probably resulted also in the formation of considerable syngenite; the unreacted calcium sulfate was present in all three states of hydration—anhydrite, hemihydrate, and gypsum.

Evaluation of Method

Because of the uncertainties introduced by line broadening, interferences, and reactions occurring during the preparation of the sample, it is difficult to estimate the accuracy of the x-ray method of analysis. The accuracy probably is best determined by comparison of the chemical composition computed from the results of the x-ray analysis with that

obtained by chemical analysis, as in Table VIII. Compositions computed from x-ray analysis are usually lower than those determined by chemical analysis, and the difference was as large as 18% for total phosphorus. Errors in the x-ray method are to be expected because of the presence of small but significant amounts of such compounds as iron and aluminum phosphates in colloidal forms that are not detected by x-ray.

It appears that the uncertainty in the x-ray results for most major constituents is between 5 and 10%, whereas for monocalcium phosphate monohydrate, apatite, and some of the solid solutions the uncertainty may be as high as 25%. Even with these uncertainties, however, the x-ray method of analysis yields valuable information on the mineralogical composition of mixed fertilizers.

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