

solution to 10 litres. The solution keeps better if 5 gr. of salicylic acid are added. To control the acid concentration of this mother liquor, dilute 50 c.c. to 500 c.c. and take 50 c.c., corresponding to 0,5 gr. of citric acid. Titrate with  $n/4$  soda in the presence of phenolphthalein. As citric acid ( $C_6H_8O_7 - H_2O$ ) has a molecular weight of 210,11 and neutralizes 42,03 of nitrogen, and as these two numbers are almost exactly in the ratio of 5 to 1, the quantity of citric acid contained in 1 litre of mother liquor has the same number as the quantity of nitrogen, expressed in mg., corresponding to the volume of soda used for neutralization. Example: 3,502 mg. of nitrogen correspond to 1 c.c. of soda. To neutralize 50 c.c. of citric acid diluted as stated, 28,57 c.c. is used. Therefore, 1 litre of mother liquor necessarily contains  $3,502 \times 28,57 = 100,0$  gr. of citric acid.

One vol. of mother liquor is diluted to 5 vols. with water and 2% citric acid is thus obtained.

#### a) Treatment of basic slag with citric acid.

Place 5 gr. of slag which will pass through a 2 mm. mesh, in a dry 500 c.c. Stohmann flask. The neck of the flask must have an inner diameter of at least 2 cm. and must be at least 8 cm. long above the mark, to allow enough room for shaking. To avoid sticking, rinse the flask before introducing the material with alcohol and shake well. After inserting the material, fill to the mark with 2% citric acid solution at 17,5° C, shaking constantly; seal tightly with a rubber stopper. Place the flask in a Wagner mechanical shaker, turning at 30–40 r. p. m.

Filter at once through a pleated filter of about 24 cm. diameter into a glass vessel, dry or rinsed with the first portion of the filtrate. The filtrate should always be perfectly clear. Transfer 50 c.c. (= 0,5 gr. of material) with a pipette into a thick-sided beaker and precipitate phosphoric acid.

#### b) Treatment of compound fertilizers (e.g. superphosphate and ammonia) with citric acid.

First pass the sample through a 1 mm. mesh sieve. Shake 5 gr. of the sample with 500 c.c. of 2% citric acid solution — as for basic slag — for half an hour in the mechanical shaker. Filter, take an aliquot part of the filtrate and proceed by the V. Lorenz method.

### II. Precipitation of phosphoric acid

#### 1. N. V. Lorenz phospho-molybdate method.

Reagents: 1. Sulpho-molybdate reagent. — Place 500 gr. of ammonium sulphate and 4500 c.c. of nitric acid ( $d = 1,40$ ) in a bottle over 10 litres capacity, marked at 10 litres, and shake vigorously. Secondly, place 750 gr. of powdered ammonium molybdate in a 3-litre flask, add 2 litres of boiling water and shake until dissolved. Treat another identical quantity of ammonium molybdate in the same way. If a large residue remains undissolved, the ammonium molybdate is not suitable for the purpose. Allow to cool to room temperature, and decant slowly into the nitric acid containing ammonium sulphate, shaking constantly. After cooling, fill to the 10-litre mark and homogenize thoroughly. The prepared reagent should be kept in a brown flask in a cool, dark place.

To precipitate the phosphoric acid present in the reagent, leave the solution for two days before using. Filter before use.

2. Nitric acid,  $d = 1,20$ .

3. Nitric acid,  $d = 1,40$ .

4. Nitric acid containing sulphuric acid. Pour 30 c.c. of sulphuric acid ( $d = 1,84$ ) into 1 litre of nitric acid ( $d = 1,20$ ) and homogenize.

5. 2% ammonium nitrate solution. If the solution does not give a slightly acid reaction, acidify with a few drops of nitric acid until such a reaction is obtained. Use very pure ammonium nitrate crystals.

6. Acetone (very pure). The acetone must be kept in a brown flask. To be suitable for use, it must form a clear mixture

with the same quantity of water, give a neutral reaction, contain no part distillate at more than 60° C, and satisfy the following tests for absence of significant quantities of water, ammonia and aldehyde.

Water test. When shaken up with anhydrous copper sulphate, the acetone should be at the most pale blue in colour. Otherwise, shake with potassium carbonate and distil. The petroleum test is also recommended.

Ammonia test. A moistened strip of red litmus paper hanging over the acetone and secured by the stopper of the acetone bottle should not turn blue if left for some time; otherwise the acetone should be shaken with a little finely ground oxalic acid and distilled.

Aldehyde test. Heat 10 c.c. of acetone and 5 c.c. of ammonia-cal silver nitrate solution for 15 minutes in a boiling water-bath under a reflux condenser. The liquid should not turn brown.

#### Method of precipitating phosphoric acid

Measure the stated volume of phosphoric acid solution with an officially calibrated pipette, and pour into a 250 c.c. beaker. If the fertilizer in solution contains sulphuric acid, make up the measured volume of phosphoric acid solution to 50 c.c. with nitric acid ( $d = 1,20$ ), using an accurately graduated test-tube. In all other cases, make up the measured volume of the fertilizer solution to 50 c.c. with nitric acid containing sulphuric acid.

Heat the 50 c.c. of liquid — the volume regularly used for precipitation — in a beaker standing on a metal gauze, without stirring, until it begins to boil; remove from the flame and shake for a few seconds to stop overheating the sides of the beaker; drop the sulphomolybdate reagent immediately from a 50 c.c. graduated test-tube into the middle of the solution, and cover. As soon as most of the precipitate has settled, and in any case after not more than 5 minutes, stir briskly with a rod for half a minute. With practice, stirring can be replaced by swirling for the same length of time. After 2 to 18 hours (if less than 3 mg. of  $P_2O_5$  are needed, after 12 to 18 hours) filter on a Gooch crucible.

After draining off the supernatant liquid, wash immediately at least five times with a 2% ammonium nitrate solution, taking care to transfer to the crucible particles of yellow precipitate clinging to the precipitation vessel with a rubber-tipped rod.

Fill the crucible once completely and then half-fill twice with acetone, sucking off the liquid completely each time. Carefully wipe the outside of the crucible and place immediately in a high vacuum, pressure in no case to exceed 150 mm. (vacuum desiccator). After half an hour, either weigh the crucible immediately or place until weighing in a desiccator, prepared with a mixture of equal parts of water and sulphuric acid. In this case, the ammonium phosphomolybdate contains 3,29% of  $P_2O_5$ , so that its weight multiplied by 0,03295 gives the quantity of phosphoric acid present.

#### 2. Ammonium citrate method

Reagents: 1. Ammonium citrate solution (for total and water-soluble phosphoric acid). First prepare a solution of citric acid containing 800 gr. of citric acid crystals per litre. Slowly pour 1,25 l. of the solution through a narrow funnel into a 10 litre vessel containing 3,5 l. of ammonia ( $d = 0,91$ ) and about 4 litres of water, frequently shaking and cooling. Any loss of ammonia is thus avoided. After cooling, make the liquid up to 10 litres with water. If the ammonia content of the citrate solution is too low, errors are liable to arise. 100 c.c. of citrate solution, prepared and kept without any loss, contain 10 gr. of citric acid and 7,96 gr. of total ammonia, corresponding to 6,55 gr. of nitrogen. The 7,96 gr. contain 5,53 gr. of free ammonia, corresponding to 4,54 gr. of nitrogen. To check this solution, dilute 25 c.c. of the ammonium citrate solution to 1 litre (it is best measured with a small graduated lipped flask, which must be rinsed). Take 50 c.c. for the determination of ammonia, corresponding to 1,25 c.c. of the original citrate solution. Excluding losses, it should contain 0,0818 gr. of ammoniacal nitrogen.

2. Ferrous citrate solution (for slag phosphoric acid soluble in citric acid and phosphate solutions rich in silicic acid). Use the citric acid solution described in paragraph 1, containing 800 gr. of citric acid per litre. Add to 1,25 l. of this solution 30 gr. of ferrous chloride (not decomposed, easily soluble and giving a clear solution), dissolved by heating slightly in about 50 c.c. of water, and rinse with very little water. Pour the solution very slowly through a narrow funnel, shaking carefully and cooling, into a 5-litre vessel containing 3,5 litres of ammonia solution ( $d = 0,91$ ); after cooling completely to room temperature, fill to the mark and homogenize. The ferrous citrate solution will contain twice as much citric acid and ammonia as solution 1. To check, proceed exactly as before, but instead of 50 c.c., take 25 c.c. of the dilute solution (25 c.c. in 1 litre). Excluding losses, this should also contain 0,0818 of ammoniacal nitrogen.

3. Magnesia liquor. Dissolve 550 gr. of magnesium chloride crystals, 700 gr. of ammonium chloride and 2,5 litres of ammonia ( $d = 0,91$ ) in enough water to give 10 litres.

a) Precipitation of water-soluble phosphoric acid from superphosphate and mixtures containing it.

Mix 50 c.c. (= 1 gr. of material) of the superphosphate solution shaken with water with 50 c.c. of ammonium citrate solution prepared as for the citrate method, then pour into a thick-sided beaker with 25 c.c. of the magnesia solution.

The latter should be added quickly and immediately mixed with the solution by stirring. Shake mechanically for half an hour. Filter, wash and calcine the precipitate as usual.

b) Precipitation of water-soluble phosphoric acid from double superphosphates.

For superphosphates and double superphosphates with a phosphoric acid content of more than 20%, take only 25 c.c. (= 0,5 gr. of material), but use the same quantities of reagent as in paragraph a). For double superphosphates, boil 25 c.c. for 10 minutes with 10 c.c. of nitric acid ( $d = 1,40$ ) to convert any meta- or pyrophosphoric acids present into the precipitable ortho form. After pouring in the ammonium citrate solution, add a quantity of ammonia corresponding to the amount of nitric acid used, cool and proceed as for ordinary superphosphates.

c) Precipitation of total phosphoric acid (e.g. basic slag).

Neutralize 50 c.c. (= 0,5 gr. of material) of the filtrate obtained from ammonia ( $d = 0,91$ ) until the liquid begins to cloud. Add 50 c.c. ammonium citrate solution, then 25 c.c. of the magnesia liquor, and place immediately on the agitator. It is usually more difficult to obtain total precipitation than, for instance, in superphosphate solutions; it is therefore preferable to shake for one hour.

### D. Analysis of lime improvers

#### 1. Determination of total CaO.

a) Lime improvers with a low  $SiO_2$ , Al and Fe content.

Reagents: 1. Hydrochloric acid  $d = 1,20$ . 2. Nitric acid  $d = 1,40$ . 3. Ammonia 10%. 4. Acetic acid 10%. 5. Ammonium oxalate 10%.

Method: Place 5 gr. of lime improver in a 500 c.c. flask with 50 c.c. of water, 50 c.c. of hydrochloric acid ( $d = 1,2$ ) and 5 c.c. of nitric acid and boil until completely dissolved. When the mixture is cool fill up to the mark and filter. To 10 c.c. (= 0,1 gr. of material) of the filtrate add some phenolphthalein; add a few drops of ammonia to make it slightly alkaline and then a slight excess of acetic acid to make it slightly acid. Dilute to 100 c.c. and precipitate the lime at boiling point with ammonium oxalate. Boil for a few minutes and allow to settle. If required, the precipitate can be collected immediately by filtering. Rinse with hot or cold water. The precipitate must be very carefully calcined. If this procedure is used with ordinary lime improvers, the precipitate

contains only small quantities of iron and other impurities. As a rule, the weight of the calcined precipitate for the analysis of lime should not exceed 0,1 gr.

b) Lime improvers with a fairly high  $SiO_2$  content.

Reagents: 1. Hydrochloric acid  $d = 1,20$ . 2. Nitric acid  $d = 1,40$ . 3. Ammonia 10%. 4. Acetic acid 10%. 5. Ammonium oxalate 10%.

Method: In a 500 c.c. flask mix 5 gr. of lime improver cautiously with 100 c.c. of dilute hydrochloric acid and boil for half-an-hour; cool, fill up to the mark and filter. Evaporate in a water-bath 200 c.c. of the filtrate (= 2,0 gr. of material) in a porcelain dish and calcine slightly. Dissolve with nitric acid and, in order to eliminate the silicic acid, twice with concentrated hydrochloric acid, and calcine slightly again; then moisten with concentrated hydrochloric acid, mix with hot water and filter into a 500 c.c. flask. To eliminate iron and alumina hydroxides, add excess ammonia to the filtrate, eliminate excess ammonia by evaporation, add a few drops of acetic acid, fill up to the mark and filter. Precipitate the lime in 50 c.c. of the filtrate (= 0,2 gr. of material) with ammonium oxalate. Filter off the precipitate and determine the lime in the form of CaO by gravimetric or titrimetric methods with a potassium permanganate solution.

#### 2. Determination of total MgO.

B. Schmitz method.

Reagents: 1. 2N sodium phosphate solution. 2. Ammonium acetate 10%. 3. Ammonia 2%. 4. Dilute hydrochloric acid, about 1 : 10.

Method: The filtrate obtained in the previous section is reduced to about 50 c.c. and then slightly acidified with a few drops of dilute hydrochloric acid. Then mix the solution with about 50 c.c. of ammonium acetate and excess sodium phosphate. Bring the liquid to boiling point, pour in 2,5% ammonia by means of a burette in the presence of phenolphthalein, stirring constantly with a glass rod until the mixture becomes cloudy, slightly milky and opalescent. If possible, avoid touching the sides of the flask with the rod. As soon as the cloudiness appears, stop adding ammonia and keep stirring until the cloudiness disappears and the precipitate has become crystalline, which will take about a minute. Then continue to add ammonia, stirring all the while; but proceed so that each drop falling into the liquid is visible to the naked eye.

As soon as a slight red tinge appears, again stop adding ammonia, rinse the stirring rod in dilute hydrochloric acid and go on pouring ammonia until the liquid turns slightly red. Then allow the liquid to cool completely, add about 1/5th by volume of concentrated ammonia, stir vigorously and filter after a few minutes. Collect the precipitate in a Neubauer-Gooch crucible, wash carefully first with a 2,5% ammonia solution, and then twice with pure alcohol. Start to dry over a very low flame and finally calcine in the electric furnace; weigh in the form of magnesium pyrophosphate ( $Mg_2P_2O_7$ ).

#### 3. Determination of $CO_2$ .

Fresenius-Classen method.

Reagents: 1. Calcium chloride. 2. Soda lime. 3. Hydrochloric acid (1 : 3).

Method: The Fresenius-Classen method is regarded as the most accurate way of analysing  $CO_2$  in lime improvers. The apparatus used consists of a reaction flask of about 400 c.c. fitted with a cooling system, three drying tubes and two graduated absorption tubes (soda lime). The first drying tube which is attached directly to the flask contains glass beads standing in concentrated sulphuric acid; this is followed by two tubes containing pellets of calcium chloride, then two tubes of soda lime and, finally, a safety U tube with the left arm filled with calcium chloride and the right arm filled with soda lime.