

To carry out the analysis place 1 gr. of the improver in the dry reaction flask and sprinkle a very little water to prevent the material from crumbling into dust. Then pass CO₂-free air slowly through to drive out any traces of CO₂ in the reaction flask and the three drying tubes. While the air is passing through the apparatus, weigh the soda lime tubes, then stop the air flow, connect the soda lime tubes at one end to the calcium chloride tube and at the other to the end safety tube and pour hydrochloric acid slowly through a funnel on to the material, which immediately gives off CO₂. When all the hydrochloric acid has been added, heat over a low flame and while the liquid is boiling gently, bubble air through slowly. No more than 3 or 4 bubbles per second should pass through the sulphuric acid tube. Throughout the operation, cold water should flow through the cooling system; in this way the entrained steam is condensed and returned to the flask. When all the CO₂ has been extracted, extinguish the flame and bubble air through fairly quickly for a further 20 minutes, then remove the soda lime tube and weigh after 30 minutes.

E. Methods recommended by the International Commission for Testing

1. Methods of nitrogen analysis

1. Analysis of ammonia with NaOCl (Literature: Kolthoff, I. M. «Die Massanalyse», 1931, pages 512—513).
2. Analysis of ammonia with MgO (Literature: Schmitt L., «Die Untersuchung von Düngemitteln», 1954, page 14).
3. Analysis of nitric nitrogen.
 - a) by the K. Ulsch method (Literature: Schmitt L., «Die Untersuchung von Düngemitteln», 1954, page 13);
 - b) by the Th. Arnd method (Literature: Schmitt L., «Die Untersuchung von Düngemitteln», 1954, page 12).

Prélèvements d'échantillons d'engrais

par M. A. Daujat

L'analyse des engrais justifiée par la nécessité de contrôler les fournitures commerciales de ces produits, n'a de signification qu'à condition de pouvoir affirmer formellement l'identité entre l'échantillon remis au laboratoire et la masse du lot, objet du contrat.

Le prélèvement d'échantillons est donc, de ce fait, une opération très délicate et qui influe considérablement sur le résultat donné par le laboratoire.

Certains principes en vigueur dans le commerce des engrais sont à prendre en considération pour effectuer correctement les prélèvements:

Premier principe: Les produits sont vendus en l'état et, par conséquent, la garantie de titre n'est généralement pas établie sur produits secs, c'est là une première difficulté qui exigera certaines précautions spéciales pour la prise d'échantillons.

Deuxième principe: Le fournisseur, sauf convention contraire, est réputé avoir livré correctement lorsqu'il a fourni dans l'engrais la quantité de matières utiles garanties, donc, lorsqu'il a fourni le dosage moyen garanti. Il s'ensuit que la prise d'échantillons devra permettre l'établissement de cette moyenne, sans se soucier outre mesure de l'homogénéité parfaite du lot échantillonné.

Troisième principe de transaction commerciale: l'identification des échantillons soumis à l'analyse, doit être faite, à la fois de l'expéditeur et du destinataire; c'est pourquoi nous trouverons toujours soit ces deux personnes associées dans le pré-

2. Method of potash analysis

Analysis of potash with the flame photometer (The literature contains many proposals from different sources).

3. Methods of phosphoric acid analysis

1. Ferrous citrate method (Literature: Schmitt L., «Die Untersuchung von Düngemitteln», 1954, page 34).

2. Colorimetric methods.

a) With molybdenum blue (Literature: O.E.E.C. documentation, page 173).

b) With ammonium phosphovanadomolybdate.

F. Literature used in studying the proposals

1. SCHMITT L.: Die Untersuchung von Düngemitteln — Neumann Verlag, Radebeul und Berlin II. Auflage 1954.
2. O.E.E.C. documentation: Fertilisers — Methods of Analysis used in O.E.E.C. countries — 1952.
3. GERICKE S.: Analytische Chemie der Düngemittel — Ferdinand Enke Verlag, Stuttgart, 1949.
4. LEROUX D.: Engrais amendements produits pour la protection des cultures — Etude et analyse — Gauthier-Villiers Ed., Paris, 1951.
5. GELLI P.: Determinazione Fotometrica del Titolo dei concimi Fosfatici. Annali Sperimentazione Agraria, nuova serie Vol. VI n. 2. 347—358 (1952).
6. EPPS E. A., Jr.: Photometric Determination of Available Phosphorus Pentoxide in Fertilisers. Analytical Chemistry, vol. 22; No. 8. 1062—1063 (1950).
7. GELLI P.: Sulla determinazione del titolo dei concimi potassici col metodo «alla fiamma». Annali Sperimentazione Agraria, nuova serie Vol. VI, n. 2. 359—365 (1952).

lèvement et dans la signature d'un procès-verbal de prélèvement, soit la présence de l'un d'entre eux accompagné d'un témoin impartial, peseur juré au départ, ou témoin d'impartialité authentique à l'arrivée (Commissaire de Police, fonctionnaire assermenté ou administrateur communal).

Je tiens à remercier les quelques personnes qui ont bien voulu m'adresser des documents concernant les méthodes de prélèvement d'échantillons dans leur pays: Monsieur WINDORF qui m'a fourni les méthodes utilisées en Allemagne, Monsieur BONDORFF qui m'a fait remettre les instructions d'échantillonnage établies en 1939 par le Ministère de l'Agriculture danois, Monsieur le Professeur FABBRIS qui m'a transmis les extraits du décret-loi réglementant les fraudes en Italie, Monsieur GILLEN qui m'a donné les réglementations de la prise d'échantillons de scories Thomas en Luxembourg, et Monsieur LEHR qui m'a fourni les instructions de la station agronomique de Maastricht. Ainsi que MM. BOXUS et HOED qui m'ont adressé le 16 avril des renseignements sur l'échantillonnage en Belgique.

A cette documentation, j'ai pu joindre les instructions à son personnel, données par le Service des Fraudes en France et, enfin, la «norme» adoptée par l'Association Française de Normalisation qui a été homologuée le 30 avril 1953.

Suivant les pays, le prélèvement d'échantillons est, soit purement contractuel, soit une disposition du régime de contrôle légal des services de répression des fraudes. Dans tous les pays, on observe le processus général suivant:

15 c.c. of alcohol on to the residue as soon as cool, and crush to a fine powder with a glass rod. The residue must be very carefully crushed, to ensure that the potassium perchlorate does not dissolve. Allow to stand for a short time and filter. If left too long, the results obtained will be too low owing to the hygroscopicity of the product. Pour the liquid covering the precipitate into a Gooch crucible or a glass filter crucible; crush the residue twice more in the presence of perchloric alcohol, and pour the liquid into the crucible. Lastly, transfer the precipitate to the crucible and rinse with perchloric alcohol. Dry by depression, then rinse the potassium perchlorate again with about 4 to 5 c.c. of pure alcohol 96 %.

The filtrate must not be more than 75 c.c. in volume. Dry the precipitate for 30 minutes at 130° C and weigh after cooling in the desiccator.

C. Analysis of phosphate fertilisers

I. Dissolution of phosphates and preparation of P₂O₅ precipitate

1. Total P₂O₅.

a) In the absence of organic substances.

Reagents: Concentrated H₂SO₄ d = 1,84.

Method: Place 5 gr. of material in a 500 c.c. Pyrex flask, moisten with about 15 c.c. of water, and heat with 30 c.c. of H₂SO₄, shaking frequently, for about 20 minutes until completely dissolved. Dilute the hot solution with water and shake to break up any crust that may have formed. After cooling, fill to the mark, shake well and filter on a dry pleated filter. Take an aliquot part of the filtrate and precipitate the phosphoric acid by the Lorenz method or the citrate method (cf. C. II).

b) In the presence of organic substances (rock phosphate, bone-meal, guano, etc.).

Reagents: 1. Ground copper sulphate. 2. H₂SO₄ d = 1,84. 3. Nitric acid d = 1,40.

Method: Place 5 gr. of material in a 500 c.c. Pyrex flask, moisten with about 15 c.c. of water and add 20 c.c. of nitric acid, after adding a few small grains of copper sulphate (about 0,5 gr.). Add cautiously 30 to 40 c.c. of H₂SO₄. This procedure usually provokes a violent initial reaction; when the effervescence has died down, begin to heat slowly until the contents of the flask are gently boiling. Continue to boil until the organic matter has decomposed and a clear liquid is obtained. If necessary, add further small quantities of nitric acid, allowing to boil for some time after each addition. After evaporation of the excess nitric acid and complete dissolution, boil, shaking frequently, until the nitrous fumes cease and white fumes of H₂SO₄ are given off. After cooling the contents of the flask, add about 200 c.c. of water, shaking all the time, and fill to the mark when the solution is quite cold, homogenise and filter on a dry pleated filter. Discard the first few cubic centimetres obtained. Take 15 c.c. of filtrate (= 0,15 gr.) and proceed by the Lorenz method (cf. C. II).

Remark. Substances containing carbonates (e.g. rock phosphate) should be first moistened with water, then treated with 20 c.c. of nitric acid. When the effervescence has died down, add 40 c.c. of sulphuric acid. Proceed as above.

In presence of bones, fish-bones, etc., allow the flask to stand for some time, or heat until completely dissolved.

2. Water-soluble phosphoric acid.

a) In superphosphate and mixtures containing it.

Place 10 gr. of material in a 500 c.c. Stohmann flask, add about 200 c.c. of water and shake briskly to prevent the material from sticking to the sides of the flask and caking. Fill to the mark with water and shake in the mechanical shaker for 30 minutes at room temperature. Filter through a dry pleated filter and precipitate P₂O₅ in 50 c.c. of the filtrate (= 1 gr. of material) by the citrate method (cf. C. II).

b) In double superphosphates

Extract as follows: shake 20 gr. with about 800 c.c. of water in a 1-litre flask for 30 minutes in the mechanical shaker; fill to the mark and filter. Boil 25 c.c. of filtrate with 10 c.c. of nitric acid (d = 1,40) for 10 minutes to convert any pyrophosphoric acid that may be present into orthophosphoric acid. After adding ammonium citrate solution, add a quantity of liquid ammonia corresponding to the amount of nitric acid added; cool and proceed as for ordinary superphosphates.

c) In NPK ternary fertilizers (e.g. nitrophoska).

Place 10 gr. of the sample in a 500 c.c. graduated Stohmann flask and add 400 c.c. of water. Shake the flask for 30 minutes in the mechanical shaker at 30 to 40 r.p.m. Fill to the mark, shake again thoroughly and filter. Pour 250 c.c. of this solution into a 500 c.c. graduated flask and fill to the mark. Draw off 10 c.c. of this solution (0,10 gr. of material) with a pipette and add 40 c.c. of nitric acid containing sulphuric acid. Treat the 50 c.c. of liquid by the Lorenz method.

3. Phosphoric acid soluble in ammonium citrate.

Petermann method.

Reagents: 1. Crystallized citric acid, fresh (not decomposed) (free from lead). 2. Ammonia, d = 0,910.

Preparation of the ammonium citrate solution: Dissolve 173 gr. of citric acid per litre of the solution to be prepared, and slowly add liquid ammonia of a concentration determined by titration or distillation, to yield when cool 420 gr. of ammoniacal nitrogen per litre of solution prepared. Cool to 15° C and make up the volume with water at 15° C. The specific gravity of the solution must be between 1,082 and 1,083. Avoid any loss of ammonia. Pour the citric acid slowly into the cooled ammonia solution through a narrow funnel, hermetically sealing the neck of the flask containing the liquid ammonia. The air escaping from the flask must pass through the citric acid solution in the narrow funnel, where it leaves its ammonia.

To control the final solution, determine the nitrogen content as well as the specific gravity. Dilute 25 c.c. to 250 c.c. and take 25 c.c., corresponding to 2,5 c.c. of the original solution. The nitrogen content should be 0,1050 gr.

a) Treatment of oven-dried phosphates (phospal) with an ammonium citrate solution.

Place 2,5 gr. of oven-dried phosphate, unground, of less than 1 mm. fineness, in a dry 250 c.c. Stohmann flask with enough room above the mark to shake the liquid thoroughly. Pour the ammonium citrate solution on to the sample and shake briskly to prevent sticking. Fill to the mark with the citrate solution and shake in the mechanical shaker for 2 hours at 30—40 r.p.m. The temperature should be kept as near as possible to 20° C. After shaking, filter immediately. Use 10 c.c. of the filtrate (= 0,1 gr. of material) to determine P₂O₅ by the Lorenz method.

b) Treatment of superphosphate, dicalcium phosphate, KP binary and NPK ternary fertilizers with an ammonium citrate solution.

Grind 1,0 gr. of material in a mortar with 100 c.c. of the Petermann ammonium citrate solution and wash in a 250 c.c. flask. Do not use more than 100 c.c. of the citrate solution for crushing and washing. Shake in the mechanical shaker for 3 hours and leave to digest for one hour more in a water-bath at 40° C. After cooling, fill to the mark with water, filter, take 25 c.c. of this solution (0,1 gr. of material) and precipitate P₂O₅ by the Lorenz method.

4. Phosphoric acid soluble in citric acid, P. Wagner method.

Reagents: Fresh crystallized citric acid, not decomposed (free from lead).

Preparation of the 2% citric acid solution: A 2% citric acid solution here means an aqueous solution, containing 2 parts of citric acid by weight to 100 parts in volume. First prepare a mother liquor 5 times more highly concentrated, i.e. 10%, by dissolving 1 kg. of citric acid in water and making up the