NOTE ON

“BERICHT ÜBER DIE ARBEITEN DER INTERNATIONALEN KOMMISSION FÜR DIE ANALYSE DER KUNSTDÜNGER UND FUTTERMITTEL DES V. INTERNATIONALEN KON- GRESSES FÜR ANGEWANDTE CHEMIE ZU BERLIN, 1903.”

By T. B. WOOD, M.A.

At the beginning of October, 1904, many agricultural chemists in England received copies of the above publication from the Secretary of the commission, Dr M. Ullmann, of Hamburg, together with a letter asking all who were willing to agree with the recommendations printed in the report to signify their assent to him. Copies of the report were circulated to members of the Chemical Committee of the Agricultural Education Association, and the recommendations were informally discussed at a meeting of the committee on Dec. 8th. It was suggested that a note should be published in order to call the attention of agricultural chemists to the subject, and facilitate further discussion.

The history of the matter is briefly as follows:—At the first International Congress of Applied Chemistry held at Brussels in 1894 the subject was brought forward, and was again discussed at the Paris Congress in 1896. At the Vienna Congress in 1898 a committee was appointed to investigate the methods of analysis used for manures and feeding stuffs in various countries, and to draw up a series of recommendations with a view to securing international uniformity of method. This committee presented an incomplete report at the Paris Congress in 1900, and its powers were prolonged in order that the final report might be presented at the Berlin Congress in 1903.

This was done, and the report and recommendations were presented and unanimously accepted.

The English translation of the recommendations is printed below:—

METHODS FOR THE ANALYSIS OF ARTIFICIAL MANURES
AND FEEDING STUFFS ADOPTED AT THE GENERAL
MEETING AT BERLIN ON JUNE 3, 1903, OF THE FIFTH
INTERNATIONAL CONGRESS OF APPLIED CHEMISTRY.

The following publications are cited as references :

- Die landwirtschaftlichen Versuchsstationen*, Berlin, Paul Parey,
for artificial manures Bd. 38, 41, 43, 51, 52,
for feeding stuffs ... Bd. 36, 37, 38, 45, 49, 51.
- Methoden zur Untersuchung der Kunstdüngemittel*, 3. Aufl., Berlin, 1903,
Weidemannsche Buchhandlung, herausgegeben vom Verein Deutscher
Dünger-Fabrikanten.
- U. S. Dept. of Agric. Div. of Chem.*, Washington, Bull. 46, 65, 81.
- König, *die Untersuchung landw. und gewerbl. wichtiger Stoffe*, Berlin,
1898, Paul Parey.
- Wiley, *Principles and Practice of Agricultural Analysis*, Vol. II.
and III.
- Sidersky, D., *Analyse des engrais*, Paris, 1901, Béranger.
- Petermann, A., *Méthodes suivies dans l'analyse des matières fertilisantes*,
Gembloux, 1901.

INTERNATIONAL REGULATIONS FOR SAMPLING WHOLESALE QUANTITIES
OF RAW MATERIALS AND PRODUCTS OF THE FERTILISER INDUSTRY.

1. Samples not drawn in accordance with these regulations are to be refused by the official analysts, such refusal being recorded on the certificate.

2. Samples are only to be considered as properly taken, if drawn during unloading on railway or quay, in the presence of representatives of both parties, or by a sworn sampler, and in accordance with these regulations.

3. In the case of manufactured products, a sample is to be taken by means of a sampling iron from every tenth bag, or if the material is in bulk, from at least ten different places throughout the parcel.

4. In the case of shiploads of raw materials every 50th bag or bucketful during discharge (corresponding to 2% of the whole) is to be set aside, and from this, after first crushing to at least the size of a hazel-nut, a sample is to be taken for the determination of moisture;

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a further sample for the determination of the constituents of value is to be taken in the same way as in the case of manufactured products, after the sample has been reduced to a fine state by grinding and sifting.

5. The samples—in weight about 300 grams—are to be filled loosely into strong, clean and absolutely dry glass bottles.

6. At least three samples are to be taken. The bottles are to be hermetically closed and sealed by the persons conducting the sampling.

7. The labels are to be signed by the persons taking the sample and are to be attached by means of the wax used in sealing the bottles.

8. The samples are to be kept in a cool, dark, and dry place.

9. Materials of heterogeneous composition must be sufficiently reduced in size and mixed before bottling.

PREPARATION OF SAMPLES.

(a) Dry samples of phosphates or other artificial manures may be simply sifted and then mixed.

(b) In the case of damp materials, where the above procedure is not possible, the preparation must be confined to a careful mixing by hand.

(c) In the case of raw phosphates and animal charcoal, a water determination is to be made, as confirmatory evidence.

(d) In dealing with substances which are apt to lose water during grinding, the moisture is to be determined both before and after the preparation of the sample, the results of the analysis being afterwards calculated back into the original hygroscopic condition of the sample as received.

METHODS OF ANALYSIS.

A. Artificial Fertilisers.

I. DETERMINATION OF MOISTURE.

Ten grams of the substance are used; the drying is conducted at 100° C. to constant weight; substances containing gypsum are dried three hours.

For potash salts the regulations of the Kalisyndicat at Leopoldshall-Stassfurt hold good.

II. DETERMINATION OF INSOLUBLE MATTER.

Ten grams of the substance are used.

A. When the substance is dissolved in mineral acids, the silica is rendered insoluble and the total residue ignited.

B. When the substance is dissolved in water, the residue is dried at 100° C. to constant weight.

III. DETERMINATION OF PHOSPHORIC ACID.

A. *Method of making the Solutions.*

1. In the case of water-soluble P_2O_5 , twenty grams of the substance are to be agitated for 30 minutes with about 800 c.cm. water in a litre bottle and then filled up to 1000 c.cm. The solution of so-called double superphosphates must be boiled with HNO_3 previous to precipitation of the P_2O_5 , whereby any pyrophosphoric acid, which may be present, is converted into orthophosphoric acid.

For every 25 c.cm. of solution of double superphosphate 10 c.cm. concentrated HNO_3 must be taken.

N.B. When the amount of citrate-soluble phosphoric acid in superphosphates is required, the determination must be made according to Petermann's method.

2. For total phosphoric acid 5 grams of the substance are boiled with aqua regia or 20 c.cm. HNO_3 and 50 gms. concentrated H_2SO_4 for 30 minutes and made up to 500 c.cm.

3. P_2O_5 in Basic slag¹.

(a) Citric-soluble P_2O_5 .

Five grams of the substance are placed in a 500 c.cm. flask with 5 c.cm. of alcohol to prevent caking and shaken with 2% citric acid solution for one half-hour at 17°5 C. in a rotary apparatus which makes 30—40 revolutions per minute.

(b) Total P_2O_5 .

Ten grams of the substance are placed in a 500 c.cm. flask, thoroughly mixed with a few c.cm. of water and boiled for 30 minutes with 50 c.cm. concentrated H_2SO_4 , the flask being frequently shaken.

¹ Basic slag, which appears to contain coarse particles, is passed through a 2 mm. sieve; the portion, which remains behind, is slightly crushed. The determination of P_2O_5 is made in the portion which passes through the sieve, the result being calculated so as to include the portion which remains behind.

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B. *Analysis of the Solutions.*

1. Molybdate-method according to Fresenius and P. Wagner.
2. Citrate method.
3. Free acid.

- (a) Total of free acid: The aqueous solution A 1 is titrated with a solution of NaOH, using methyl orange as an indicator, or
- (b) Free phosphoric acid: An alcoholic solution is used for making a gravimetric determination.

IV. DETERMINATION OF FERRIC OXIDE AND ALUMINA.

This determination must be made either according to the method of Eugen Glaser¹ as improved by R. Jones², or, in the case of the determination of alumina, according to Henri Lasne³. The method adopted must be mentioned.

V. DETERMINATION OF NITROGEN.

1. *Nitric Nitrogen.*

Only direct methods must be used.

- (a) Reduction methods according to Böttcher⁴, Ulsch, Devarda and Kjeldahl-Jodlbauer.
- (b) Gasometric methods. Lunge, Schloesing-Grandeau.

2. *Nitrogen present as Ammonia.*

The determination must be made by distillation with magnesia. With ammonia-superphosphates the solution given under III. A. 1 must be used.

3. *Total Nitrogen.*

In presence of nitrates this determination must be made according to Kjeldahl-Jodlbauer.

4. *Organic Nitrogen.*

In the absence of nitrates and ammonia the determination must be made according to Kjeldahl or by combustion with soda lime.

¹ Glaser, *Zeitschr. f. angew. Chemie*, 1889, S. 636, s. a. *Landw. Vers.-Stat.*, Bd. 38, S. 284.

² R. Jones, *Zeitschr. f. angew. Chemie*, 1891, S. 3, s. a. *Fresenius Zeitschr.*, 30, S. 743.

³ Lasne, *Bull. Soc. Chim.*, T. 15, S. 146 u. 237, s. a. *Chem. Ztg.*, Repert. 1896, S. 47 u. 65.

⁴ Early method of Kühn, *Landw. Vers.-Stat.*, Bd. 41, S. 165 u. 379.

VI. DETERMINATION OF POTASH.

This determination must always be made with platinum chloride or with perchloric acid. The method adopted must be specified.

VII. DETERMINATION OF LIME AND MAGNESIA.

In lime used as a fertiliser and in chalky clay this determination can be made either according to the titration method of Tacke or by the usual gravimetric method. The method adopted must be mentioned.

B. Feeding Stuffs.

Preparation of samples.

Samples of all feeding stuffs must be passed through a 1 mm. sieve, if possible.

I. DETERMINATION OF MOISTURE.

Five grams of the substance are dried for three hours at 100° C.
As regards linseed cake see III. 1.

II. DETERMINATION OF PROTEIN¹.1. *Determination of Crude Protein.*

1—5 grams of the substance are taken. The nitrogen determination is made according to Kjeldahl or Gunning-Atterberg and the amount of nitrogen found is multiplied by 6.25. In the case of feeding stuffs which are difficult to dissolve, such as cotton-seed meal, peanut meal, etc. an addition of phosphoric anhydride is recommended.

2. *Determination of Albuminoid Nitrogen.*

The determination is made according to Stutzer or Kellner. The method employed must be specified.

3. *Determination of the Digestible Protein.*

Stutzer's method improved by G. Kühn is to be used. Instead of gastric juice commercial pepsin can be employed, with restrictions according to Wedemeyer.

¹ In feeding stuffs, where the carbohydrates have an accepted nutritive value, the determination of the value of the nutritive constituents from a commercial standpoint is made on the basis of the ratio 3 : 3 : 1 for Protein : Fat : Carbohydrates. (*VII Hauptversammlung des Verbandes landwirtschaftlicher Versuchstationen im Deutschen Reiche*, Kiel, 1895.)

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III. DETERMINATION OF THE FAT.

1. Feeding stuffs must be dried for three hours at 95° and in no case above 100°. In the case of linseed cake and other cake containing drying oils this can be done in an atmosphere of hydrogen or coal gas or only one hour at 100°. The ether used for the extraction must contain neither alcohol nor water. The extraction must be a complete one. The dried extract need not be soluble in ether.

2. Molasses feeds. 25 grams of substance are to be dried for three hours at 80° C. and ground when cool. Five grams of the powder must be washed out in a Gooch crucible with about 100 c.cm. cold water, added drop by drop. The residue to be dried at 95° and extracted by ether.

IV. DETERMINATION OF NITROGEN-FREE EXTRACT.

(a) This is usually obtained by difference after all the other constituents have been determined.

(b) For the determination of sugar the regulations of the International Sugar Commission hold good.

V. DETERMINATION OF CRUDE FIBRE.

According to Weende's method, three grams of substance, from which the fat (if present) has been extracted, are boiled with 200 c.cm. H_2SO_4 of 1.25% and 200 c.cm. of potassium hydrate solution of 1.25%. Each boiling must last $\frac{1}{2}$ hour, water being added to replace the evaporated portion. Each treatment with acid or alkali must be followed by a boiling with water. The residue to be washed with hot alcohol, then with ether, and dried to a constant weight. The ash of the residue must be subtracted.

VI. DETERMINATIONS OF THE ASH.

Five grams of the substance are incinerated and the residue is carefully weighed.

VII. DETERMINATION OF THE SAND OR MINERAL INGREDIENTS.

The examination of all feeding stuffs for sand or mineral admixtures is obligatory. When the preliminary examination shows the presence of more than normal amounts a quantitative determination must be made. The result to be communicated to the remitter of the sample when the preliminary examination is ratified, at all events in all cases where the contents show more than 1%.

The acceptance of these methods for the analysis of artificial manures and feeding stuffs at the general meeting of sections I and VII on Thursday, June 4, 1903, and at the general meeting of the Congress on

Monday, June 8, 1903, constitutes a second reading, the first reading having taken place at Paris in 1900.

As will be seen the labours of the International Commission deputed by the Berlin Congress to deal with the subject of the analysis of artificial manures and feeding stuffs have resulted in a definite agreement being arrived at.

Leaving out the sections on the sampling of wholesale quantities of raw materials, and preparation of samples, the rest of the recommendations may be divided into two, those that aim at establishing uniform conventional methods (for instance A. III. 1, defining water-soluble P_2O_5 , and B. V. defining crude fibre), and those that attempt to dictate which particular one of many absolute methods shall be used (for instance A. V. 1, 2, 3, 4). With regard to the former it is no doubt desirable for many reasons that there should be a wide agreement on purely conventional methods, but the need of uniformity in the latter class is by no means apparent. It would certainly be for the general good if all analysts would agree for instance to determine fibre in the same way, for the result must vary with details of method, but no useful purpose would be served by all analysts using exactly the same method of estimating nitrogen, for the percentage of nitrogen in a substance is a fact which admits of accurate determination in more than one way.

At a meeting of the Agricultural Education Association it was decided to give the recommendations which define conventions (indicated by larger print in the accompanying text) careful consideration, as it is eminently desirable that English chemists should as far as possible fall into line.