Commission Directive 77/535/EEC of 22 June 1977 on the approximation of the laws of the Member States relating to methods of sampling and analysis for fertilizers

Official Journal L 213, 22/08/1977

THE COMMISSION OF THE EUROPEAN COMMUNITIES,
Having regard to the Treaty establishing the European Economic Community,
Having regard to Council Directive 76/116/EEC of 18 December 1975 on the approximation of the laws of the Member States relating to fertilizers (1), and in particular Article 9 (2) thereof,
Whereas that Directive provides for official controls for EEC fertilizers for the purpose of checking compliance with requirements arising under the Community provisions concerning the quality and composition of fertilizers;
Whereas the measures provided for in this Directive are in accordance with the Opinion of the Committee on the Adaptation to Technical Progress of the Directives for the Removal of Technical Barriers to Trade in Fertilizers,
HAS ADOPTED THIS DIRECTIVE:

Article 1
The Member States shall take the necessary measures to ensure that sampling and analyses for official controls of EEC fertilizers pursuant to Article 8 (1) and (2) of Council Directive 76/116/EEC of 18 December 1975 are carried out in accordance with the methods described in the Annex to this Directive.

Article 2
1. The Member States shall, not later than 19 December 1977, bring into force the laws, regulations or administrative provisions necessary to comply with this Directive. They shall forthwith notify the Commission thereof.
2. The Member States shall ensure that the texts of the provisions of national law which they adopt in the field covered by this Directive are communicated to the Commission.

Article 3
This Directive is addressed to the Member States.

Done at Brussels, 22 June 1977.
For the Commission
Étienne DAVIGNON
Member of the Commission (1)OJ No L 24, 30.1.1976, p. 21.

ANNEX I METHOD OF SAMPLING FOR THE CONTROL OF FERTILIZERS
INTRODUCTION
Correct sampling is a difficult operation which requires the greatest of care. The need to obtain a sufficiently representative sample for the official testing of fertilizers cannot, therefore, be stressed too much.
The sampling method described below must be applied with strict accuracy by specialists with experience of the conventional sampling procedure. 1. PURPOSE AND SCOPE
Samples intended for the official control of fertilizers, for quality and composition, shall be taken according to the methods described below. Samples thus obtained shall be considered as representative of the sampled portions.
2. SAMPLING OFFICERS
The samples shall be taken by specialist officers authorized for that purpose by the Member States.
3. DEFINITIONS
Sampled portion : A quantity of product constituting a unit, and having characteristics presumed to be uniform.
Incremental sample : A quantity taken from one point in the sampled portion.
Aggregate sample : An aggregate of incremental samples taken from the same sampled portion.
Reduced sample : A representative part of the aggregate sample, obtained from the latter by a process of

reduction.
Final sample : A representative part of the reduced sample.
4. APPARATUS 4.1. The sampling apparatus must be made of materials which cannot affect the characteristics of the products to be sampled. Such apparatus may be officially approved by the Member States.
4.2. Apparatus recommended for the sampling of solid fertilizers 4.2.1. Manual sampling 4.2.1.1. Flat-bottomed shovel with vertical sides.
4.2.1.2. Sampling spear with a long split or compartments. The dimensions of the sampling spear must be appropriate to the characteristics of the sampled portion (depth of container, dimensions of sack, etc.) and to the particle size of the fertilizer.
4.2.2. Mechanical sampling
Approved mechanical apparatus may be used for the sampling of moving fertilizers.
4.2.3. Divider
Apparatus designed to divide the sample into equal parts may be used for taking incremental samples and for the preparation of reduced and final samples.
5. QUANTITATIVE REQUIREMENTS 5.1. Sampled portion
The size of the sampled portion must be such that each of its constituent parts can be sampled.
6. INSTRUCTIONS FOR TAKING, PREPARING AND PACKAGING THE SAMPLES 6.1. General
The samples must be taken and prepared as quickly as possible bearing in mind the precautions necessary to ensure that they remain representative of the fertilizer sampled. Instruments and also surfaces and containers intended to receive samples must be clean and dry.
6.2. Incremental samples
Incremental samples must be taken at random throughout the whole sampled portion and they must be of approximately equal sizes. 6.2.1. Loose fertilizers
An imaginary division shall be made of the sampled portion into a number of approximately equal parts. A number of parts corresponding to the number of incremental samples required in accordance with 5.2 shall be selected at random and at least one sample taken from each of these parts. Where it is not possible to comply with the requirements of 5.1 when sampling bulk fertilizers the sampling should be carried out when the sampled portion is being moved (loading or unloading). In this case samples shall be taken from the randomly selected notional parts as defined above while these are being moved.
6.2.2. Packaged fertilizers
Having selected the required number of packages for sampling as indicated in 5.2, part of the contents of each package shall be removed. Where necessary, the samples shall be taken after emptying the packages separately.

6.3. Preparation of aggregate sample
The incremental samples shall be mixed to form a single aggregate sample.
6.4. Preparation of the final sample
The material in the aggregate sample shall be carefully mixed (1).
If necessary the aggregate sample should first be reduced to at least 2 kg (reduced sample) either by using a mechanical divider or by the quartering method.
At least three final samples shall then be prepared, of approximately the same amount and conforming to the quantitative requirements of 5.4. Each sample shall be put into an appropriate air tight container. All necessary precautions shall be taken to avoid any change in the characteristics of the sample.

7. PACKAGING OF FINAL SAMPLES
The containers or packages shall be sealed and labelled (the total label must be incorporated in the seal) in such a manner that they cannot be opened without damaging the seal.
8. SAMPLING RECORD
A record must be kept of each sampling, permitting each sampled portion to be identified unambiguously.
9. DESTINATION OF SAMPLES
For each sample portion at least one final sample shall be sent as quickly as possible to an authorized analytical laboratory, together with the information necessary for the analyst. (1)Any lumps shall be broken up (if necessary by separating them out and returning them to the sample).

ANNEX II

GENERAL OBSERVATIONS

Laboratory equipment

In the descriptions of the methods, general laboratory equipment has not been precisely defined, except that the sizes of flasks and pipettes are given. In all cases laboratory apparatus must be well cleaned, particularly when small quantities of elements are to be determined.

Control tests

Before analysis it is necessary to ensure that all apparatus functions well and that the analytical technique is carried out correctly, using where appropriate chemical compounds of known composition (e.g. ammonium sulphate, mono potassium phosphate, etc.). Nevertheless the results from analyzed fertilizers can indicate wrong chemical composition if the analytical technique is not rigorously followed. On the other hand a certain number of determinations are empirical and are relative to products of complex chemical composition. It is recommended that where available, laboratories should make use of standard reference fertilisers of well defined composition.

Method 1 PREPARATION OF THE SAMPLE FOR ANALYSIS

1. SCOPE

This document defines the procedure for the preparation of the sample for analysis, taken from the final sample.

2. PRINCIPLE

The preparation of a final sample received at the laboratory is a series of operations, usually sieving, grinding and mixing, carried out in such a way that: - on the one hand, the smallest amount weighed out laid down by the methods of analysis is representative of the laboratory sample,

- on the other hand, the fineness of the fertilizer cannot have been changed by the preparation to the extent that its solubility in the various extraction reagents is appreciably affected.

3. APPARATUS

Sample divider (optional).

Sieves with apertus of 0 72 and 0 75 mm.

250-ml flasks, stoppered.

Porcelain pestle and mortar or grinder.

4. CHOICE OF TREATMENT TO BE USED

Preliminary remark

If the product is suitable, only a representative part of the final sample need be kept. 4.1. Final samples which must not be ground

Calcium nitrate, calcium magnesium nitrate, sodium nitrate, Chile nitrate, calcium cyanamide, nitrogenous calcium cyanamide, ammonium sulphate, ammonium nitrates of over 30 % N, urea, basic slag, natural phosphate rendered partially soluble, precipitated dihydrated dicalcium phosphate, calcined phosphate, aluminium calcium phosphate, soft ground rock phosphate.

4.2. Final samples which must be divided and part of which must be ground

These are products in respect of which certain determinations are carried out without previous grinding (fineness of grinding for example) and other determinations after grinding. They include all compound fertilizers containing the following phosphate ingredients : basic slag, aluminium calcium phosphate, calcined phosphate, soft ground rock phosphate and natural phosphate rendered partially soluble. To that end, divide the final sample into two parts, which are as identical as possible, using a sample divider or by quartering.

4.3. Final samples in respect of which all determinations are carried out on a ground product

Only a representative part of the final sample need be ground. These are all the other fertilizers on the list which are not to be found under 4.1 and 4.2.

5. METHOD

The part of the final sample referred to under 4.2 and 4.3 is sieved rapidly through a sieve with apertures of 0 75 mm. The residue is ground roughly so as to obtain a product in which there is a minimum of fine particles, and it is then sieved. The grinding must be done in conditions such that the substance is not appreciably heated. The operation is repeated as many times as is necessary until there is no residue, and it

must be effected as quickly as possible in order to prevent any gain or loss of constituents (water, ammonia).
The whole ground and sieved product is placed in a clean flask which can be stoppered.
Before any weighing is carried out for the analysis, the whole sample must be thoroughly mixed.
6. SPECIAL CASES (a) Fertilizers comprising a blend of several categories of crystals
In this case, separation frequently occurs. It is therefore absolutely essential to crush and pass the sample through a sieve with apertures of 0 7200 mm. For example : mixtures of ammonium phosphate and potassium nitrate. The grinding of the whole of the final sample is recommended in the case of these products.
(b) Residue which is difficult to grind and does not contain fertilizing substances
Weigh the residue and take account of its mass when calculating the final result.
(c) Products which decompose on heating
Grinding must be carried out in such a way as to avoid any heating. It is preferable in this case to use a mortar for grinding. For example : compound fertilizers containing calcium cyanamide and urea.
(d) Products which are abnormally moist or made into a paste by grinding
To ensure homogeneity, a sieve is to be chosen which has the smallest apertures compatible with the destruction of lumps by hand or with the pestle. This may be the case of mixtures, certain ingredients of which contain water of crystallization.

Methods 2 NITROGEN
Method 2.1 DETERMINATION OF AMMONIACAL NITROGEN
1. SCOPE
This document defines the procedure for the determination of the ammoniacal nitrogen.
2. FIELD OF APPLICATION
All nitrogenous fertilizers, including compound fertilizers, in which nitrogen is found exclusively either in the form of ammonium salts, or ammonium salts together with nitrates.
It is not applicable to fertilizers containing urea, cyanamide or other organic nitrogenous compounds.
3. PRINCIPLE
Displacement of ammonia by means of an excess of sodium hydroxide ; distillation ; determining the yield of ammonia in a given volume of a standard sulphuric acid and titration of the excess acid by means of a standard solution of sodium or potassium hydroxide.
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Diluted hydrochloric acid : one volume of HCl (d = 1 718) plus one volume of water.
4.8. Sodium hydroxide solution, approximately 30 % NaOH (d = 1 733), ammonia free.
4.9. Indicator solutions. 4.9.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of sodium hydroxide solution 0 71 N and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops) of this indicator solution.
4.9.2. Methyl red indicator solution.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol. Make up to 100 ml with water and filter if necessary. This indicator may be used (four to five drops) instead of the preceding one.

4.10. Anti-bump granules of pumice stone, washed in hydrochloric acid and calcined.
4.11. Ammonium sulphate for analysis.

5. APPARATUS 5.1. Distillation apparatus consisting of a round-bottomed flask of suitable capacity connected to a condenser by means of a splash head.
Note 1
The different types of equipment approved and recommended for this determination are reproduced, showing all the features of construction, in Figures 1, 2, 3 and 4.

5.2. Pipettes of 10, 20, 25, 50, 100 and 200 ml.
5.3. A 500-ml graduated flask.
5.4. Rotary shaker (35 to 40 turns per minute).

6. PREPARATION OF THE SAMPLE
See Method 1.
7. METHOD OF ANALYSIS 7.1. Preparation of the solution
Carry out a solubility test on the sample in water at room temperature and in the proportion of 2 % (W/V). Weigh to 0 7001 g, according to the indications in Table 1, a quantity of 5 or 7 or 10 g of the prepared sample and place it in a 500-ml graduated flask. According to the result of the solubility test, proceed as follows: (a) Products completely soluble in water
Add to the flask the quantity of water needed to dissolve the sample ; shake, and when completely dissolved, make up the volume and mix thoroughly.
(b) Products not completely soluble in water
Add to the flask 50 ml of water and then 20 ml of hydrochloric acid (4.1). Shake. Leave undisturbed until the evolution of carbon dioxide has ceased. Add 400 ml of water and shake for half an hour with the rotary shaker (5.4). Make up the volume with water, mix and filter through a dry filter into a dry receptacle.

7.2. Analysis of the solution
According to the variant chosen, place in the receiving flask a measured quantity of standard sulphuric acid as indicated in Table 1. Add the appropriate quantity of the chosen indicator solution (4.9.1 or 4.9.2) and, if necessary, water in order to obtain a volume of at least 50 ml. The end of the extension tube of the condenser must be below the surface of the solution.
Transfer by precision pipette, according to the details given in the table, an aliquot portion (1) of the clear solution, into the distilling flask of the apparatus. Add water in order to obtain a total volume of about 350 ml, and several grains of pumice in order to control the boiling.
Assemble the distillation apparatus, and taking care to avoid any loss of ammonia, add to the contents of the distillation flask 10 ml of concentrated sodium hydroxide solution (4.8) or 20 ml of the reagent in the cases where one has used 20 ml hydrochloric acid (4.1) in order to dissolve the test sample. Gradually warm the flask, to avoid boiling vigorously. When boiling commences, distil at the rate of about 100 ml in 10 to 15 minutes ; the total volume of distillate should be about 250 ml (2). When no more ammonia is likely to be evolved, lower the receiving flask so that the tip of the condenser extension is above the surface of the liquid. Test the subsequent distillate by means of an appropriate reagent to ensure that all the ammonia is completely distilled. Wash the condenser extension with a little water and tirate the surplus acid with the standard solution of sodium or potassium hydroxide prescribed for the variant adopted (see Note 2).
Note 2
Standard solutions of different strengths may be used for the back titration provided that the volumes used for the titration do not, as far as possible, exceed 40 to 45 ml.
7.3. Blank
Make a blank test under the same conditions and refer to this in the calculation of the final result.
7.4. Control test
Before carrying out analyses, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a freshly prepared solution of ammonium sulphate (4.11) containing the maximum quantity of nitrogen prescribed for the chosen variant.

8. EXPRESSION OF THE RESULT
Express the result of the analysis as the percentage of ammoniacal nitrogen in the fertilizer as received for analysis.
9. ANNEXES
As specified in Note 1 in 5.1 "Apparatus", Figures 1, 2, 3 and 4 refer to construction features of the different types of equipment used in this document. (1)The quantity of ammoniacal nitrogen contained in the aliquot part taken according to Table 1 will be approximately: - 0 705 g for variant a,
- 0 710 g for variant b,
- 0 720 g for variant c.

(2)The condenser must be regulated so that a continuous flow of condensate is ensured. The distillation should be completed in 30 to 40 minutes.

Table 1
Key to Figures 1, 2, 3 and 4
Figure 1 (a) A round-bottomed, long-necked flask of 1 000 ml capacity.
(b) Distillation tube with a splash head, connected to the condenser by means of a spherical joint (No 18) (the spherical joint for the connection to the condenser may be replaced by an appropriate rubber connection).
(c) Funnel with a teflon tap for the addition of sodium hydroxide (the tap may likewise be replaced by a rubber connection with a clip).
(d) A six-bulb condenser with spherical joint (No 18) at the entrance, and joined at the issue to a glass extension tube by means of a small rubber connection (when the connection to the distillation tube is effected by means of a rubber tube, the spherical joint may be replaced by a suitable rubber bung).
(e) A 500-ml flask in which the distillate is collected.

The equipment is made of borosilicate glass.
Figure 2 (a) A round-bottomed, short-necked flask of 1 000 ml capacity with a spherical joint (No 35).
(b) Distillation tube with a splash head, equipped with a spherical joint (No 35) at the entrance and a spherical joint (No 18) at the issue, connected at the side to a funnel with a teflon tap for the addition of sodium hydroxide.
(c) A six-bulb condenser with a spherical joint (No 18) at the entrance and joined at the issue to a glass extension tube by means of a small rubber connection.
(d) A 500-ml flask in which the distillate is collected.

The equipment is made of borosilicate glass.
Figure 3 (a) A round-bottomed, long-necked flask of 750 or 1 000 ml capacity with a bell mouth.
(b) Distillation tube with a splash head and a spherical joint (No 18) at the issue.
(c) An elbow tube with a spherical joint (No 18) at the entrance, and a drip cone (the connection to the distillation tube may be effected by means of a rubber tube instead of a spherical joint).
(d) A six-bulb condenser joined at the issue to a glass extension tube by means of a small rubber connection.
(e) A 500-ml flask in which the distillate is collected.

The equipment is made of borosilicate glass.
Figure 4 (a) A round-bottomed, long-necked flask of 1 000 ml capacity with a bell mouth.
(b) Distillation tube with a splash head and a spherical joint (No 18) at the issue, connected at the side to a funnel with a teflon tap for the addition of sodium hydroxide (a suitable rubber bung may be used instead of the spherical joint ; the tap may be replaced by a rubber connection with an appropriate clip).
(c) A six-bulb condenser with a spherical joint (No 18) at the entrance, joined at the issue, by a rubber connection, to a glass extension tube (when the connection to the distillation tube is effected by means of a rubber tube, the spherical joint may be replaced by a suitable rubber bung).
(d) A 500-ml flask for the collection of the distillate.

The equipment is made of borosilicate glass.
Methods 2.2 DETERMINATION OF NITRIC AND AMMONIACAL NITROGEN
Method 2.2.1 DETERMINATION OF NITRIC AND AMMONIACAL NITROGEN ACCORDING TO ULSCH
1. SCOPE
This document defines the procedure for the determination of nitrate and ammoniacal nitrogen with reduction according to Ulsch.
2. FIELD OF APPLICATION
All nitrogenous fertilizers, including compound fertilizers, in which nitrogen is found exclusively in nitrate

form, or in ammoniacal and nitrate form.
3. PRINCIPLE
Reduction of nitrates and nitrites to ammonia by means of metallic iron in an acid medium, and displacement of the ammonia thus formed by the addition of an excess of sodium hydroxide : distillation of the ammonia, and determination of the yield of ammonia in a known volume of standard sulphuric acid solution. Titration of the excess sulphuric acid by means of a standard solution of sodium or potassium hydroxide.
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Dilute hydrochloric acid : one volume of HCl (d = 1 718) plus one volume of water.
4.2. Sulphuric acid : 0 71 N.
4.3. Sodium or potassium hydroxide solution, carbonate free : 0 71 N.
4.4. Sulphuric acid solution, approximately 30 % H_2SO_4 (W/V), ammonia free.
4.5. Powdered iron reduced in hydrogen (the prescribed quantity of iron must be able to reduce at least 0 705 g of nitrate nitrogen).
4.6. Sodium hydroxide solution, approximately 30 % NaOH (d = 1 733), ammonia free.
4.7. Indicator solutions. 4.7.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops).
4.7.2. Methyl red indicator solution.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol. Make up to 100 ml with water and filter if necessary.
This indicator may be used (four to five drops) instead of the preceding one.

4.8. Anti-bump granules of pumice stone, washed in hydrochloric acid and calcined.
4.9. Sodium nitrate for analysis.

5. APPARATUS
See Method 2.1 "Determination of ammoniacal nitrogen".
6. PREPARATION OF THE SAMPLE
See Method 1 "Preparation of the sample".
7. Method of analysis. 7.1. Preparation of the solution
See Method 2.1 "Determination of ammoniacal nitrogen".
7.2. Procedure
Place in the receiving flask an exactly measured quantity of standard sulphuric acid as indicated in Table 1 of Method 2.1 (variant a) and add the appropriate quantity of indicator solution 4.7.1 or 4.7.2. The end of the extension tube of the condenser must be below the surface of the standard acid in the receiving flask.
Using a precision pipette, transfer an aliquot part of the clear solution as indicated in Table 1 of Method 2.1 (variant a) and place it in the distilling flask of the apparatus. Add 350 ml of water, 20 ml of 30 % sulphuric acid solution (4.4) stir, and add 5 g of reduced iron (4.5). Wash the neck of the flask with several millilitres of water, and place in the neck of the flask a small, long-stemmed funnel. Heat in a boiling water bath for an hour and then wash the stem of the funnel with a few millilitres of water.
Taking care to avoid any loss of ammonia, add to the contents of the distilling flask 50 ml of concentrated sodium hydroxide solution (4.6), or in the cases where 20 ml of hydrochloric acid (1 + 1) (4.1) has been used to dissolve the sample, add 60 ml of concentrated sodium hydroxide solution (4.6). Assemble the distillation apparatus. Distil the ammonia according to the procedure given in Method 2.1.
7.3. Blank test
Carry out a blank test (omitting the sample) under the same conditions and refer to this in the calculation of the final result.
7.4. Control test
Before analysis, check that the apparatus is working properly and that the correct application of the method is used by using an aliquot part of a freshly prepared solution of sodium nitrate (4.9) containing 0 7045 to 0

7050 g of nitrogen.

8. EXPRESSION OF THE RESULT
Express the result of analysis as a percentage of nitrate nitrogen or combined ammoniacal and nitrate nitrogen contained in the fertilizer as received for analysis.

Method 2.2.2
DETERMINATION OF NITRIC AND AMMONIACAL NITROGEN ACCORDING TO ARND
1. SCOPE
This document defines the procedure for the determination of nitric and ammoniacal nitrogen with reduction according to Arnd (modified for each of the variants a, b and c).
2. FIELD OF APPLICATION
See Method 2.2.1.
3. PRINCIPLE
Reduction of nitrates and nitrites to ammonia in a neutral aqueous solution by means of a metallic alloy composed of 60 % Cu and 40 % Mg (Arnd's alloy) in the presence of magnesium chloride.
Distillation of the ammonia, and determination of the yield in a known volume of standard sulphuric acid solution. Titration of the excess acid by means of a standard solution of sodium or potassium hydroxide.
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Dilute hydrochloric acid : one volume of HCl (d = 1 718) plus one volume of water.
4.8. Sodium hydroxide solution : approximately 2 N.
4.9. Arnd's alloy for analysis : powdered so as to pass through a seive with apertures less than 1 mm square.
4.10. 20 % magnesium chloride solution.
Dissolve 200 g of magnesium chloride (MgCl2 76H2O) in approximately 600 to 700 ml of water in a one-litre, flat-bottomed flask. To prevent frothing, add 15 g of magnesium sulphate (MgSO4 77H2O).
After dissolution add 2 g of magnesium oxide and a few anti-bump granules of pumice stone, and concentrate the suspension to 200 ml by boiling, thus expelling any trace of ammonia from the reagents. Cool, make up the volume to one litre and filter.
4.11. Indicator solutions. 4.11.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops).
4.11.2. Methyl red indicator solution.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol. Make up to 100 ml with water and filter if necessary. This indicator may be used (four to five drops) instead of the preceding one.
4.11.3. Congo red indicator solution.
Dissolve 3 g of Congo red in one litre of warm water and filter if necessary after cooling. This indicator may be used, instead of the two described above, in the neutralization of acid extracts before distillation, using 0 75 ml per 100 ml of liquid to be neutralized.

4.12. Anti-bump granules of pumice stone washed in hydrochloric acid and calcined.
4.13. Sodium nitrate for analysis.

5. APPARATUS
See Method 2.1 "Determination of ammoniacal nitrogen".
6. PREPARATION OF THE SAMPLE
See Method 1.
7. METHOD OF ANALYSIS 7.1. Preparation of the solution for analysis.
See Method 2.1 "Determination of ammoniacal nitrogen".
7.2. Analysis of the solution

According to the chosen variant, place in the receiving flask the exactly measured quantity of standard sulphuric acid as indicated in Table 1 of Method 2.1. Add the appropriate quantity of chosen indicator solution (4.11.1 or 4.11.2) and finally, sufficient water to give a volume of at least 50 ml. The end of the extension tube of the condenser must be below the surface of the solution.
Using a precision pipette, take, according to Table 1, an adequate aliquot of the clear solution. Place it in the distillation flask.
Add sufficient water to obtain a total volume of about 350 ml (see Note 1), 10 g of Arnd's alloy (4.9), 50 ml of magnesium chloride solution (4.10) and a few fragments of pumice stone (4.12). Rapidly connect the flask to the distillation apparatus. Heat gently for about 30 minutes. Then increase the heating to distil the ammonia. Continue the distillation for about an hour. After this time, the residue in the flask ought to have a syrupy consistency. When the distillation has finished, titrate the quantity of excess acid in the receiving flask according to the procedure in Method 2.1.
Note 1
When the sample solution is acid (addition of 20 ml of HCl (1 + 1) (4.1) to dissolve the sample) the aliquot part taken for analysis is neutralized in the following way : to the distillation flask containing the taken aliquot part add about 250 ml of water, the necessary quantity of one of the indicators (4.11.1, 4.11.2,4.11.3) and shake carefully.
Neutralize with 2 N sodium hydroxide solution (4.8) and acidify again with a drop of hydrochloric acid (1 + 1) (4.1). Then proceed as indicated in 7.2 (second line).
7.3. Blank test
Carry out a blank test under the same conditions and refer to this in the calculation of the final result.
7.4. Control test
Before analysis, check that the apparatus is working properly and that the correct technique is applied using a freshly prepared solution of sodium nitrate (4.13) containing 0 7050 to 0 7150 g of nitrate nitrogen depending on the variant chosen.

8. EXPRESSION OF THE RESULT
See Method 2.2.1.

Method 2.2.3 DETERMINATION OF NITRIC AND AMMONIACAL NITROGEN ACCORDING TO DEVARDA
1. SCOPE
This document defines the procedure for the determination of nitrate and ammoniacal nitrogen with reduction according to Devarda (modified for each of the variants a, b and c).
2. FIELD OF APPLICATION
See Method 2.2.1.
3. PRINCIPLE
Reduction of nitrates and nitrites to ammonia in a strongly alkaline solution by means of a metallic alloy composed of 45 % Al, 5 % Zn and 50 % Cu (Devarda alloy). Distillation of the ammonia and determination of the yield in a known volume of standard sulphuric acid ; titration of the excess sulphuric acid by means of a standard solution of sodium or potassium hydroxide.
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Dilute hydrochloric acid : one volume of HCl (d = 1 718) plus one volume of water.
4.8. Devarda alloy for analysis.
Powdered so that 90 to 100 % will pass through a sieve with apertures less than 0 725 mm square, 50 to 75 % will pass through a sieve with apertures of less than 0 7075 mm square.
Pre-packed bottles containing a maximum of 100 g are recommended.
4.9. Sodium hydroxide solution, approximately 30 % NaOH (d = 1 733), ammonia free.
4.10. Indicator solutions. 4.10.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops).

4.10.2. Methyl red indicator.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol. Make up to 100 ml with water and filter if necessary.
This indicator (four to five drops) may be used instead of the preceding one.

4.11. Ethanol, 95 to 96 %.
4.12. Sodium nitrate for analysis.

5. APPARATUS
See Method 2.1. 5.1. Distillation apparatus consisting of a round-bottomed flask of suitable capacity, connected to a condenser by a distilling tube with a splash head, equipped, in addition, with a bubble trap on the receiving flask to prevent any loss of ammonia.
The type of apparatus approved for this determination is reproduced, showing all the features of construction, in Figure 5.
5.2. Pipettes of 10, 20, 25, 50, 100 and 200 ml.
5.3. A 500-ml graduated flask.
5.4. Rotary shaker (35 to 40 turns a minute).

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Preparation of the solution for analysis
See Method 2.1 "Determination of ammoniacal nitrogen".
7.2. Analysis of the solution
The quantity of nitric nitrogen present in the aliquot part of the solution must not exceed the maximum quantity expressed in Table 1.
According to the variant chosen, place in the receiving flask an exactly measured quantity of standard sulphuric acid as indicated Table 1. Add the appropriate quantity of the chosen indicator solution (4.10.1 or 4.10.2) and finally, sufficient water to give a volume of 50 ml. The end of the extension tube of the condenser should be underneath the surface of the solution. Fill the bubble trap with distilled water.
Using a precision pipette, take an aliquot part as indicated in Table 1 of Method 2.1. Place it in the distillation flask.
Add sufficient water to the distillation flask to obtain a volume of 250 to 300 ml, 5 ml ethanol (4.11) and 4 g Devarda's alloy (4.8). (See Note 2).
Taking the necessary precautions to avoid loss of ammonia, add to the flask about 30 ml of 30 % sodium hydroxide solution (4.9) and finally, in the case of acid soluble samples an additional quantity sufficient to neutralize the quantity of hydrochloric acid (4.1) present in the aliquot part taken for the analysis. Connect the distillation flask to the apparatus, ensuring the tightness of connections. Carefully shake the flask to mix the contents.
Warm gently, so that the release of hydrogen decreases appreciably over about half an hour and the liquid will boil. Continue the distillation, increasing the heat so that at least 200 ml liquid distils in about 30 minutes (do not prolong the distillation beyond 45 minutes).
When the distillation is complete, disconnect the receiving flask from the apparatus, carefully wash the extension tube and bubble trap, collecting the rinsings in the titration flask. Titrate the excess acid according to the procedure in Method 2.1.
Note 2
In the presence of calcium salts such as calcium nitrate and calcium ammonium nitrate, it is necessary to add before distillation for each gram of sample present in the aliquot, 0 7700 g sodium phosphate (Na2HPO4 72H2O) to prevent the formation of Ca(OH)2.
7.3. Blank test
Carry out a blank test under the same conditions and refer to this in the calculation of the final results.
7.4. Control test
Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot of a freshly prepared solution of sodium nitrate (4.12) containing, according to the variant chosen, 0 750 to 0 7150 g nitrate nitrogen.

8. EXPRESSION OF THE RESULT
See Method 2.2.1.

Key to Figure 5
(a) A 750-ml (1 000 ml) round-bottomed, long-necked flask with a bell mouth.
(b) Distillation tube with a splash head and an No 18 spherical joint at the issue.
(c) Elbow tube with an No 18 spherical joint at the entrance, and a drip cone at the issue (a suitable rubber connection may be used instead of the spherical joint).
(d) A six-bulb condenser with an extension tube mounted on a rubber bung holding a bubble trap.
(e) A 750-ml receiving flask.
(f) A bubble trap to prevent loss of ammonia.

The equipment is made of borosilicate glass.
Methods 2.3 DETERMINATION OF TOTAL NITROGEN
Method 2.3.1 DETERMINATION OF THE TOTAL NITROGEN IN CALCIUM CYANAMIDE NITRATE FREE
1. SCOPE
This document defines the procedure for the determination of total nitrogen in nitrate free, calcium cyanamide.
2. FIELD OF APPLICATION
Exclusively to calcium cyanamide (nitrate free).
3. PRINCIPLE
After Kjeldahl digestion, the ammoniacal nitrogen formed is displaced by sodium hydroxide, collected and estimated in a standard solution of sulphuric acid.
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Dilute sulphuric acid (d = 1 754) : one volume of sulphuric acid (d = 1 784) plus one volume of water.
4.2. Potassium sulphate for analysis.
4.3. Copper oxide (CuO) : 0 73 to 0 74 g for each estimation, or an equivalent quantity of copper sulphate pentahydrate, from 0 795 to 1 725 g for each estimation.
4.4. Sodium hydroxide solution, approximately 30 % NaOH (d = 1 733), ammonia free.
4.11. Indicator solutions. 4.11.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops).
4.11.2. Methyl red indicator.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol and make up to 100 ml with water. Filter if necessary. This indicator (four to five drops) may be used instead of the preceding one.

4.12. Anti-bump granules of pumice stone, washed in hydrochloric acid and calcined.
4.13. Potassium thiocyanate for analysis.

5. APPARATUS 5.1. Distilling apparatus, see Method 2.1 "Determination of ammoniacal nitrogen".
5.2. A long-necked Kjeldahl flask of suitable capacity.
5.3. Pipettes of 50, 100 and 200 ml.
5.4. A 250-ml graduated flask.

6. PREPARATION OF THE SAMPLE
See Method 1.

7. PROCEDURE 7.1. Preparation of the solution
Weigh, to the nearest 0 7001 g, 1 g of the sample and place it in the Kjeldahl flask. Add 50 ml of diluted sulphuric acid (4.1), 10 to 15 g of potassium sulphate (4.2), and the prescribed catalyst (4.3). Heat slowly to drive off the water, boil gently for two hours, allow to cool, and dilute with 100 to 150 ml of water. Cool again, transfer quantitatively the suspension to a graduated 250-ml flask, make up the volume with water, shake, and filter through a dry filter into a dry flask.
7.2. Analysis of the solution
With a pipette, transfer, according to the variant chosen (see Method 2.1), 50, 100 or 200 ml of the solution thus obtained, and distil the ammonia as described in Method 2.1, adding sufficient NaOH solution (4.4) to ensure a considerable excess.
7.3. Blank test
Make a blank test (omitting the sample) under the same conditions and refer to this in the calculation of the final result.
7.4. Control test
Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a standard solution of potassium thiocyanate (4.13), approximating to the concentration of nitrogen in the sample.

8. EXPRESSION OF THE RESULT
Express the result as the percentage of nitrogen (N) contained in the fertilizer as received for analysis.
Variant a : % N = (50 - A) × 0 77.
Variant b : % N = (50 - A) × 0 77.
Variant c : % N = (35 - A) × 0 7875.

Method 2.3.2 DETERMINATION OF TOTAL NITROGEN IN CALCIUM CYANAMIDE CONTAINING NITRATES
1. SCOPE
This document defines the procedure for the determination of total nitrogen in calcium cyanamide.
2. FIELD OF APPLICATION
The method is applicable to calcium cyanamide containing nitrates.
3. PRINCIPLE
The direct application of Kjeldahl's method cannot be applied to calcium cyanamides containing nitrates. For this reason the nitrate nitrogen is reduced to ammonia with metallic iron and stannous chloride before Kjeldahl digestion.
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Sulphuric acid (d = 1 784).
4.2. Powdered iron reduced in hydrogen.
4.3. Potassium sulphate, finely pulverized, for analysis.
4.10. Indicator solutions. 4.10.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Take 0 75 ml (10 drops) of this indicator solution.
4.10.2. Methyl red indicator.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol, make up to 100 ml with water and filter if necessary. This indicator (four to five drops) may be used instead of the preceding one.

4.11. Solution of stannous chloride.
Dissolve 120 g of $SnCl_2\ 72H_2O$ in 400 ml of concentrated hydrochloride acid (d = 1 718) and make up to one litre with water. The solution must be completely clear and prepared immediately before use. It is essential to check the reducing power of the stannous chloride.
Note

Dissolve 0 75 g of SnCl2 72H2O in 2 ml of concentrated hydrochloric acid (d = 1 718) and make up to 50 ml with water. Then add 5 g of Rochelle salt (potassium sodium tartrate) and a sufficient quantity of sodium bicarbonate for analysis for the solution to show an alkaline reaction to a litmus paper test.
Titrate with 0 71 N iodine solution in the presence of a starch solution as an indicator.
1 ml of iodine solution 0 71 N corresponds to 0 701128 g of SnCl2 72H2O.
At least 80 % of the total tin present in the solution thus prepared must be in a bivalent form. For the titration at least 35 ml of 0 71 N iodine solution should be used.
4.12. Solution of sodium hydroxide containing about 30 % NaOH (d = 1 733), ammonia free.
4.13. Standard nitrate-ammoniacal solution.
Weigh out 2 75 g of potassium nitrate for analysis and 10 716 g of ammonium sulphate for analysis and place them in a 250-ml graduated flask. Dissolve in water and make up to 250 ml. 1 ml of this solution contains 0 701 g of nitrogen.
4.14. Pumice-stone anti-bump granules, washed in hydrochloric acid and calcined.

5. APPARATUS
See Method 2.3.1.
6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Preparation of the solution
Weigh, to the nearest 0 7001 g, 1 g of the sample and place in the Kjeldahl flask. Add 0 75 g of powdered iron (4.2) and 50 ml of the stannous chloride solution (4.11), stir and leave standing for half an hour. During the time it is left standing, stir again after 10 and 20 minutes. Then add 10 g of potassium sulphate (4.3) and 30 ml of sulphuric acid (4.1). Boil and carry on the process for an hour after the appearance of white fumes. Leave to cool and dilute with 100 to 150 ml of water. Transfer the suspension quantitatively into a 250-ml graduated flask, cool and make up the volume with water, stir and filter through a dry filter into a dry container. Instead of then siphoning off the suspension in order to apply the variant a, b or c, used in Method 2.1, the ammoniacal nitrogen in this solution may also be distilled directly, after adding sufficient sodium hydroxide to ensure a large surplus (4.12).
7.2. Analysis of the solution
With a pipette, transfer, according to the variant a, b or c, used in Method 2.1, 50, 100 or 200 ml of the solution thus obtained. Distil the ammonia according to the process described in Method 2.1, taking care to add to the distillation flask sufficient sodium hydroxide solution (4.12) to ensure a large excess.
7.3. Blank test
Make a blank test (omitting the sample) under the same conditions and refer to this in the calculation of the final result.
7.4. Control test
Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used with a standard solution containing quantities of ammoniacal and nitrate nitrogen comparable to the quantities of cyanamide and nitrate nitrogen contained in nitrated calcium cyanamide.
For this purpose place 20 ml of the standard solution (4.13) in the Kjeldahl flask.
Carry out the analysis according to the method described in 7.1 and 7.2.

8. EXPRESSION OF THE RESULT
The result of the analysis must be expressed as the percentage of total nitrogen (N) contained in the fertilizer as received for analysis.
Variant a : % N = (50 - A) × 0 77.
Variant b : % N = (50 - A) × 0 77.
Variant c : % N = (35 - A) × 0 7875.

Method 2.3.3 DETERMINATION OF TOTAL NITROGEN IN UREA
1. SCOPE
This document defines the procedure for the determination of total nitrogen in urea.
2. FIELD OF APPLICATION
This method is applied exclusively to urea fertilizers which are nitrate free.
3. PRINCIPLE

Urea is transformed quantitatively into ammonia by boiling in the presence of sulphuric acid. The ammonia thus obtained is distilled from an alkaline medium, the distillate being collected in an excess of standard sulphuric acid. The excess acid is titrated by means of a standard alkaline solution.

4. REAGENTS

Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Sulphuric acid, concentrated (d = 1 784).

4.2. Sodium hydroxide solution, approximately 30 % NaOH (d = 1 733), ammonia free.

4.9. Indicator solutions. 4.9.1. Mixed indicator.

Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.

Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.

Mix one volume of A with two volumes of B.

This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops).

4.9.2. Methyl red indicator solution.

Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol, and make up to 100 ml with water. Filter if necessary. This indicator (four to five drops) may be used instead of the preceding one.

4.10. Anti-bump granules of pumice stone, washed in hydrochloric acid and calcined.

4.11. Urea, for analysis.

5. APPARATUS 5.1. Distillation apparatus, see Method 2.1 "Determination of ammoniacal nitrogen".

5.2. A 500-ml graduated flask.

5.3. Pipettes of 25, 50 and 100 ml.

6. PREPARATION OF THE SAMPLE

See Method 1.

7. PROCEDURE 7.1. Preparation of the solution

Weigh, to the nearest 0 7001 g, 2 75 g of the prepared sample, place it in a 300-ml Kjeldahl flask and moisten with 20 ml water. Stir in 20 ml of concentrated sulphuric acid (4.1) and add a few glass beads to prevent bumping. To prevent splashing, place a long-stemmed glass funnel in the neck of the flask. Heat, slowly at first, then increase the heat until white fumes are observed (30 to 40 minutes).

Cool and dilute with 100 to 150 ml water. Quantitatively transfer to a 500-ml volumetric flask, discarding any sediment. Allow to cool to room temperature. Make up the volume with water, mix and, if necessary, filter through a dry filter into a dry receptacle.

7.2. Analysis of the solution

With a precision pipette, transfer 25, 50 or 100 ml of the solution thus obtained into the distillation flask, according to the variant chosen (see Method 2.1). Distil the ammonia as described in Method 2.1, adding sufficient NaOH (d = 1 733) (4.2) to the distilling flask to ensure a considerable excess.

7.3. Blank test

Carry out a blank test (omitting the sample) under the same conditions and refer to this in the calculation of the final result.

7.4. Control test

Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used, using an aliquot part of a freshly prepared solution of urea (4.11).

8. EXPRESSION OF THE RESULT

Express the result as the percentage of nitrogen (N) contained in the fertilizer as received for analysis.

Variant a : % N = (50 - A) × 1 712.

Variant b : % N = (50 - A) × 1 712.

Variant c : % N = (35 - A) × 1 740.

Method 2.4 DETERMINATION OF CYANAMIDE NITROGEN

1. SCOPE
This document defines the procedure for the determination of cyanamide nitrogen.
2. FIELD OF APPLICATION
Calcium cyanamide and calcium cyanamide/nitrate mixtures.
3. PRINCIPLE
Cyanamide nitrogen is precipitated as a silver complex and estimated in the precipitate by Kjeldahl's method.
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and all nitrogenous compounds. 4.1. Glacial acetic acid.
4.2. Ammonia solution containing 10 % of ammonia gas by weight (d = 0 796).
4.3. Ammoniacal silver solution, according to Tollens.
Mix 500 ml of 10 % silver nitrate ($AgNO_3$) solution in water with 500 ml of 10 % ammonia (4.2).
Do not expose unnecessarily to light, heat or air. The solution normally keeps for years. As long as the solution remains clear, the reagent is of good quality.
4.4. Concentrated sulphuric acid (d = 1 784).
4.5. Potassium sulphate for analysis.
4.6. Copper oxide (CuO), 0 73 to 0 74 g for each estimation, or an equivalent quantity of copper sulphate pentahydrate from 0 795 to 1 725 g for each estimation.
4.7. Sodium hydroxide solution, approximately 30 % NaOH (d = 1 733), ammonia free.
4.8. Sulphuric acid : 0 71 N.
4.9. Sodium or potassium hydroxide solution : 0 71 N.
4.10. Indicator solutions. 4.10.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops).
4.10.2. Methyl red indicator solution.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol and make up to 100 ml with water. Filter if necessary. This indicator (four to five drops) may be used instead of the proceding one.

4.11. Anti-bump granules of pumice stone, washed in hydrochloric acid and calcined.
4.12. Potassium thiocyanate for analysis.

5. APPARATUS 5.1. Distillation apparatus, see Method 2.1 "Determination of ammoniacal nitrogen".
5.2. A 500-ml graduated flask (e.g. Stohmann).
5.3. A long-necked Kjeldahl flask of suitable capacity (300 to 500 ml).
5.4. A 50-ml pipette.
5.5. A rotary shaker (35 to 40 turns per minute).

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Safety precaution
When using any ammoniacal silver solution safety goggles must be worn. As soon as a thin membrance forms on the surface of the liquid, an explosion may be produced by agitation and the greatest caution is essential.
7.2. Preparation of the solution for analysis
Weigh, to the nearest 0 7001 g, 2 75 g of the sample and place it in a small glass mortar. Grind the sample three times with water, pouring off the water after each grinding into a 500-ml graduated Stohmann flask. Transfer quantitatively the sample into the 500-ml graduated Stohmann flask, washing the mortar, pestle and funnel with water. Make up with water to approximately 400 ml. Add 15 ml of acetic acid (4.1). Shake on the rotary shaker (5.5) for two hours.
Make up to 500 ml with water, mix and filter.

The analysis must be carried out as quickly as possible.
7.3. Analysis of the solution
Transfer 50 ml of the filtrate, into a 250-ml beaker.
Add ammonia solution (4.2) until slightly alkaline and add 30 ml of warm ammoniacal silver nitrate (4.3) in order to precipitate the yellow silver complex of the cyanamide.
Leave overnight, filter and wash the precipitate with cold water until it is completely free of ammonia.
Place the filter and the precipitate, still moist, in a Kjeldahl flask, add 10 to 15 g of potassium sulphate (4.5), the catalyst (4.6) in the prescribed proportion, then 50 ml of water and 25 ml of concentrated sulphuric acid (4.4).
Warm the flask slowly, while shaking it gently until the contents come to the boil. Increase the heat, boil until the contents of the flask become colourless or pale green.
Continue boiling for one hour, then leave to cool.
Transfer the liquid quantitatively from the Kjeldahl flask to the distilling flask, add a few anti-bump granules of pumice stone (4.11) and make up with water to a total volume of approximately 350 ml. Mix and cool.
Distil the ammonia according to Method 2.1, variant a, adding sufficient NaOH solution (4.7) to ensure the presence of a considerable excess.
7.4. Blank test
Make a blank test (omitting the sample) under the same conditions and refer to this in the calculation of the final result.
7.5. Control test
Before carrying out the analysis, check that the apparatus is working properly and that the correct application of the method is used using an aliquot part of a standard solution of potassium thiocyanate (4.12) corresponding to 0 705 g of nitrogen.

8. EXPRESSION OF THE RESULT
Express the result as the percentage of cyanamide nitrogen contained in the fertilizer as received for analysis.
% N = (50 - A) × 0 756.

Method 2.5 SPECTROPHOTOMETRIC DETERMINATION OF BIURET IN UREA
1. SCOPE
This document defines the procedure for the determination of biuret in urea.
2. FIELD OF APPLICATION
The method is applied exclusively to urea.
3. PRINCIPLE
In an alkaline medium, in the presence of potassium sodium tartrate, biuret and bivalent copper from a violet cupric compound. The optical density of the solution is measured at a wave length of about 546 nm (nanometer).
4. REAGENTS
Distilled or demineralized water, free from carbon dioxide and ammonia. The quality of this water is particularly important in this determination. 4.1. Methanol.
4.2. Sulphuric acid solution, about 0 71 N.
4.3. Sodium hydroxide solution, about 0 71 N.
4.4. Alkaline solution of potassium sodium tartarate.
In a graduated one-litre flask dissolve 40 g of sodium hydroxide in 500 ml of water and leave to cool. Add 50 g of potassium sodium tartrate (NaKC4H4O6 74H2O). Make up to the mark. Leave standing 24 hours before use.
4.5. Solution of copper sulphate.
In a graduated one-litre flask dissolve 15 g of copper sulphate (CuSO4 75H2O) in 500 ml of water. Make up to the mark.
4.6. Freshly prepared biuret standard solution.
In a 250-ml graduated flask, dissolve 0 7250 g of pure biuret (1) in water. Make up to 250 ml. 1 ml of this solution contains 0 7001 g of biuret.
4.7. Indicator solution.
In a graduated 100-ml flask, dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol, make up to 100 ml with water. Filter if any insolubles remain.

5. APPARATUS 5.1. Spectrophotometer or photometer with filters of a sensitivity and precision to permit measures of less than 0 75 % T to be reproduced (2).
5.2. Graduated flasks of 100, 250 and 1 000 ml.
5.3. Graduated pipettes of 2, 5, 10, 20, 25 and 50 ml or a 25 ml burette, graduated to 0 705 ml.
5.4. A 250-ml beaker.

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Preparation of the standard curve
Transfer 0, 2, 5, 10, 20, 25 and 50 ml of aliquots of biuret standard solution (4.6) into a series of seven graduated 100-ml flasks. Make up the volumes to about (1)Biuret can be purified beforehand by washing with an ammoniacal solution (10 %), then with acetone and drying in a vacuum. (2)See point 9 "Appendix". 50 ml with water, add one drop of indicator (4.7) and neutralize, if necessary, with sulphuric acid 0 71 N (4.2). Stir in 20 ml of the alkaline tartrate solution (4.4) then 20 ml of the copper sulphate solution (4.5).
Note
These solutions must be measured in with two precision burettes or better still with pipettes.
Make up to 100 ml with distilled water, mix and leave standing for 15 minutes at 30 ± 2 ºC.
With the "O" biuret solution as reference, measure the absorbance of each solution at a wavelength of about 546 nm using cells of a suitable thickness.
Plot the calibration curve, using the absorbances as the ordinates and the corresponding quantities of biuret, in milligrams, as the abscissae.
7.2. Preparation of the solution to be analyzed
Weigh, to the nearest 0 7001 g, 10 g of the prepared sample ; dissolve in about 150 ml of water in a 250-ml graduated flask, and make up to the mark. Filter if necessary.
Remark 1
If the sample for analysis contains more than 0 7015 g of ammoniacal nitrogen, dissolve it, in a 250-ml beaker, in 50 ml of methanol (4.1). Reduce by evaporation to a volume of about 25 ml. Transfer quantitatively to a graduated 250-ml flask. Make up to the mark with water. Filter, if necessary, through a dry fluted filter into a dry container.
Remark 2
Elimination of the opalescence : if any colloid substance is present difficulties may arise during filtering. The solution intended for analysis is in that case prepared as follows : dissolve the sample for analysis in 150 ml of water, add 2 ml of 1 N hydrochloric acid, and filter the solution through two flat very fine filters into a graduated 250-ml flask. Wash the filters with water and make up to volume. Continue the process according to the method described in 7.3 "Determination".
7.3. Determination
According to the presumed biuret content, transfer 25 or 50 ml from the solution mentioned in 7.2 with a pipette, place this quantity in a 100-ml graduated flask and neutralize if necessary with a 0 71 N reagent (4.2 or 4.3) as required, using methyl red as an indicator and add, with the same accuracy as that used when drawing up a standardization curve, 20 ml of the alkaline solution of potassium sodium tartrate (4.4) and 20 ml of the copper solution (4.5). Make up to volume, mix thoroughly and leave standing for 15 minutes at 30 ± 2 ºC.
Then carry out the photometric measurements and calculate the quantity of biuret present in the urea.

8. EXPRESSION OF THE RESULT
Where "C" is the weight, in milligrams, of biuret, read from the standardization graph, "V" the volume of the aliquot:
9. APPENDIX
where:
s = thickness of the layer in centimetres.
c = concentration in milligrams per litre.
k = specific factor for each substance in the Lambert-Beer law.

Methods 2.6 DETERMINATION OF DIFFERENT FORMS OF NITROGEN IN THE SAME SAMPLE

Method 2.6.1 DETERMINATION OF DIFFERENT FORMS OF NITROGEN IN THE SAME SAMPLE IN FERTILIZERS CONTAINING NITROGEN AS NITRIC, AMMONIACAL, UREA AND CYANAMIDE NITROGEN

1. SCOPE

This document defines the procedure for the determination of any one form of nitrogen in the presence of any other form.

2. FIELD OF APPLICATION

Any fertilizer provided for in Directive 76/116/EEC containing nitrogen in various forms.

3. PRINCIPLE 3.1. Total soluble and insoluble nitrogen

According to the list of standard fertilizers (Annex I to Directive 76/116/EEC), this determination is applicable to products containing calcium cyanamide. 3.1.1. In the absence of nitrates, the test sample is mineralized by direct Kjeldahl digestion.

3.1.2. In the presence of nitrates, the test sample is mineralized by Kjeldahl digestion after reduction with the aid of metallic iron and stannous chloride.

In both cases, the ammonia is determined according to Method 2.1.

Note

If analysis shows an insoluble nitrogen content of more than 0 75, one concludes that the fertilizer contains other forms of insoluble nitrogen not included in the list in Directive 76/116/EEC.

3.2. Forms of soluble nitrogen

The following are determined from different aliquots taken from the same solution of the sample: 3.2.1. total soluble nitrogen: 3.2.1.1. in the absence of nitrates, by direct Kjeldahl digestion,

3.2.1.2. in the presence of nitrates, by Kjeldahl digestion on an aliquot part taken from the solution after reduction according to Ulsch, the ammonia being determined in both cases, as described in Method 2.1;

3.2.2. total soluble nitrogen with the exception of nitrate nitrogen by Kjeldahl digestion after elimination in an acid medium of nitrate nitrogen with ferrous sulphate, the ammonia being determined as described in Method 2.1;

3.2.3. nitrate nitrogen by difference: 3.2.3.1. in the absence of calcium cyanamide, between 3.2.1.2 and 3.2.2 or between total soluble nitrogen (3.2.1.2) and the sum of ammoniacal nitrogen and ureic organic nitrogen (3.2.4 + 3.2.5),

3.2.3.2. in the presence of calcium cyanamide, between 3.2.1.2 and 3.2.2 or between 3.2.1.2 and the sum of 3.2.4 + 3.2.5 + 3.2.6;

3.2.4. ammoniacal nitrogen: 3.2.4.1. solely in the presence of ammoniacal nitrogen and ammoniacal plus nitrate nitrogen, by applying Method 1,

3.2.4.2. in the presence of urea nitrogen and/or cyanamide nitrogen by cold distillation after making slightly alkaline, the ammonia being absorbed in a standard solution of sulphuric acid and determined as described in Method 2.1;

3.2.5. urea nitrogen: 3.2.5.1. by conversion using urease, into ammonia which is titrated with a standard solution of hydrochloric acid,

or

3.2.5.2. by gravimetry with xanthydrol : the co-precipitated biuret can be counted with urea nitrogen without great error, its content remaining generally low in absolute value in compound fertilizers,

or

3.2.5.3. by difference according to the following table:

3.2.6. cyanamide nitrogen, by precipitation as a silver compound, the nitrogen being estimated in the precipitate by the Kjeldahl method.

4. REAGENTS

Distilled or demineralized water. 4.1. Potassium sulphate for analysis.

4.2. Iron powder, reduced with hydrogen (the prescribed quantity of iron must be able to reduce at least 50 mg of nitrate nitrogen).

4.3. Potassium thiocyanate for analysis.

4.4. Potassium nitrate for analysis.

4.5. Ammonium sulphate for analysis.

4.6. Urea for analysis.

4.7. Dilute sulphuric acid 1 : 1 by volume.

4.8. Standard solution of sulphuric acid : 0 72 N.

4.9. Concentrated sodium hydroxide solution. Aqueous solution at about 30 % (W/V) of NaOH, free from ammonia.

4.10. Standard solution of sodium or potassium hydroxide : 0 72 N, free from carbonates.
4.11. Stannous chloride solution.
Dissolve 120 g of SnCl2 72H2O in 400 ml of concentrated hydrochloric acid (d = 1 718) and make up to one litre with water. The solution must be perfectly clear and prepared immediately before its use.
Note
It is essential to check the reducing power of stannous chloride : dissolve 0 75 g of SnCl2 72H2O in 2 ml of concentrated hydrochloric acid (d = 1 718) and make up to 50 ml with water. Then add 5 g of Rochelle salt (potassium sodium tartrate), then a sufficient quantity of sodium bicarbonate for the solution to be alkaline to litmus paper.
Titrate with a 0 71 N iodine solution in the presence of a starch solution as an indicator.
1 ml of 0 71 N iodine solution corresponds to 0 701128 g of SnCl2 72H2O.
At least 80 % of the total tin present in the solution thus prepared must be in bivalent form. For the titration at least 35 ml of 0 71 N iodine solution must therefore be used.
4.12. Sulphuric acid (d = 1 784).
4.13. Dilute hydrochloric acid : 1 : 1 by volume.
4.14. Acetic acid : 96 to 100 %.
4.15. Sulphuric acid solution containing about 30 % of H2SO4 (W/V).
4.16. Ferrous sulphate : crystalline, Fe SO4 77H2O.
4.17. Standard sulphuric acid solution : 0 71 N.
4.18. Octyl alcohol.
4.19. Saturated solution of potassium carbonate.
4.20. Standard solution of sodium or potassium hydroxide : 0 71 N (free from carbonates).
4.21. Saturated solution of barium hydroxide.
4.22. Sodium carbonate solution : at 10 % (W/V).
4.23. Hydrochloric acid : 2 N.
4.24. Standard solution of hydrochloric acid : 0 71 N.
4.25. Urease solution.
Suspend 0 75 g of active urease in 100 ml of distilled water. Using hydrochloric acid 0 71 N (4 724), adjust the pH to 5 74, measured by a pH meter.
4.26. Xanthydrol.
Solution at 5 % in ethanol or methanol (4.31) (do not use products giving a high proportion of insoluble matter). The solution may be kept for three months in a well-stoppered bottle, away from the light.
4.27. Copper oxide (CuO) : 0 73 to 0 74 g per estimation or an equivalent quantity of copper sulphate pentahydrate of 0 795 to 1 725 g per estimation.
4.28. Anti-bump granules washed in hydrocloric acid and calcined.
4.29. Indicator solutions. 4.29.1. Mixed indicator solution.
Solution A : Dissolve 1 g of methyl red in 37 ml of sodium hydroxide solution 0 71 N and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution and green in alkaline solution. Use 0 75 ml (10 drops) of this indicator solution.
4.29.2. Methyl red indicator solution.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol. Make up to 100 ml with water and filter if necessary. This indicator (four to five drops) can be used instead of the previous one.
4.30. Indicator papers.
Litmus, bromothymol blue (or other papers sensitive to pH 6 to 8).
4.31. Ethanol or methanol : solution 95 %.
5. APPARATUS 5.1. Distillation apparatus.
See Method 2.1.
5.2. Apparatus for the estimation of ammoniacal nitrogen according to analytical technique 7.2.5.3 (see Figure 6).
The apparatus is made up of a specially shaped receptacle with a ground glass neck, with a side neck, a connecting tube with a splash head and a perpendicular tube for the introduction of air. The tubes can be connected to the receptacle by means of a simple perforated rubber bung. It is important to give a suitable shape to the end of the tubes introducing air, since the bubbles of gas must be perfectly distributed throughout the solutions contained in the receptacle and the absorber. The best arrangement consists of small

mushroom-shaped pieces with an external diameter of 20 mm and six openings of 1 mm around the periphery.
5.3. Apparatus for the estimation of urea nitrogen according to the urease technique (7.2.6.1).
It consists of a 300 ml Erlenmeyer flask, with a separating funnel and a small absorber (see Figure 7).
5.4. Rotary shaker (35 to 40 turns per minute).
5.5. A pH meter.
5.6. Adjustable oven.
5.7. Glassware: - pipettes of 2, 5, 10, 20, 25, 50 and 100 ml,
- long-necked Kjeldahl flasks of 300 and 500 ml,
- graduated flasks of 100, 250, 500 and 1 000 ml,
- crucibles of sintered glass, pore diameter, 5 to 15 ¶,
- mortars.
6. PREPARATION OF THE SAMPLE
See Method 1.
7. ANALYTICAL TECHNIQUE 7.1. Total soluble and insoluble nitrogen 7.1.1. In the absence of nitrates
7.1.1.1. Digestion
Weigh out, to an accuracy of 0 7001 g, a quantity of the sample containing 100 mg of nitrogen at the most. Place it in the flask of the distillation apparatus (5.1). Add 10 to 15 g of potassium sulphate (4.1), the catalyst (4.27), and a few anti-bump granules (4.28). Then add 50 ml of dilute sulphuric acid (4.7), and mix thoroughly. First heat gently mixing from time to time, until foam no longer forms. Then heat so that the liquid boils regularly and keep it boiling for one hour after the solution has become clear, preventing any organic matter from sticking to the sides of the flask. Allow to cool. Carefully add about 350 ml of water, with mixing. Ensure that the dissolution is as complete as possible. Allow to cool and connect the flask to the distillation apparatus (5.1).
7.1.1.2. Distillation of ammonia
Transfer with a precision pipette, into the receiver of the apparatus, 50 ml of a standard solution of sulphuric acid 0 72 N (4.8). Add the indicator (4.29.1 or 4.29.2). Ensure that the tip of the condenser is at least 1 cm below the level of the solution.
Taking the necessary precautions to avoid any loss of ammonia, carefully add to the distillation flask enough of the concentrated sodium hydroxide solution (4.9) to make the liquid strongly alkaline (120 ml is generally sufficient ; check by adding a few drops of phenolphthalein. At the end of the distillation the solution in the flask must still be clearly alkaline). Adjust the heating of the flask so as to distil 150 ml in half an hour. Test with indicator paper (4.30) that the distillation has been completed. If it has not, distil a further 50 ml and repeat the test until the supplementary distillate reacts neutrally to the indicator paper (4.30). Then lower the receiver, distil a few millilitres more and rinse the tip of the condenser. Titrate the excess of acid with a standard solution of potassium or sodium hydroxide 0 72 N (4.10) until the indicator changes colour.
7.1.1.3. Blank test
Carry out a blank test in identical conditions and take account of it when calculating the final result.
7.1.1.4. Expression of the result
where:
a = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the blank, carried out by pipetting into the receiver of the apparatus (5.1), 50 ml of standard solution of sulphuric acid 0 72 N (4 78),
A = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the analysis,
M = weight of the test sample, in grams.
7.1.2. In the presence of nitrate 7.1.2.1. Test sample
Weigh out, to an accuracy of 0 7001 g, a quantity of the sample containing not more than 40 mg of nitrate nitrogen.
7.1.2.2. Reduction of the nitrate
Mix the test sample in a small mortar with 50 ml of water. Transfer with the minimum amount of distilled water into a 500-ml Kjeldahl flask. Add 5 g of reduced iron (4.2) and 50 ml of stannous chloride solution (4.11). Shake and leave it to stand for half an hour. During the time it is standing, stir again after 10 and 20 minutes.
7.1.2.3. Kjeldahl digestion
Add 30 ml of sulphuric acid (4.12), 5 g of potassium sulphate (4.1), the prescribed quantity of catalyst (4.27) and some anti-bump granules (4.28). Heat gently with the flask slightly tilted. Increase the heat slowly and shake the solution frequently to keep the mixture suspended : the liquid darkens and then clears with the formation of a yellow-green anhydrous iron sulphate suspension. Then continue heating for one hour after

obtaining a clear solution, maintaining it at simmering point. Leave to cool. Cautiously take the contents of the flask up in a little water and add little by little 100 ml of water. Mix and transfer the contents of the flask into a 500-ml graduated flask. Make up the volume with water. Mix. Filter through a dry filter into a dry receptacle.

7.1.2.4. Analysis of the solution

Transfer by pipette, into the flask of the distillation apparatus (5.1), an aliquot containing 100 mg of nitrogen at the most. Dilute to about 350 ml with distilled water, add a few anti-bump granules (4.28), connect the flask to the distillation apparatus and continue the estimation as described in 7.1.1.2.

7.1.2.5. Blank test

See 7.1.1.3.

7.1.2.6. Expression of the result

where:

a = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the blank, carried out by pipetting into the receiver of the apparatus (5.1), 50 ml of the standard solution of sulphuric acid 0 72 N (4.8),

A = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the analysis,

M = weight of the sample, expressed in grams, present in the aliquot part taken in 7.1.2.4.

7.2. Forms of soluble nitrogen 7.2.1. Preparation of the solution to be analyzed

Weigh out, to an accuracy of 1 mg, 10 g of the sample and place it in a 500-ml graduated flask. 7.2.1.1. In the case of fertilizers not containing cyanamide nitrogen

Add to the flask 50 ml of water and then 20 ml of dilute hydrochloric acid (4.13). Shake and leave it to stand until the evolution of carbon dioxide ceases. Then add 400 ml of water and shake for half an hour on the rotary shaker (5.4). Make up to the volume with water, mix and filter through a dry filter into a dry receptacle.

7.2.1.2. In the case of fertilizers containing cyanamide nitrogen

Add to the flask 400 ml of water and a few drops of methyl red (4.29.2). If necessary make the solution acid by using acetic acid (4.14). Add 15 ml of acetic acid (4.14). Shake on the rotary shaker for two hours (5.4). If necessary, reacidify the solution during the operation, using acetic acid (4.14). Make up to the volume with water, mix, filter immediately through a dry filter into a dry receptacle and immediately estimate the cyanamide nitrogen.

In both cases, estimate the various soluble forms of nitrogen the same day the solution is made up, starting with the cyanamide nitrogen and urea nitrogen if they are present.

7.2.2. Total soluble nitrogen 7.2.2.1. In the absence of nitrate

Pipette into a 300-ml Kjeldahl flask, an aliquot of the filtrate (7.2.1.1 or 7.2.1.2), containing 100 mg of nitrogen at the most. Add 15 ml of concentrated sulphuric acid (4.12), 0 74 g of copper oxide or 1 725 g of copper-sulphate (4.27) and a few anti-bump granules (4.28). First heat gently to begin the digestion and then at a higher temperature until the liquid become colourless or slightly greenish and white fumes are clearly apparent. After cooling, quantitatively transfer the solution into the distillation flask, dilute to about 500 ml with water, and add a few anti-bump granules (4.28). Connect the flask to the distillation apparatus (5.1) and continue the determination as described in 7.1.1.2.

7.2.2.2. In the presence of nitrate

Transfer with a precision pipette into a 500-ml Erlenmeyer, an aliquot of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 40 mg of nitrate nitrogen. At this stage of the analysis the total quantity of nitrogen is not important. Add 10 ml of sulphuric acid at 30 % (4.15), 5 g of reduced iron (4.2), and immediately cover the Erlenmeyer with a watch glass. Heat gently until the reaction is steady but not vigorous. At this juncture stop the heating and allow the flask to stand for at least three hours at ambient temperature. With water, quantitatively transfer the liquid into a 250-ml graduated flask, leaving behind the undissolved iron - make up to the mark with the water. Mix thoroughly, and transfer by precision pipette into a 300-ml Kjeldahl flask, an aliquot containing 100 mg of nitrogen at the most. Add 15 ml of concentrated sulphuric acid (4.12), 0 74 g of copper oxide or 1 725 g of copper sulphate (4.27) and some anti-bump granules (4.28). First heat gently to begin the digestion and then at a higher temperature until the liquid becomes colourless or slightly greenish and white fumes are clearly apparent. After cooling, quantitatively transfer the solution into the distillation flask, dilute to approximately 500 ml with water and add some anti-bump granules (4.28). Connect the flask to the distillation apparatus (5.1) and continue the determination as described in 7.1.1.2.

7.2.2.3. Blank

See 7.1.1.3.

7.2.2.4. Expression of the result

where:
a = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the blank, carried out by placing into the receiver of the apparatus (5.1), 50 ml of standard solution of sulphuric acid 0 72 N (4.8),
A = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the analysis,
M = weight of the sample, expressed in grams, present in the aliquot part taken in 7.2.2.1 or 7.2.2.2.
7.2.3. Total soluble nitrogen with the exception of nitrate nitrogen
Transfer with a precision pipette into a 300-ml Kjeldahl flask, an aliquot sample of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 50 mg of nitrogen to be determined. Dilute to 100 ml with water, add 5 g of ferrous sulphate (4.16), 20 ml of concentrated sulphuric acid (4.1) and some anti-bump granules (4.28). First heat gently and then increase the heat until white fumes appear. Continue the digestion for 15 minutes. Stop the heating, introduce copper oxide (4.27) as a catalyst and keep it at a temperature such that white fumes are emitted for a further 10 to 15 minutes. After cooling, quantitatively transfer the contents of the Kjeldahl flask into the distillation flask of the apparatus (5.1). Dilute to approximately 500 ml with water and add a few anti-bump granules (4.28). Connect the flask to the distillation apparatus and continue the determination as described in 7.1.1.2. 7.2.3.1. Blank
See 7.1.1.3.
7.2.3.2. Expression of the result
where:
a = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the blank, carried out by placing into the receiver of the apparatus (5.1), 50 ml of the standard sulphuric acid solution 0 72 N (4.8),
A = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the analysis,
M = weight of the sample, expressed in grams, present in the aliquot part taken for the estimation.
7.2.4. Nitrate nitrogen 7.2.4.1. In the absence of calcium cyanamide
Is obtained by the difference between the results obtained in 7.2.2.4 and 7.2.3.2 and/or the result obtained in 7.2.2.4 and the sum of the results obtained in (7.2.5.2 or 7.2.5.5) and (7.2.6.3 or 7.2.6.5 or 7.2.6.6).
7.2.4.2. In the presence of calcium cyanamide
Is obtained by the difference between the results obtained in 7.2.2.4 and 7.2.3.2 and between the result obtained in 7.2.2.4 and the sum of the results obtained in (7.2.5.5), (7.2.6.3 or 7.2.6.5 or 7.2.6.6) and (7.2.7).
7.2.5. Ammoniacal nitrogen 7.2.5.1. Solely in the presence of ammoniacal nitrogen and ammoniacal plus nitrate nitrogen
Transfer with a precision pipette into the flask of the distillation apparatus (5.1), an aliquot sample of the filtrate (7.2.1.1) containing 100 mg of ammoniacal nitrogen at the most. Add water to obtain a total volume of about 350 ml and some anti-bump granules (4.28) to facilitate boiling. Connect the flask to the distillation apparatus, add 20 ml of sodium hydroxide solution (4.9) and distil as described in 7.1.1.2.
7.2.5.2. Expression of the result
where:
a = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the blank, carried out by pipetting into the receiver of the apparatus (5.1), 50 ml of standard sulphuric acid solution 0 72 N (4.8),
A = ml of standard solution of sodium or potassium hydroxide 0 72 N, used for the analysis,
M = weight of the sample, expressed in grams, present in the aliquot part taken for the estimation.
7.2.5.3. In the presence of urea and/or cyanamide nitrogen
Transfer with a precision pipette, into the dry flask of the apparatus (5.2), an aliquot sample of the filtrate (7.2.1.1 or 7.2.1.2) containing 20 mg of ammoniacal nitrogen at the most. Then assemble the apparatus. Pipette, into the 300-ml Erlenmeyer, 50 ml of the standard sulphuric acid solution 0 71 N (4.17) and enough distilled water for the level of the liquid to be approximately 5 cm above the opening of the delivery tube. Introduce, through the side neck of the reaction flask, distilled water so as to make up the volume to about 50 ml. Mix. To avoid foaming during aeration, add a few drops of octyl alcohol (4.18). Then make the solution alkaline by using 50 ml of saturated potassium carbonate solution (4.19) and immediately begin to expel the ammonia thus liberated from the cold suspension. The strong current of air necessary to that end (flow of approximately three litres per minute) is purified beforehand by passing it through washing flasks containing dilute sulphuric acid and dilute sodium hydroxide. Instead of using pressurized air, it is also possible to work in a vacuum (water pump) provided that the inflow tube is connected in a sufficiently airtight manner to the receptacle used to recover the ammonia. The elimination of the ammonia is generally complete after three hours. It is nevertheless wise to make sure of that by changing the receiving flask. When the operation is finished, separate the flask from the apparatus, rinse the tip of the tube and the sides of the flask with a little distilled water. Titrate the excess of acid with a standard solution of sodium hydroxide 0 71 N (4.20) until the indicator turns grey (4.29.1).

7.2.5.4. Blank test
See 7.1.1.3.
7.2.5.5. Expression of the result
where:
a = ml of standard solution of sodium or potassium hydroxide 0 71 N, used for the blank, carried out by pipetting into the 300-ml Erlenmeyer of the apparatus (5.2), 50 ml of the standard solution of sulphuric acid 0 71 N (4.17),
A = ml of standard solution of sodium or potassium hydroxide 0 71 N, used for the analysis,
M = weight of the sample, expressed in grams, present in the aliquot part taken for the analysis.
7.2.6. Urea nitrogen 7.2.6.1. Urease method
Transfer with a precision pipette, into a 500-ml graduated flask, an aliquot of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 250 mg of urea nitrogen. To precipitate the phosphates add some saturated barium hydroxide solution (4.21) until no further precipitation occurs. Then eliminate the excess of barium ions (and any dissolved calcium ions) with the aid of the sodium carbonate solution at 10 % (4.22).
Leave it to settle and check whether total precipitation has occurred. Make up to the mark, mix and filter through a pleated filter. Pipette 50 ml of the filtrate into the 300-ml Erlenmeyer of the apparatus (5.3). Acidify the filtrate with hydrochloric acid 2 N (4.23) until a pH of 3 measured by the pH meter is obtained (5.5). Then raise the pH to 5 74 with sodium hydroxide 0 71 N (4.20).
To avoid losses of ammonia during decomposition by the urease, close the Erlenmeyer with a stopper provided with a separating funnel and a small bubble trap containing exactly 2 ml of a standard solution of hydrochloric acid 0 71 N (4.24). Introduce through the separating funnel 20 ml of urease solution (4.25), and leave it to stand for one hour at 20 to 25 ºC. Then pipette 25 ml of the standard solution of hydrochloric acid 0 71 N (4.24) into the separating funnel, allow it to run through into the solution and then rinse with a little water. In the same way quantitatively transfer the contents of the protective receptacle into the solution contained in the Erlenmeyer. Titrate the excess of acid with the standard solution of sodium hydroxide 0 71 N (4.20), until a pH of 5 74 is obtained, measured by the pH meter.
7.2.6.2. Blank test
See 7.1.1.3.
7.2.6.3. Expression of the result
where:
a = ml of standard solution of sodium or potassium hydroxide 0 71 N, used for the blank, carried out exactly in the same conditions as the analysis,
A = ml of standard solution of sodium or potassium hydroxide 0 71 N, used for the analysis,
M = weight of the sample, expressed in grams, present in the aliquot part taken for the analysis.
Remarks 1. After precipitation by the solutions of barium hydroxide and sodium carbonate, make up to the mark, filter and neutralize as rapidly as possible.
2. The titration test may also be carried out with the indicator (4.29.2), but the end point is then more difficult to observe.

7.2.6.4. Gravimetric method with xanthydrol
Transfer with a precision pipette, into a 250-ml beaker, an aliquot of the filtrate (7.2.1.1 or 7.2.1.2) containing not more than 20 mg of urea. Add 40 ml of acetic acid (4.14). Stir with a glass rod for one minute, leave any precipitate to settle for five minutes. Filter on a flat bed into a 100-ml beaker, wash with several millilitres of acetic acid (4.14), then add to the filtrate drop by drop, 10 ml of xanthydrol (4.26), stirring continuously with a glass rod. Leave it to settle until the precipitate appears, at that juncture, stir again for one or two minutes. Leave it to stand for one and a half hours. Filter through a glass filtering crucible, which has been previously dried and weighed, pressing it down slightly ; wash three times with 5 ml of ethanol (4.31) without trying to eliminate all the acetic acid. Place it in the oven and keep it at a temperature of 130 ºC for an hour (do not go above 145 ºC). Leave it to cool in a desiccator and weigh.
7.2.6.5. Expression of the result
where:
m1 = weight of the precipitate obtained, in grams,
M2 = weight of the sample, expressed in grams, present in the aliquot part taken for the estimation.
Correct for a blank. Biuret may, generally speaking, be measured with the urea nitrogen without any great error, since its content remains small in absolute value in compound fertilizers.
7.2.6.6. Method by difference

7.2.7. Cyanamide nitrogen
Take one aliquot part of the filtrate (7.2.1.2), containing 10 to 30 mg of cyanamide nitrogen and place it in a 250-ml beaker. Continue the analysis according to Method 2.4.
8. VERIFICATION OF THE RESULTS 8.1. In certain cases, a difference may be found between the total nitrogen obtained directly from a weighed out sample (7.1) and total soluble nitrogen (7.2.2). Nevertheless, the difference should not be greater than 0 75 %. If this is not the case, the fertilizer contains forms of insoluble nitrogen not contained in the list in Directive 76/116/EEC.
8.2. Before each analysis, check that the apparatus is working properly and that the correct application of the method is used, with a standard solution including the various forms of nitrogen in proportions similar to those of the test sample. This standard solution is prepared from standard solutions of potassium thiocyanate (4.3), potassium nitrate (4.4), ammonium sulphate (4.5) and urea (4.6).

Method 2.6.2
DETERMINATION OF DIFFERENT FORMS OF NITROGEN IN FERTILIZERS CONTAINING NITROGEN ONLY AS NITRIC AMMONIACAL AND UREA NITROGEN
1. OBJECT
The purpose of the present document is to specify a simplified method for the determination of different forms of nitrogen in fertilizers containing nitrogen only as nitric ammoniacal and urea nitrogen.
2. FIELD OF APPLICATION
The present method can be used for all fertilizers mentioned in Directive 76/116/EEC which contain exclusively nitric, ammoniacal or urea nitrogen.
3. PRINCIPLE
The following determinations are made on different portions of a single sample solution: 3.1. total soluble nitrogen: 3.1.1. in the absence of nitrates, by direct Kjeldahl digestion of the solution,
3.1.2. in the presence of nitrates, by Kjeldahl digestion of a portion of the solution after reduction by the Ulsch method ; ammonia is determined in both cases as described in Method 2.1;

3.2. total soluble nitrogen except nitric nitrogen, by Kjeldahl digestion after elimination of nitric nitrogen in acid medium by means of ferrous sulphate ; ammonia is determined as described in Method 2.1;
3.3. nitric nitrogen, by the difference between 3.1.2 and 3.2 or between total soluble nitrogen (3.1.2) and the sum of ammoniacal and urea nitrogen (3.4 + 3.5);
3.4. ammoniacal nitrogen, by cold distillation after slight alkalinization ; the ammonia is obtained in a solution of sulphuric acid and determine as in Method 2.1;
3.5. urea nitrogen, either: 3.5.1. by transformation using urease, into ammonia, which is determined by titration with a standard solution of hydrochloric acid,
3.5.2. by gravimetry using xanhydrol : co-precipitated biuret can be taken with urea nitrogen with little error ; its level is usually of small absolute value in compound fertilizers,
3.5.3. by difference, following the table:
4. REAGENTS
Distilled or demineralized water. 4.1. Potassium sulphate for analysis.
4.2. Iron for analysis, hydrogen reduced (the specified amount of iron must be able to reduce at least 50 mg nitric N).
4.3. Potassium nitrate for analysis.
4.4. Ammonium sulphate for analysis.
4.5. Urea for analysis.
4.6. Sulphuric acid solution : 0 72 N.
4.7. Concentrated sodium hydroxide solution : approximately 30 % (W/V) aqueous solution of NaOH, free of ammonia.
4.8. Sodium or potassium hydroxide solution : 0 72 N, free of carbonates.
4.9. Sulphuric acid density (d20 = 1 784).
4.10. Dilute hydrochloric acid : 1 : 1 by volume.
4.11. Acetic acid : 96 to 100 %.
4.12. Sulphuric acid solution containing approximately 30 % H_2SO_4 (W/V), free of ammonia.
4.13. Ferrous sulphate : crystalline $FeSO_4\ 77H_2O$.
4.14. Titrated sulphuric acid solution : 0 71 N.

4.15. Octyl alcohol.
4.16. Saturated potassium carbonate solution.
4.17. Sodium or potassium hydroxide solution : 0 71 N.
4.18. Saturated barium hydroxide solution.
4.19. Sodium carbonate solution : 10 % (W/V).
4.20. Hydrochloric acid : 2 N.
4.21. Hydrochloric acid solution : 0 71 N.
4.22. Urease solution.
Make a suspension of 0 75 g of active urease in 100 ml of distilled water, using 0 71 N hydrochloric acid (4 721), adjust pH to 5 74, measured with pH meter.
4.23. Xanthydrol.
5 % solution in ethanol or methanol (4.28) (do not use products giving a high proportion of insoluble material) ; the solution can be kept for three months in a carefully stoppered bottle in darkness.
4.24. Catalyst.
Copper oxide (CoO) : 0 73 to 0 74 g per determination, or an equivalent amount of copper sulphate 5H2O of 0 795 to 1 725 g determination.
4.25. Pumice stone granules washed with hydrochloric acid and calcined.
4.26. Indicator solutions. 4.26.1. Mixed indicator.
Solution A : Dissolve 1 g of methyl red in 37 ml of 0 71 N sodium hydroxide solution and make up to one litre with water.
Solution B : Dissolve 1 g of methylene blue in water and make up to one litre.
Mix one volume of A with two volumes of B.
This indicator is violet in acid solution, grey in neutral solution, and green in alkaline solution. Use 0 75 ml (10 drops) of this indicator.
4.26.2. Methyl red indicator solution.
Dissolve 0 71 g of methyl red in 50 ml of 95 % ethanol. Make up to 100 ml with water and filter if necessary. Four to five drops of this indicator can be used instead of the previous one.

4.27. Indicator papers.
Litmus, bromothymol blue (or other papers sensitive to pH 6 to 8).
4.28. Ethanol or methanol : 95 % (W/V).

5. APPARATUS 5.1. Distillation apparatus
See Method 2.1.
5.2. Apparatus for determination of ammoniacal nitrogen (7.5.1).
See Method 2.6.1 and Figure 6.
5.3. Apparatus for determination of urea nitrogen by the urease method (7.6.1).
See Method 2.6.1 and Figure 7.
5.4. Rotary shaker (35 to 40 turns per minute).
5.5. A pH meter.
5.6. Glassware: - precision pipettes of 2, 5, 10, 25, 50 and 100 ml,
- long-necked Kjeldahl flasks of 300 and 500 ml,
- graduated flask of 100, 250, 500 and 1 000 ml,
- crucibles of sintered glass, pore diameter, 5 to 15 ¶m,
- mortar.

6. PREPARATION OF THE SAMPLE
See Method 1.
7. METHODS 7.1. Preparation of solution for analysis
Weigh out, to an accuracy of 1 mg, 10 g of sample, and transfer to a 500-ml graduated flask. Add 50 ml water and then 20 ml dilute hydrochloric acid (4.10). Shake. Allow to rest until any CO2 release comes to an end. Add 400 ml of water ; shake for half an hour ; make up to volume with water, homogenize, filter on a

dry filter into a dry container.
7.2. Total nitrogen 7.2.1. In absence of nitrates
Pipette into a 300-ml Kjeldahl flask a portion of the filtrate (7.1), containing a maximum of 100 mg N. Add 15 ml of concentrated sulphuric acid (4.9), 0 74 g of copper oxide or 1 725 g of copper sulphate (4.24), and a few glass beads to control boiling. Heat moderately at first in order to initiate the reaction, then more strongly until the liquid becomes colourless or slightly greenish and white fumes unmistakably appear. After cooling, transfer the solution into the distillation flask, dilute to approximately 500 ml with water and add a few granules of pumice stone (4.25). Connect the flask to the distillation apparatus (5.1) and carry out the determination as described in 7.1.1.2, Method 2.6.1.
7.2.2. In the presence of nitrates
Pipette into 500-ml-Erlenmeyer a portion of the filtrate (7.1) containing not more than 40 mg of nitric N. At this stage of the analysis, the total quantity of N is unimportant. Add 10 ml of 30 % sulphuric acid (4.12), 5 g of reduced iron (4.2), and immediately cover the Erlenmeyer with a watch glass. Heat gently until the reaction becomes strong but not violent. Stop heating and leave for at least three hours at ambient temperature. Transfer the liquid quantitatively to a 250-ml graduated flask, ignoring undissolved iron. Make up to the mark with water. Homogenize carefully. Pipette a portion containing a maximum of 100 mg N into a 300-ml Kjeldahl flask. Add 15 ml of concentrated sulphuric acid (4.9), 0 74 g of copper oxide or 1 725 g of copper sulphate (4.24), and some glass beads for the control of boiling. Heat moderately at first in order to initiate the reaction, then more strongly until the liquid becomes colourless or slightly greenish and white fumes unmistakably appear. After cooling, transfer the solution quantitatively to the distillation flask, dilute to approximately 500 ml with water, and add a few granules of pumice stone (4.25). Connect the flask to the distillation apparatus (5.1) and continue the determination as described in 7.1.1.2, Method 2.6.1.
7.2.3. Blank test
Carry out a blank test in the same conditions, and use the result in calculating the final result.
7.2.4. Expression of the result
where:
a = ml of titrated 0 72 N sodium or potassium hydroxide solution (4 78), used in the blank test, carried out by placing 50 ml of titrated 0 72 N sulphuric acid solution into the receiver of the apparatus (4.6),
A = ml of titrated 0 72 N sodium or potassium hydroxide solution (4.8), used for the analysis,
M = weight of the test sample, in grams, present in the aliquot (7.2.1 or 7.2.2).

7.3. Total nitrogen excluding nitric N 7.3.1. Analysis
Pipette into a 300-ml Kjehldahl flask an aliquot of filtrate (7.1) containing not more than 50 mg N to be determined. Dilute to 100 ml with water, add 5 g of ferrous sulphate (4.13), 20 ml of concentrated sulphuric acid (4.9), and a few glass beads to control boiling. Heat moderately at first, then more strongly until white fumes appear. Continue the reaction for 15 minutes. Stop heating, introduce 0 74 g of copper oxide or 1 725 g of copper sulphate (4.24) as catalyst. Resume heating and maintain production of white fumes for 10 to 15 minutes. After cooling, transfer the contents of the Kjeldahl flask quantitatively to the distillation flask (5.1). Dilute to approximately 500 ml with water, and add a few granules of pumice stone (4.2). Connect the flask to the distillation apparatus and continue the determination as in 7.1.1.2, Method 2.6.1.
7.3.2. Blank test
See 7.2.3.
7.3.3. Expression of the result
where:
a = ml of titrated 0 72 N sodium or potassium hydroxide solution (4.8), used in the blank test, carried out by pipetting 50 ml of titrated 0 72 N sulphuric acid solution (4.6) into the receiver of the apparatus (4.8),
A = ml of titrated 0 72 N sodium or potassium hydroxide solution (4.8), used for the analysis,
M = weight of the test sample, in grams, present in the aliquot used in the determination.

7.4. Nitric nitrogen
Is obtained the by difference between:
7.2.4 - (7.5.3 + 7.6.3),
or
7.2.4 - (7.5.3 + 7.6.5),
or

7.2.4 - (7.5.3 + 7.6.6).
7.5. Ammoniacal nitrogen 7.5.1. Analysis
Pipette into the dry flask of the apparatus (5.2) a portion of filtrate (7.1) containing a maximum of 20 mg of ammoniacal N. Connect up the apparatus. Pipette into the 300-ml Erlenmeyer exactly 50 ml of titrated 0 71 N sulphuric acid solution (4.14) and an amount of distilled water so that the level of the liquid is approximately 5 cm above the opening of the intake tube. Introduce through the side neck of the reaction flask, distilled water so as to bring the volume to approximately 50 ml. Shake. In order to avoid the formation of froth on the introduction of the gaseous flow, add several drops of octyl alcohol (4.15). Add 50 ml of saturated potassium carbonate solution (4.16), and immediately begin to expel the ammonia thus released from the cold suspension. The intense air flow required for this purpose (flow rate of approximately three litres per minute) is previously purified by passage through washing flasks containing dilute sulphuric acid and dilute sodium hydroxide. Instead of using air under pressure, a vacuum may be used (water suction pump) provided that the connections between the apparatus are air tight.
The elimination of ammonia is generally completed after three hours.
However, it is desirable to make certain of this by changing the Erlenmeyer. When the process is finished, separate the Erlenmeyer from the apparatus, rinse the end of the intake tube and the Erlenmeyer walls with a little distilled water, and titrate the excess acid against a standard 0 71 N sodium hydroxide solution (4.17).
7.5.2. Blank test
See 7.2.3.
7.5.3. Expression the result
where:
a = ml of titrated 0 71 N sodium or potassium hydroxide solution (4.17), used in the blank test, carried out by pipetting into the 300-ml Erlenmeyer of the apparatus (5.2) 50 ml of titrated 0 71 N sulphuric acid solution (4.14),
A = ml of titrated 0 71 N sodium or potassium hydroxide solution, used for the analysis (4.17),
M = sample weight, in grams, present in the aliquot used for the analysis.

7.6. Urea nitrogen 7.6.1. Urease method
Pipette into a 500-ml graduated flask a portion of filtrate (7.1) containing not more than 250 mg of urea nitrogen. To precipitate phosphates, add a suitable quantity of saturated barium hydroxide solution (4.18) until further addition does not cause the production of more precipitate. Eliminate excess barium ions (and any dissolved calcium ions) by means of 10 % sodium carbonate solution (4.19). Allow to settle and check whether precipitation is complete. Make up to the mark, homogenize, and filter through a folded filter. Pipette 50 ml of filtrate into the 300-ml Erlenmeyer of the apparatus (5.3). Acidify with 2 N hydrochloric acid (4.20) to pH 3, measured by means of pH meter. Raise the pH to 5 74 by means of 0 71 N sodium hydroxide (4.17). To avoid ammonia losses when hydrolysis by urease occurs, close the Erlenmeyer by means of a stopper attached to a dropping funnel and a small protective container holding exactly 2 ml of 0 71 N hydrochloric acid solution (4.21). By way of the dropping funnel, introduce 20 ml of urease solution (4.22). Leave for one hour at 20 to 25 ºC. Pipette 25 ml of the standard 0 71 N hydrochloric acid solution (4.2) into the dropping funnel, allow to run into the solution, then rinse with a little water. Also transfer quantitatively the contents of the protective container to the solution held in the Erlenmeyer. Titrate the excess acid using the standard 0 71 N sodium hydroxide solution (4.17), until a pH of 5 74 is obtained, measured on the pH meter.
Remarks 1. After precipitation by the barium hydroxide and sodium carbonate solutions, make up to the mark, filter, and neutralize as quickly as possible.
2. The titration may also be assessed using the indicator (4.26), although the change of colour is more difficult to observe.

7.6.2. Blank test
See 7.2.3.
7.6.3. Expression of result
where:
a = ml of titrated 0 71 N sodium or potassium hydroxide solution (4.17), used in the blank test, carried out in exactly the same conditions as the analysis,
A = ml of 0 71 N sodium or potassium hydroxide solution (4.17), used in the analysis,

M = sample weight, in grams, present in the aliquot used for the analysis.
7.6.4. Gravimetric method with xanthydrol
Pipette into a 100-ml beaker a portion of filtrate (7.1) containing not more than 20 mg of urea. Add 40 ml of acetic acid (4.11). Stir with a glass rod for one minute. Allow any precipitate to settle for five minutes. Filter, wash with a few millilitres of acetic acid (4.11). Add 10 ml of xanthydrol to the filtrate drop by drop (4.23), stirring continually with a glass rod. Leave it to settle until the precipitate appears, and at that juncture stir again for one to two minutes. Leave for one and a half hours. Filter on a glass filtration crucible, previously dried and weigh, using a slight reduction of pressure ; wash three times with 5 ml of ethanol (4.28), without aiming to eliminate all the acetic acid. Transfer to oven and maintain at 130 ºC for one hour (do not exceed 145 ºC). Allow to cool in a desiccator and weigh.
7.6.5. Expression of the result
where:
m = weight of precipitate obtained, in grams,
M = weight of the sample, in grams, present in the aliquot used in the determination.
Make the corrections for the blank. Biuret can generally be taken with urea nitrogen without large error, its level being of small absolute value in compound fertilizers.
7.6.6. Difference method

8. VERIFICATION OF THE RESULT
Before each analysis, check the functioning of the apparatus and the correct application of the methods used with a standard solution containing the different forms of nitrogen in proportions similar to those in the sample. This standard solution is prepared from titrated solutions of potassium nitrate (4.3), ammonium sulphate (4.4) and urea (4.5).

Methods 3 PHOSPHORUS
Methods 3.1 EXTRACTIONS
Method 3.1.1 EXTRACTION OF PHOSPHORUS SOLUBLE IN MINERAL ACIDS
1. SCOPE
This document describes the procedure for the determination of phosphorus soluble in mineral acids.
2. FIELD OF APPLICATION
Applicable exclusively to the phosphate fertilizers listed in Annex I to Directive 76/116/EEC.
3. PRINCIPLE
Extraction of the phosphorus in the fertilizer with a mixture of nitric acid and sulphuric acid.
4. REAGENTS
Distilled or demineralized water. 4.1. Sulphuric acid (d20 = 1 784).
4.2. Nitric acid (d20 = 1 740).

5. EQUIPMENT
Standard laboratory equipment. 5.1. A Kjeldahl flask, with a capacity of at least 500 ml, or a 250-ml round-bottomed flask with a glass tube forming a reflux condenser.
5.2. A 500-ml graduated flask.

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Sample
Weigh, to the nearest 0 7001 g, 2 75 g of the prepared sample and place it in a dry Kjeldahl flask.
7.2. Extraction
Add 15 ml of water and stir so as to suspend the substance. Add 20 ml of nitric acid (4.2) and carefully add 30 ml of sulphuric acid (4.1).
When the initial violent reaction has ceased, slowly bring the contents of the flask to boiling and boil for 30 minutes. Allow to cool and than carefully add with mixing about 150 ml of water. Continue boiling for 15 minutes.
Cool completely and transfer the liquid quantitatively to a 500-ml graduated flask. Make up to volume, mix and filter through a dry pleated filter, free from phosphates, discarding the first portion of the filtrate.
7.3. Determination

The determination of the phosphorus will be carried out by Method 3.2 on an aliquot part of the solution thus obtained.

Method 3.1.2 EXTRACTION OF THE PHOSPHORUS SOLUBLE IN 2 % FORMIC ACID (20 g per litre)
1. SCOPE
This document defines the procedure for the determination of phosphorus soluble in 2 % formic acid (20 g per litre).
2. FIELD OF APPLICATION
Soft natural phosphates exclusively.
3. PRINCIPLE
To differentiate between hard natural phosphates and soft natural phosphates, phosphorus soluble in formic acid is extracted in specific conditions.
4. REAGENT 4.1. Formic acid, 2 % (20 g per litre).
Note
Make 82 ml of formic acid (concentration 98 to 100 % ; d20 = 1 722) up to five litres with distilled water.

5. APPARATUS
Standard laboratory equipment. 5.1. A 500-ml graduated flask (e.g. Stohmann).
5.2. Rotary shaker (35 to 40 turns per minute).

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Sample
Weigh, to the nearest 0 7001 g, 5 g of the prepared sample and place it in a dry 500-ml graduated Stohmann flask (5.1) with a wide neck.
7.2. Extraction
While continuously rotating the flask by hand, add the formic acid at 20 ± 1 ºC (4.1) until it is approximately 1 cm below the graduation mark and make up to the volume. Close the flask with a rubber stopper and shake for 30 minutes at 20 ± 2 ºC on a rotary shaker (5.2).
Filter the solution through a dry pleated filter, free from phosphates, into a dry glass receptacle. Discard the first portion of the filtrate.
7.3. Determination
Determine the phosphorus according to Method 3.2 in an aliquot part of the completely clear filtrate.

Method 3.1.3 EXTRACTION OF PHOSPHORUS SOLUBLE IN 2 % CITRIC ACID (20 g per litre)
1. SCOPE
This document describes the procedure for the determination of phosphorus soluble in 2 % citric acid (20 g per litre).
2. FIELD OF APPLICATION
Only applicable to types of Basic slag (see Annex I A to the Directive).
3. PRINCIPLE
Extraction of phosphorus from the fertilizer with a 2 % citric acid solution (20 g per litre) in given conditions.
4. REAGENT
Distilled or demineralized water. 4.1. 2 % citric acid solution (20 g per litre), prepared from crystalized, citric acid ($C_6H_8O_7$ $7H_2O$).
Note
Verify the concentration of this citric acid solution by titrating 10 ml of the latter with a sodium hydroxide standard solution 0 71 N, using phenolphtalein as an indicator.
If the solution is correct 28 755 ml of the standard solution should be used.

5. APPARATUS 5.1. Rotary shaker (35 to 40 turns per minute).

6. PREPARATION OF THE SAMPLE
The analysis is carried out on the product as received after carefully mixing the original sample to ensure it is homogeneous. See Method 1.
7. PROCEDURE 7.1. Sample
Weigh, to the nearest 0 7001 g, 5 g of the prepared sample and place it in a dry flask with a sufficiently wide neck, with a capacity of 600 ml, allowing the liquid to be shaken thoroughly.
7.2. Extraction
Add 500 ± 1 ml of the citric acid solution at 20 ± 1 ºC. When adding the first millilitres of the reagent shake vigorously by hand to stop the formation of lumps and to prevent the substance sticking to the sides. Close the flask with a rubber stopper and shake it in the rotary shaker (5.1) for exactly 30 minutes at a temperature of 20 ± 2 ºC.
Filter immediately through a dry pleated filter, free of phosphates, into a dry glass receiver and discard the first 20 ml of the filtrate. Continue the filtering until a sufficient quantity of filtrate is obtained to carry out the phosphorus determination.
7.3. Determination
The determination of the phosphorus extract will be carried out according to Method 3.2 on an aliquot part of the solution thus obtained.

Method 3.1.4 EXTRACTION OF PHOSPHORUS WHICH IS SOLUBLE IN NEUTRAL AMMONIUM CITRATE
1. SCOPE
This document defines the procedure for the determination of phosphorus soluble in neutral ammonium citrate.
2. FIELD OF APPLICATION
All fertilizers in respect of which solubility in neutral ammonium citrate is laid down (see Annex I to Directive 76/116/EEC).
3. PRINCIPLE
Extraction of phosphorus at a temperature of 65 ºC using a neutral ammonium citrate solution (pH 7) under specific conditions.
4. REAGENTS
Distilled or demineralized water. 4.1. Neutral ammonium citrate solution (pH 7).
This solution must contain per litre 185 g of crystallized citric acid and must have a specific gravity of 1 709 at 20 ºC and a pH of 7.
The reagent is prepared as follows.
Dissolve 370 g of crystalline citric acid ($C_6H_8O_7$ $7H_2O$) in about 1 75 litres of water and make an approximately neutral solution by adding 345 ml of ammonium hydroxide solution (28 to 29 % of NH_3). If the NH_3 concentration is lower than 28 % add a correspondingly larger quantity of ammonium hydroxide solution and dilute the citric acid in correspondingly smaller quantities of water.
Cool and make exactly neutral by keeping the electrodes of a pH meter immersed in the solution. Add the ammonia, at 28 to 29 % of NH_3, drop by drop, stirring continuously (with a mechanical stirrer) until obtaining exactly a pH of 7 at a temperature of 20 ºC. At this point make up the volume to two litres and test the pH again. Keep the reagent in a closed container and check the pH at regular intervals.

5. APPARATUS 5.1. A two-litre beaker.
5.2. A pH meter.
5.3. A 200 or 250-ml Erlenmeyer flask.
5.4. 500-ml graduated flasks and a 2 000-ml graduated flask.
5.5. Water bath which can be set thermostatically at 65 ºC, equipped with a suitable stirrer (see Figure 8).

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Sample
Transfer 1 or 3 g of the fertilizer to be analyzed (see Annex I A and B to the Directive) into a 200 or 250-ml Erlenmeyer flask containing 100 ml of ammonium citrate solution previously heated to 65 ºC.
7.2. Analysis of the solution
Stopper the Erlenmeyer flask and shake in order to suspend the fertilizer without forming lumps. Remove the stopper for an instant in order to balance the pressure and close the Erlenmeyer flask again. Place the flask in a water bath set to maintain the contents of the flask at exactly 65 ºC and connect it to the stirrer (see Figure 8). During stirring, the level of the suspension in the flask must stay constantly below the level of the water in the water bath (1). Mechanical stirring will be regulated so as to ensure complete suspension.
After stirring for exactly one hour, remove the Erlenmeyer flask from the water bath.
Cool immediately under running water to ambient temperature and, immediately, quantitatively transfer the contents from the Erlenmeyer flask into a graduated 500-ml flask with a jet of water (wash bottle). Make up the volume with water. Mix thoroughly. Filter through a dry pleated filter (medium speed phosphate free) into a dry container, discarding the first part of the filtrate (about 50 ml).
About 100 ml of clear filtrate will then be collected.
7.3. Determination
Determine the phosphorus of the extract thus obtained according to Method 3.2. (1)If no mechanical stirrer is available, the flask may be shaken hand every five minutes.

Methods 3.1.5 EXTRACTION BY ALKALINE AMMONIUM CITRATE
Method 3.1.5.1 Extraction of soluble phosphorus according to Petermann at 65 ºC
1. SCOPE
This document defines the procedure for the determination of soluble phosphorus in alkaline ammonium citrate.
2. FIELD OF APPLICATION
Exclusively to precipitated dihydrated dicalcium phosphate (CaHPO4 72H2O).
3. PRINCIPLE
Extraction of phosphorus at a temperature of 65 ºC with an alkaline solution of ammonium citrate (Petermann) under specified conditions.
4. REAGENTS
Distilled water, or demineralized water having the same characteristics as distilled water. 4.1. Petermann's solution.
4.2. Characteristics
Citric acid (C6H8O7 7H2O) : 173 g per litre.
Ammonia : 42 g per litre of ammoniacal nitrogen.
pH between 9 74 and 9 77.
Preparation from diammonium citrate
Preparation from citric acid and ammonia
Check the ammoniacal nitrogen content as follows
Transfer 25 ml of the solution into a 250-ml standard flask and make up to volume with distilled water. Mix.
Determine the ammoniacal nitrogen content on 25 ml of this solution following Method 2.1. If the solution is correct, one must use 15 ml of 0 75 N H2SO4.
If the strength of ammoniacal nitrogen is greater than 42 g per litre, NH3 can be expelled by a stream of inert gas or by moderate heating to bring back the pH to 9 77. Carry out a second determination.
If the strength of ammoniacal nitrogen is less than 42 g per litre, it will be necessary to add a weight of ammonia solution:
If V is less than 25 ml, add it directly to the five-litre flask with a weight of V x 0 7173 g powdered citric acid.
If V is greater than 25 ml, it will be convenient to make a new litre of reagent in the following way.
Weigh 173 g of citric acid. Dissolve it in 500 ml of water. And, taking the precautions indicated, add not more than 225 + V × 1 206 ml of ammonia solution which was used to prepare the five litres of reagent.
Make up to volume with water. Mix.
Mix this litre with the 4 975 ml previously prepared.

5. APPARATUS 5.1. Water bath which can be maintained at a temperature of 65 ± 1 ºC.
5.2. A 500-ml graduated flask (e.g. Stohmann).

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Sample
Weigh, to the nearest 0 7001 g, 1 g of the prepared sample and transfer to the 500-ml graduated flask (5.2).
7.2. Extraction
Add 200 ml of alkaline ammonium citrate solution (4.1). Stopper the flask and shake vigorously by hand to avoid the formation of lumps and to prevent any adherence of the substance to the sides.
Place the flask in the water bath set at 65 ºC and shake every five minutes during the first half an hour. After each shaking, raise the stopper to equilibrate the pressure. The level of water in the water bath ought to be above the level of solution in the flask. Allow the flask to remain in the water bath a further hour at 65 ºC and shake every 10 minutes. Remove the flask, cool to a temperature of about 20 ºC, make up to a volume of 500 ml with water. Mix and filter through a dry fluted filter paper, free from phosphates, rejecting the first portion of filtrate.
7.3. Determination
The determination of phosphate extracted will be carried out by Method 3.2 on an aliquot part of the solution thus obtained.

Method 3.1.5.2 Extraction of the soluble phosphorus according to Petermann at ambient temperature
1. SCOPE
This document defines the procedure for the determination of phosphorus soluble in cold alkaline ammonium citrate.
2. FIELD OF APPLICATION
Disintegrated phosphates exclusively.
3. PRINCIPLE
Extraction of phosphorus at a temperature about 20 ºC with an alkaline solution of ammonium citrate (Petermann's solution) in specific conditions.
4. REAGENT
See Method 3.1.5.1.
5. APPARATUS 5.1. Standard laboratory equipment, and a 250-ml graduated flask (e.g. Stohmann).
5.2. Rotary shaker (35 to 40 turns per minute).

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Sample
Weigh, to the nearest 0 7001 g, 2 75 g of the prepared sample and place it in a 250-ml graduated flask (5.1).
7.2. Extraction
Add a little of Petermann's solution at 20 ºC, shake very hard in order to stop the formation of lumps and to prevent any of the substance adhering to the side of the flask. Make up to the graduation mark with Petermann's solution and close the flask with a rubber stopper.
Shake for two hours in the rotary shaker (5.2). Filter immediately through a dry pleated filter, free from phosphate, into a dry container, discarding the first portion of the filtrate.
7.3. Determination
The phosphorus determination will be carried out by Method 3.2 on an aliquot part of the solution thus obtained.

Method 3.1.5.3 Extraction of the phosphorus soluble in Joulie's alkaline ammonium citrate
1. SCOPE

This document defines the procedure for the determination of phosphorus soluble in Joulie's alkaline ammonium citrate.

2. FIELD OF APPLICATION

All the straight and compound phosphate fertilizers, in which the phosphate occurs in an alumino-calcic form.

3. PRINCIPLE

Extraction by shaking vigorously with an alkaline solution of ammonium citrate of defined specification (and where appropriate in the presence of oxine) at about 20 ºC.

4. REAGENTS

Distilled or demineralized water. 4.1. Joulie's alkaline solution of ammonium citrate.

This solution contains 400 g of citric acid and 153 g of NH3 per litre. Its free ammonia content is approximately 55 g per litre. It can be prepared by one of the methods described below. 4.1.1. In a one-litre graduated flask, dissolve 400 g of citric acid (C6H8O7 7H2O) in approximately 600 ml of ammonia (d20 = 0 7925, i.e. 200 g of NH3 per litre). The citric acid is added successively in quantities of 50 to 80 g maintaining the temperature below 50 ºC. Make up the volume to one litre with ammonia.

4.1.2. In a one-litre graduated flask, of dissolve 432 g of dibasic ammonium citrate (C6H14N2O7) in 300 ml of water. Add 440 ml of ammonia (d20 = 0 7925). Make the volume up to one litre with water.

Note

Verification of the total ammonia content.

Take a 10-ml sample of the citrate solution and place it in a 250-ml flask. Make up the volume with distilled water. Determine the ammoniacal nitrogen content on 25 ml of this solution according to Method 2.1.

1 ml of H2SO4 0 75 N = 0 7008516 g of NH3

In these conditions, the reagent is considered to be correct when the number of millilitres found upon titration lies between 17 77 and 18 ml.

If this is not so add 4 725 ml of ammonia (d20 = 0 7925) per 0 71 ml below 18 ml indicated above.

4.2. Powdered 8-hydroxyquinoline (oxine).

5. APPARATUS 5.1. Standard laboratory equipment and small mortar in glass or porcelain with pestle.

5.2. 500-ml graduated flasks.

5.3. A 1 000-ml graduated flask.

5.4. Rotary shaker (35 to 40 turns per minute).

6. PREPARATION OF THE SAMPLE

See Method 1.

7. PROCEDURE 7.1. Sample

Weigh, to the nearest 0 70005 g, 1 g of the prepared sample and place in a small mortar. Add about 10 drops of citrate (4.1) to moisten it and break it up very carefully with the pestle.

7.2. Extraction

Add 20 ml of ammonium citrate (4.1) and mix to a paste, leave it to settle for about one minute.

Decant the liquid into a 500-ml graduated flask, straining off particles which might have escaped the preceding moist disintegration. Add 20 ml of citrate solution (4.1) to the residue, grind as above and decant the liquid into the graduated flask. Repeat the process four times, so that by the end of the fifth time all the product can be poured into the flask. The total quantity of citrate used for these processes must be approximately 100 ml.

Rinse the pestle and mortar above the graduated flask with 40 ml of distilled water.

The stoppered flask is shaken for three hours on the rotary shaker (5.4).

Leave the flask standing for 15 to 16 hours, shake it again under same conditions for three hours. The temperature during the whole process is kept at 20 ± 2 ºC.

Make up to the graduation mark with distilled water. Filter through a dry filter, discard the first portion of the filtrate and collect the clear filtrate in a dry flask.

7.3. Determination

The estimation of the extracted phosphorus will be carried out according to Method 3.2 on an aliquot part of the solution thus obtained.

8. APPENDIX

The use of oxine makes it possible to apply this method to fertilizers containing magnesium. This use is

recommended when the ratio of magnesium and phosphoric anhydride contents is higher than 0 703 (Mg/P2O5 > 0 703). If this is the case, add 3 g of oxine to the moistened sample for analysis. The use of oxine in the absence of magnesium is not, moreover, likely to interfere subsequently with the determination. In the known absence of magnesium it is, however, possible not to use oxine.

Method 3.1.6 EXTRACTION OF WATER SOLUBLE PHOSPHORUS
1. SCOPE
This document defines the procedure for the determination of water soluble phosphorus.
2. FIELD OF APPLICATION
All fertilizers, including compound fertilizers, where water soluble phosphorus is to be determined.
3. PRINCIPLE
Extraction in water by shaking under specific conditions.
4. REAGENT
Distilled or demineralized water.
5. APPARATUS 5.1. A 500-ml graduated flask (e.g. Stohmann).
5.2. Rotary shaker (35 to 40 turns per minute).
6. PREPARATION OF THE SAMPLE
See Method 1.
PROCEDURE 7.1. Sample
Weigh, to the nearest 0 7001 g, 5 g of the prepared sample and place it in a 500-ml graduated flask (5.1).
7.2. Extraction
Add to the flask 450 ml of water, the temperature of which must be between 20 and 25 ºC.
Shake in the rotary shaker (5.2) for 30 minutes.
Then make up to the mark with water, mix thoroughly by shaking and filter through a dry pleated filter, tree of phosphate, into a dry container.
7.3. Determination
The estimation of phosphorus will be carried out on an aliquot part of the solution thus obtained by Method 3.2.
Method 3.2 DETERMINATION OF EXTRACTED PHOSPHORUS (Gravimetric method using quinoline phosphomolybdate)
1. SCOPE
This document defines the procedure for the determination of phosphorus in the extracts from fertilizers.
2. FIELD OF APPLICATION
The method is applicable to all extracts of fertilizers (1) for the determination of the different forms of phosphorus.
3. PRINCIPLE
After possible hydrolysis, phosphorus is precipitated in an acid media in the form of quinoline phosphomolybdate.
After filtering and washing, the precipitate is dried at 250 ºC and weighed.
In the abovementioned conditions no interfering action is exerted by the compounds likely to be found in the solution (mineral and organic acids, ammonium ions, soluble silicates, etc.) if a reagent based on sodium molybdate or ammonium molybdate is used in the precipitation.
4. REAGENTS
Distilled or demineralized water. 4.1. Concentrated nitric acid (d20 = 1 740).
4.2. Preparation of reagent. 4.2.1. Preparation of the reagent based on sodium molybdate.
Solution A : Dissolve 70 g of sodium molybdate dihydrate in 100 ml of distilled water.
Solution B : Dissolve 60 g of citric acid monhydrate in 100 ml of distilled water and add 85 ml concentrated nitric acid (4.1).
Solution C : Stir solution A into solution B to obtain solution C.
Solution D : To 50 ml of distilled water add 35 ml of concentrated nitric acid (4.1), then 5 ml of freshly distilled quinoline. Add this solution to solution C, mix thoroughly and leave standing overnight in the dark. After this make up to 500 ml with distilled water, mix again, and filter through a sintered glass funnel (5.6).
4.2.2. Preparation of the reagent based on ammonium molybdate.
Solution A : In 300 ml of distilled water dissolve 100 g of ammonium molybdate while heating gently and stirring from time to time.
Solution B : Dissolve 120 g of citric acid monohydrate in 200 ml of distilled water, add 170 ml of concentrated nitric acid (4.1). (1)Phosphorus soluble in mineral acids, water soluble phosphorus, phosphorus

soluble in solutions of ammonium citrate, phosphorus soluble in 2 % citric acid and phosphorus soluble in 2 % formic acid.
Solution C : Add 10 ml of freshly distilled quinoline to 70 ml of concentrated nitric acid (4.1).
Solution D : Slowly pour, stirring well, solution A into solution B. After thoroughly mixing add solution C to this mixture and make up to one litre. Leave standing for two days in a dark place and filter through a sintered glass funnel (5.6).
The reagents 4.2.1 and 4.2.2 can be used in the same way ; both must be kept in the dark in stoppered polyethylene bottles.

5. APPARATUS 5.1. Standard laboratory equipment and a 500-ml Erlenmeyer flask with a wide neck.
5.2. Graduated pipettes of 10,25 and 50 ml.
5.3. Filter crucible with porosity of 5 to 20 ¶.
5.4. Buchner flask.
5.5. Drying oven regulated at 250 ± 10 ºC.
5.6. Sintered glass funnel with porosity of 5 to 20 ¶.

6. PROCEDURE 6.1. Treatment of the solution
With a pipette, take an aliquot part of fertilizer extract (see Table 2) containing about 0 701 g of P2O5 and put it in a 500-ml Erlenmeyer flask. Add 15 ml of concentrated nitric acid (1) (4.1) and dilute with water to about 100 ml.
Table 2 21 ml when the solution to be precipitated contains more than 15 ml of citrate solution (neutral citrate, Petermann or Joulie alkaline citrate).
6.2. Hydrolysis
If the presence of metaphosphates, pyrophosphates or polyphosphates is suspected in the solution, hydrolysis is carried out as follows.
Bring the contents of the Erlenmeyer flask to the boil slowly and keep at this temperature until hydrolysis is completed (this usually takes one hour). Care must be taken to avoid losses by splashing and excessive evaporation which would reduce the initial volume by more than half, by fitting a reflux condenser. After hydrolysis make up to the initial volume with distilled water.
6.3. Weighing the crucible
Dry the filter crucible (5.3) for at least 15 minutes in the drying oven set at 250 ± 10 ºC. Weigh it after it has been cooled in a desiccator.
6.4. Precipitation
The acid solution contained in the Erlenmeyer flask is heated until it begins to boil then precipitation of the quinoline phosphomolybdate is started by adding 40 ml of the precipitating reagent (reagent 4.2.1 or 4.2.2) (1) drop by drop, stirring continuously. Place the Erlenmeyer flask in a steam bath, leave it there for 15 minutes, shaking it from time to time. The solution can be filtered immediately or after it has cooled down.
6.5. Filtering and washing
Filter the solution under vacuum by decantation. Wash the precipitate in the Erlenmeyer flask with 30 ml of water. Decant and filter the solution. Repeat this process five times. Quantitatively transfer the rest of the precipitate into the crucible washing it with water. Wash four times with 20 ml of water, allowing the liquid to drain from the crucible before each addition. Dry the precipitate thoroughly.
6.6. Drying and weighing
Wipe the outside of the crucible with a filter paper. Place this crucible in a drying oven and keep it there until its weight remains constant, at a temperature of 250 ºC (5.5) (usually 15 minutes) ; leave it to cool in the desiccator at ambient temperature and weigh rapidly.
6.7. Blank test
For each series of determinations, carry out a blank test using only the reagents and solvents in the proportions used in the extraction (citrate solution, etc.) and allow for them in the calculation of the final result.
6.8. Verification
Carry out the determination using an aliquot part of a potassium dihydrogen phosphate solution containing 0 701 g of P2O5. (1)To precipitate phosphate solutions containing more than 15 ml of citrate solution (neutral, Petermann or Joulie) which have been acidified with 21 ml of concentrated nitric acid (see footnote to 6.1) use 80 ml of the precipitating reagent.

7. EXPRESSION OF THE RESULT
If the samples for analysis and dilutions shown in Table 2 are used, the following formula applies:
% P in the fertilizer = (A - a) × F'
or
% P2O5 in the fertilizer = (A - a) × F
where:
A = weight, in grams, of the quinoline phosphomolybdate,
a = weight, in grams, of the quinoline phosphomolybdate obtained in the blank test,
F and F' = factors given in the last two columns of Table 2.
With samples for analysis and dilutions which differ from those of Table 2, the following formula applies:
where:
f and f' = conversion factors of quinoline phosphomolybdate into P2O5 = 0 7032074, (f) or into P = 0 7013984 (f').
D = dilution factor.
M = weight, in grams, of the sample analyzed.

Method 4 POTASSIUM
Method 4.1 DETERMINATION OF THE WATER SOLUBLE POTASSIUM CONTENT
1. SCOPE
This document defines the procedure for the determination of water soluble potassium.
2. FIELD OF APPLICATION
All the potassium fertilizers listed in Annex I to Directive 76/116/EEC.
3. PRINCIPLE
The potassium in the sample to be analyzed is dissolved in water. After eliminating or fixing the substances which might interfere with the quantitative determination, the potassium is precipitated in a slightly alkaline medium in the form of potassium tetraphenylborate.
4. REAGENTS
Distilled or demineralized water. 4.1. Formaldehyde.
Clear formaldehyde solution at 25 to 35 %.
4.2. Potassium chloride for analysis.
4.3. Sodium hydroxide solution : 10 N.
Care should be taken to ensure that only potassium free sodium hydroxide is used.
4.4. Indicator solution.
Dissolve 0 75 g of phenolphthalein in ethanol at 90 % and make the volume up to 100 ml.
4.5. EDTA solution.
Dissolve 4 g of the dihydrated disodium salt of ethylenediaminetetraacetic acid in water in a 100-ml graduated flask. Make up the volume and mix.
Store this reagent in a plastic container.
4.6. STPB solution.
Dissolve 32 75 g of sodium tetraphenylborate in 480 ml of water add 2 ml of the sodium hydroxide solution (4.3) and 20 ml of a magnesium chloride solution (100 g of MgCl2 76H2O per litre).
Stir for 15 minutes and filter through a fine, ashless filter.
Store this reagent in a plastic container.
4.7. Liquid for washing.
Dilute 20 ml of the STPB solution (4.6) to 1 000 ml with water.
4.8. Bromine water.
Saturated bromine solution in water.

5. APPARATUS 5.1. 1 000-ml graduated flasks.
5.2. A 250-ml beaker.
5.3. Filter crucibles with a porosity of 5 to 20 ¶.
5.4. Oven regulated at 120 ± 10 ºC.
5.5. Desiccator.

6. PREPARATION OF THE SAMPLE
See Method 1.
In the case of potassium salts the sample must be ground fine enough in order that a representative sample is obtained for analysis. For these products Method 1 (6) (a) must be used.
7. PROCEDURE 7.1. Sample
Weigh, to the nearest 0 7001 g, 10 g of the prepared sample (5 g for potassium salts containing more than 50 % of potassium oxide). Place this test sample in a 600-ml beaker with approximately 400 ml of water.
Bring to the boil and allow it to boil for 30 minutes. Cool, transfer quantitatively into a 1 000-ml graduated flask, make up the volume, mix and filter into a dry receiver. Discard the first 50 ml of the filtrate (see 7.6, note on procedure).
7.2. Preparation of the aliquot part for precipitation
Transfer by pipette an aliquot part of the filtrate containing 25 to 50 mg of potassium (see Table 3) and place it in a 250-ml beaker. If required make up to 50 ml with water.
To remove any interferences, add 10 ml of the EDTA solution (4.5), several drops of the phenolphthalein solution (4.4) and stir in, drop by drop, sodium hydroxide solution (4.3) until it turns red, then finally add a few more drops of sodium hydroxide to ensure an excess (usually 1 ml of sodium hydroxide is sufficient to neutralize the sample and ensure an excess).
To eliminate most of the ammonia (see 7.6 (b), note on procedure) boil gently for 15 minutes.
If necessary add water to make the volume up to 60 ml.
Bring the solution to the boil, remove the beaker from the heat and add 10 ml of formaldehyde (4.1). Add several drops of phenolphthalein and, if necessary, some more sodium hydroxide, until a distinct red colour appears. Cover the beaker with a watch glass and place it on a steam bath for 15 minutes.
7.3. Weighing the crucible
Dry the filter crucible (see 5 "Apparatus") constant weight (about 15 minutes) in the oven at 120 ºC (5.4). Allow the crucible to cool in a desiccator and then weigh it.
7.4. Precipitation
Remove the beaker from the steam bath, stir in drop by drop 10 ml of the STPB solution (4.6). This addition takes about two minutes. Wait for at least 10 minutes before filtering.
7.5. Filtering and washing
Filter under vacuum into the weighed crucible, rinse the beaker with the liquid for washing (4.7), wash the precipitate three times with the liquid for washing (60 ml in all of the liquid for washing) and twice with 5 to 10 ml of water.
Dry the precipitate thoroughly.
7.6. Drying and weighing
Wipe the outside of the crucible with a filter paper. Place the crucible with its contents in the oven for one and a half hours at a temperature of 120 ºC. Allow the crucible to cool in a desiccator to ambient temperature and weigh rapidly.
Note on procedure (a) If the filtrate is dark in colour, transfer by pipette, an aliquot part containing at the most 100 mg of K_2O and place in a 100-ml graduated flask, add bromine water and bring to the boil to eliminate any surplus bromine. After cooling make up the volume, filter and quantitatively determine the potassium in an aliquot part of the filtrate.
(b) Where there is little or no ammoniacal nitrogen present, there is no need to boil for 15 minutes.

7.7. Aliquot parts to be taken as samples and conversion factors
Table 3
7.8. Blank test
For each series of determinations, carry out a blank test using only the reagents in the proportions used in the analysis and allow for this when calculating the final result.
7.9. Control test
In order to obtain a control for the method of analysis, carry out a determination on an aliquot part of an aqueous solution of potassium chloride, containing at the most 40 mg of K_2O.

8. EXPRESSION OF THE RESULT
If one uses the samples for analysis and the dilutions shown in Table 3, the formula to apply is the following:

% K2O in the fertilizer = (A - a) × F
or
% K in the fertilizer = (A - a) × F'
where:
A = weight, in grams, of the precipitate from the sample,
a = weight, in grams, of the precipitate from the blank,
F and F' = factors (see Table 3).
With samples and dilutions which differ from those shown in Table, 3 use the following formula: where:
f = conversion factor, KTPB into K2O = 0 71314,
f' = conversion factor, KTPB into K = 0 7109,
D = dilution factor,
M = weight, in grams, of sample for analysis.

Method 5 MAGNESIUM
Method 5.1 DETERMINATION OF WATER SOLUBLE MAGNESIUM
1. SCOPE
This document defines the procedure for the determination of water soluble magnesium.
2. FIELD OF APPLICATION
Exclusively to straight fertilizers in respect of which Annex I A to Directive 76/116/EEC provides for the indication of water soluble magnesium.
3. PRINCIPLE
Solution of magnesium by boiling a test sample in water.
First titration with EDTA of Ca + Mg in the presence of eriochrome black-T. Second titration with EDTA of Ca in the presence of calcein or of colcon carbonic acid. Determination of magnesium by difference.
4. REAGENTS
Distilled or demineralized water. 4.1. Standard 0 705 molar solution of magnesium.
Weigh out 2 7016 g of magnesium oxide, previously calcined at 600 ºC for two hours. Place it in a beaker with 100 ml of water. Stir in 120 ml of approximately 1 N hydrochloric acid. After dissolution, transfer quantitatively into a graduated one-litre flask, make up the volume with water and mix.
Check the strength of the solution gravimetrically as the phosphate.
1 ml of the solution should contain 0 71216 g of Mg (= 0 72016 g of MgO).
4.2. 0 705 molar solution of EDTA.
Weigh out 18 761 g of the dihydrated disodium salt of ethylenediaminetetraacetic (C10H14N2Na2O8 72H2O), place it in a litre beaker and dissolve in 600 to 800 ml of water. Transfer the solution quantitatively into a graduated one-litre flask. Make up the volume and mix. Check this solution with the standard solution (4.1) by taking a sample of 20 ml of the latter and by titration according to analytical procedure (7.4.1).
1 ml of the EDTA solution should correspond to 1 7216 mg of Mg or 2 7016 mg of MgO and to 2 7004 mg of Ca or 2 7804 mg of CaO (see 9.1 and 9.6).
4.3. 0 705 molar standard solution of calcium.
Weigh out 5 7004 g of dry calcium carbonate. Place it in a beaker with 100 ml of water. Progressively stir in 120 ml of approximately 1 N hydrochloric acid.
Bring to the boil in order to drive off the carbon dioxide, cool, transfer quantitatively into a graduated one-litre flask, make up the volume with water and mix. Check this solution against the EDTA solution (4.2) following analytical procedure 7.4.2. 1 ml of this solution should contain 2 7004 mg of Ca (= 2 7804 mg of CaO) and should correspond to 1 ml of the 0 705 molar EDTA solution.
4.4. Calcein indicator.
Carefully mix in a mortar 1 g of calcein with 100 g of sodium chloride. Use 10 mg of this mixture. The indicator changes from green to orange. Titration must be carried out until an orange is obtained which is free from green tinges.
4.5. Calcon carbonic acid indicator.
Dissolve 400 mg of calcon carbonic acid in 100 ml of methanol. Use three drops of this solution. The indicator changes from red to blue. Titration must be carried out until a blue is obtained which is free from red tinges.
4.6. Eriochrome black-T indicator.
Dissolve 300 mg of eriochrome black-T in a mixture of 25 ml of propyl alcohol and 15 ml of triethanolamine. Use three drops of this solution. This indicator turns from red to blue and titration must be carried out until a blue is obtained which is free from red tinges. It changes colour only when magnesium is

present. If necessary add 0 71 ml of the standard solution (4.1).
When both calcium and magnesium are present the EDTA first forms a complex with the calcium and then with the magnesium. In that case these two elements are determined concurrently.
4.7. Potassium cyanide.
Aqueous solution of KCN at 2 %.
4.8. Solution of potassium hydroxide and potassium cyanide.
Dissolve 280 g of KOH and 66 g of KCN in water, make up the volume to one litre and mix.
4.9. pH 10 buffer solution.
Dissolve 33 g of ammonium chloride in 200 ml of water, add 250 ml of ammonia (d = 0 791) make up the volume to 500 ml with water and mix. Test the pH of this solution regularly.

5. APPARATUS 5.1. Magnetic or mechanical stirrer.
5.2. A pH meter.
5.3. 500-ml graduated flasks.
5.4. 300-ml beakers.

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Sample
Place 5 g of the prepared sample weighed out to an accuracy of 1 mg in a 500-ml graduated flask.
7.2. Solution
Add about 300 ml water and boil for half an hour. Cool, make up the volume, mix and filter.
7.3. Control test
Carry out a determination on aliquots parts of solutions (4.1) and (4.3) such that the Ca/Mg ratio is equal to that expected from the sample.
To this end take (a) millilitres of standard solution (4.3) and (b - a) millilitres of standard solution (4.1).
(a) and (b) are the numbers of millilitres of EDTA solution used in the two titrations when analyzing the sample. This procedure is correct only if the standard solutions of EDTA, calcium and magnesium are exactly equivalent. If this is not the case, it is necessary to make the appropriate corrections.
7.4. Determination 7.4.1. Titration in the presence of eriochrome black-T
Pipette an aliquot part of the solution to be analyzed (7.5) into a 300-ml beaker and dilute with water to about 100 ml. Add 5 ml of the buffer solution (4.9). The pH measured by the meter must be 10 75 ± 0 71. Add 2 ml of the potassium cyanide solution (4.7) and three drops of the eriochrome black-T indicator (4.6). Stir gently and titrate with the EDTA solution (4.2) (9.2, 9.3 and 9.4). Let "b" be the number of millilitres of 0 705 molar EDTA solution.
7.4.2. Titration in the presence of calcein or of calcon carbonic acid
Pipette an aliquot part of the solution to be analyzed equal to that taken for the above titration and place it in a beaker. Dilute with water to about 100 ml. Add 10 ml of the KOH/KCN solution (4.8) and the indicator (4.4 or 4.5). Stir gently and titrate with the EDTA solution (9.2, 9.3 and 9.4). Let "a" be the number of millilitres of 0 705 molar EDTA solution.
7.5. Aliquot parts to be taken as a sample for titration
Note 1. For all these fertilizers the test sample is 5 g and the total volume of the solution to be analyzed is 500 ml.
2. For titration with eriochrome black-T, the titration must not exceed much more than the 25 ml of EDTA, or else the volume of the aliquot part must be reduced.
However, it is possible to increase the latter.

8. EXPRESSION OF THE RESULT where:
T = strength of the EDTA solution,
T' = strength of the EDTA solution.
If it is exactly 0 705 M, T is equal to 0 72016 g MgO or T' is equal to 0 71216 g Mg.
M = the weight of the sample, expressed in grams, present in the aliquot part taken as a sample (7.5).
9. REMARKS 9.1. The stoichiometric ratio of EDTA-metal in complexometric analyses is always 1 : 1, whatever the valency of the metal, although EDTA is quadrivalent. The titration solution of EDTA and the standard solutions will therefore be molar and not normal.

9.2. Complexometric indicators are often sensitive to the action of air and solutions may turn pale during titration. One or two drops of the indicator must then be added. This effect is observed when eriochrome black and calcon carbonic acid are used.
9.3. The metal-indicator complexes are sometimes relatively stable and the colour change can take some time.
The last drops of EDTA must therefore be added slowly and one must ensure that the colour change point has not been passed by adding one drop of the 0 705 molar magnesium solution (4.1) or calcium solution (4.3).
This is especially the case for the eriochrome-magnesium complex.
9.4. The colour change of the indicator must not be observed from above but horizontally through the solution and the beaker must be placed against a white background in a well-lit position,
The colour change can also be observed easily by placing a beaker on a frosted glass plate lit from below (25-watt lamp).
9.5. This analysis requires a certain amount of experience from the chemist. The latter should take pains inter alia to observe the colour changes with the standard solutions (4.1 and 4.3).
It is advisable to have the determinations carried out always by the same chemist.
9.6. The use of an EDTA solution of a guaranteed strength (Titrisol or Normex for example) can simplify the testing of the equivalence of the standard solutions (4.1, 4.2 and 4.3).

Method 6 CHLORINE
Method 6.1 DETERMINATION OF CHLORIDES IN THE ABSENCE OF ORGANIC MATERIAL
1. SCOPE
This document defines the procedure for the determination of chloride, in the absence of organic material.
2. FIELD OF APPLICATION
All fertilizers which are free from organic material.
3. PRINCIPLE
The chlorides, dissolved in water, are precipitated in an acid medium by an excess of standard solution of silver nitrate. The excess is titrated with a solution of ammonium thiocyanate in the presence of ferric ammonium sulphate (Volhard's method).
4. REAGENTS
Distilled or demineralized water, free from chlorides. 4.1. Nitrobenzene or diethyl ether.
4.2. Nitric acid : 10 N.
4.3. Indicator solution.
Dissolve 40 g of ferric ammonium sulphate Fe2(SO4)3 7(NH4)2SO4 724H2O, in water and make up to one litre.
4.4. Silver nitrate standard solution : 0 71 N.
4.5. Ammonium thiocyanate standard solution : 0 71 N.
Preparation.
Since this salt is hygroscopic and cannot be dried without risk of decomposition, it is advisable to weigh out approximately 9 g, dissolve in water and make up the volume to one litre. Adjust to 0 71 N strength by titration of AgNO3 0 71 N.

5. APPARATUS 5.1. Rotary shaker (35 to 40 turns per minute).
5.2. Burettes.
5.3. A 500-ml graduated flask.
5.4. Conical (Erlenmeyer) flask of 250 ml.

6. PREPARATION OF THE SAMPLE
See Method 1.
7. PROCEDURE 7.1. Sample and preparation of the solution
Place 5 g of the sample, weighed out to nearest 0 7001 g, in a 500-ml graduated flask and add 450 ml of water. Mix for half an hour on the shaker (5.1) ; make up to 500 ml with distilled water ; mix and filter into a beaker.

7.2. Determination
Take an aliquot part of the filtrate containing not more than 0 7150 g of chloride. For example 25 ml (0 725 g), 50 ml (0 75 g) or 100 ml (1 g). If the sample taken is smaller than 50 ml it is necessary to make up the volume to 50 ml with distilled water.
Add 5 ml of nitric acid 10 N (4.2), 20 ml of indicator solution (4.3), and two drops of ammonium thiocyanate standard solution (a sample of this latter reagent is taken with a burette adjusted to zero for this purpose). With a burette then add silver nitrate standard solution (4.4) until there is an excess of 2 to 5 ml. Add 5 ml of nitrobenzene or 5 ml of diethyl ether (4.1) and shake well to agglomerate the precipitate. Titrate the excess silver nitrate with ammonium thiocyanate 0 71 N (4.5) until a red-brown colour appears which remains after the flask has been shaken slightly.
Note
Nitrobenzene or diethyl ether (but above all nitrobenzene) prevents the silver chloride from reacting with thiocyanate ions. Thus a clear colour change is obtained.
7.3. Blank test
Make a blank test in the same conditions and allow for it when calculating the final result.
7.4. Control test
Before carrying out the estimations check the accuracy of the method by using an aliquot part of a freshly prepared solution of potassium chloride, such that this part contains a known quantity in the order of 100 mg of chloride.

8. EXPRESSION OF THE RESULT
Express the result of the analysis as a percentage of chloride contained in the sample as it has been received for analysis.
Calculate the percentage of chloride (Cl) with the formula: where:
Vz = number of millilitres of silver nitrate 0 71 N,
Vcz = number of millilitres of silver nitrate 0 71 N, used in the blank test,
Va = number of millilitres of ammonium thiocyanate 0 71 N,
Vca = number of millilitres of ammonium thiocyanate 0 71 N, used in blank test,
M = weight, in grams, of the sample taken (7.2).

Methods 7 FINENESS OF GRINDING
Method 7.1 DETERMINATION OF FINENESS OF GRINDING (DRY PROCEDURE)
1. SCOPE
This document defines the dry procedure, for the determination of the fineness of grinding.
2. FIELD OF APPLICATION
All EEC type fertilizers in which requirements are given of fineness of grinding using 0 763 and 0 7160 mm sieves.
3. PRINCIPLE
By mechanical sieve shaking, the quantities of product with a granule size greater than 0 763 mm and those with a granule size between 0 716 and 0 763 mm are determined, and the percentage of fineness of grinding is calculated.
4. APPARATUS 4.1. Mechanical sieve shaker.
4.2. Sieves with apertures of 0 716 and 0 763 mm respectively of standard ranges (20 cm diameter and 5 cm high).

5. PROCEDURE
Weigh, to the nearest 0 705 g, 50 g of the substance. Assemble the two sieves and the collecting container on the shaker (4.1), the sieve with the larger apertures being placed on top. Place the sample for analysis on the top. Sieve for 10 minutes and remove the part collected on the bottom. Start the apparatus up again and after one minute check that the amount collected on the bottom during this time is not more than 250 mg. Repeat the process (for one minute each time) until the amount collected is less than 250 mg. Weigh the residual material on both sieves separately.
6. EXPRESSION OF THE RESULT
% fineness of the sample shown by the sieve, with 0 763 mm apertures = (50 - M1) × 2
% fineness of the sample shown by the sieve, with 0 716 mm apertures = (50 - (M1 + M2)) × 2

where:
M1 = weight, in grams, of residue on the sieve, with 0 763 mm apertures,
M2 = weight, in grams, of residue on the sieve, with 0 716 mm apertures.
The reject from the sieve, with 0 763 mm apertures having been already eliminated.
The results of these calculations are rounded up to the nearest unit.

Method 7.2 DETERMINATION OF THE FINENESS OF GRINDING OF SOFT NATURAL PHOSPHATES
1. SCOPE
This method is for determining the fineness of grinding of soft natural phosphates.
2. FIELD OF APPLICATION
Soft natural phosphates.
3. PRINCIPLE
For samples of fine particle size, agglomeration may occur thus making dry sieving difficult. For this reason, wet sieving is normally used.
4. REAGENTS
Sodium hexametaphosphate solution : 1 %.
5. APPARATUS 5.1. Sieves with apertures of 0 7063 and 0 7125 mm respectively of standard ranges (diameter 20 cm and height 5 cm) ; collecting containers.
5.2. Glass funnel of 20 cm diameter mounted on a stand.
5.3. 250-ml beakers.
5.4. Drying oven.

6. METHOD OF ANALYSIS 6.1. Sampling
Weigh, to the nearest 0 705 g, 50 g of the substance. Wash both sides of the sieve with water and place the sieve with 0 7125 mm apertures above the 0 7063 mm sieve.
6.2. Procedure
Place the sample for analysis on the top sieve. Sieve under a small jet of cold water (tap water can be used) until the water is practically clear when it passes through. Care should be taken to ensure that the flow of water is such that the lower sieve never fills with water.
When the residue on the top sieve seems to remain more or less constant, remove this sieve, and place, in the meanwhile on a collecting container.
Continue the wet sieving through the lower sieve for a few minutes, until the water passing through is nearly clear.
Replace the 0 7125 mm sieve over the 0 7063 mm sieve. Transfer any deposit from the collecting container to the top sieve and begin sieving again under a small jet of water until this water becomes almost clear once more.
Quantitatively transfer each of the residues into a different beaker by means of the funnel. Suspend each residue by filling the beakers with water. Leave to stand for about one minute, decant, as much water as possible.
Place the beakers in the drying oven at 150 ºC for two hours.
Allow them to cool, detach the residues with a brush and weigh them.

7. EXPRESSION OF THE RESULT
The results of the calculations are rounded up to the nearest unit.
% fineness shown by the residue left on the 0 7125 mm sieve = (50 - M1) × 2
% fineness shown by the residue left on the 0 7063 mm sieve = (50 - (M1 + M2)) × 2
where:
M1 = weight, in grams, of the residue on the 0 7125 mm sieve,
M2 = weight, in grams, of the residue on the 0 7063 mm sieve.
8. REMARKS
If the presence of lumps is observed after sieving the analysis should be carried out again in the following way.
Slowly pour 50 g of the sample into a one-litre flask containing 500 ml of the sodium hexametaphosphate solution stirring continuously. Stopper the flask and shake vigorously by hand to break up the lumps.

Transfer the whole suspension into the top sieve and wash the flask thoroughly. Continue the analysis as described in 6.2.