SCHEDULE 2

METHODS OF ANALYSIS

PART I

16.

METHODS OF ANALYSIS AND TEST PROCEDURES FOR AMMONIUM NITRATE FERTILISERS CONTAINING MORE THAN 28% NITROGEN BY WEIGHT

A.Methods for the Application of Thermal Cycles

SCOPE AND FIELD OF APPLICATION

1. This method defines the procedures for the application of thermal cycles prior to the execution of the oil retention test in straight ammonium nitrate fertilisers containing more than 28% nitrogen by weight.

THERMAL CYCLES

Field application

Field application

2.—(2.1) This procedure is for thermal cycling prior to determining the oil retention of the fertiliser.

Principle and definition

(2.2) In an Erlenmeyer flask, heat the sample from ambient temperature to 50°C and maintain at this temperature for a period of two hours (phase at 50°C). Thereupon, cool the sample until a temperature of 25°C is acheived and maintain at that temperature for two hours (phase at 25°C). The combination of the successive phases at 50°C and 25°C forms one thermal cycle. After being subjected to two thermal cycles, the test sample is held at a temperature of 20±3°C for the determination of the oil retention value.

Apparatus

(2.3) Normal laboratory apparatus, in particular

— Water baths thermostated at 25 (±1) and 50 (±1)°C respectively.

— Erlenmeyer flasks with an individual capacity of 150 ml.

Procedure

(2.4) Put each test sample of 70(±5) grams into an Erlenmeyer flask which is then sealed with a stopper.

Move each flask every two hours from the 50°C bath to the 25°C bath and vice versa.

Maintain the water in each bath at constant temperature and keep in motion by rapid stirring to ensure the water level comes above the level of the sample. Protect the stopper from condensation by a foam rubber cap.

B.Determination of Oil Retention

SCOPE AND FIELD OF APPLICATION

1. This method defines the procedure for the determination of oil retention of straight ammonium nitrate fertilisers containing more than 28% nitrogen by weight.

The method is applicable to both prilled and granular fertilisers which do not contain oil-soluble materials.

DEFINITION

2. Oil retention of a fertiliser: the quantity of oil retained by the fertiliser determined under the operating conditions specified and expressed as a percentage by mass.

PRINCIPLE

3. Total immersion of the test portion in gas oil for a specified period, followed by the draining away of surplus oil under specified conditions. Measurement of the increase in mass of the test portion.

REAGENT

4.

Gas oil	
Viscosity max:	5 mPas at 40°C
Density:	0.8 to 0.85 g/ml at 20°C
Sulphur content:	≤1.0% (m/m)
Ash:	≤0.1% (m/m)

APPARATUS

5. Ordinary laboratory apparatus and:

(5.1) Balance, capable of weighing to the nearest 0.01 gram.

(5.2) Beakers, of capacity 500 ml.

(5.3) Funnel, of plastic materials, preferably with a cylindrical wall at the upper end, diameter approximately 200 mm.

(5.4) Test sieve, aperture 0.5 mm, fitting into the funnel (5.3).

Note The size of the funnel and sieve is such as to ensure that only a few granules lie one above another and the oil is able to drain away.

(5.5) Filter paper, rapid filtering grade, creped, soft, weight 150g/m^2.

(5.6) Absorbent tissue (laboratory grade).

PROCEDURE

6.—(6.1) Two individual determinations are carried out in quick succession on seperate portions of the same test sample.

(6.2) Remove particles smaller than 0.5 mm using the test sieve (5.4). Weigh to the nearest 0.01 gram approximately 50 grams of the sample into the beaker (5.2). Add sufficient gas oil (Section 4)

to cover the prills completely and stir carefully to ensure that the surfaces of all the prills are fully wetted. Cover the beaker with a watch galss and leave to stand for one hour at 25(±2)°C.

(6.3) Filter the entire contents of the beaker through the funnel (5.3) containing the test sieve (5.4). Allow the portion retained by the sieve to remain there for one hour so that most of the excess oil can drain away.

(6.4) Lay two sheets of filter paper (5.5) (about 500 × 500 mm) on top of each other on a smooth surface; fold the four edges of both filter papers upwards to a width of about 40 mm to prevent the prills from rolling away. Place two layers of absorbent tissue (5.6) in the centre of the filter papers. Pour the entire contents of the sieve (5.4) over the absorbent tissues and spread the prills evenly with a sof flat brush. After two minutes lift one side of the tissues to transfer the prills to the filter papers beneath and spread them evenly over these with the brush. Lay another sheet of filter paper, similarly with its edges turned upward, on the sample and roll the prills between the filter papers with circular movements while exerting a little pressure. Pause after every eight circular movements to lift the opposite edges of the filter papers and return to the centre the prills that have rolled to the periphery. Keep to the following procedure: make four complete circular movements first clockwise and then anticlockwise. Then roll the prills back to the centre as described above. This procedure to be carried out three times (24 circular movements, edges lifted twice). Carefully insert a new sheet of filter paper between the bottom sheet and the one above it and allow the prills to roll onto the new sheet by lifting the edges of the upper sheet. Cover the prills with a new sheet of filter paper and repeat the same procedure as described above. Immediately after rolling, pour the prills into a tared dish and reweigh to the nearest 0.01 gram to determine the weight of the quantity of gas oil retained.

Repeating the rolling procedure and reweighing

(6.5) If the quantity of gas oil retained in the portion is found to be greater than 2.00 grams, place the portion on a fresh set of filter papers and repeat the rolling procedure, lifting the corners in accordance with Section 6.3 (two times eight circular movements, lifting once). Then reweigh the portion.

EXPRESSION OF RESULTS

Method of calculation and formula

Method of calculation and formula

7.—(7.1) The oil retention, from each determination (6.1) expressed as a percentage by mass of the sieved test portion, is given by the equation:

$$\text{Oil retention} = \frac{m_2 - m_1}{m_1} \times 100$$

where:

m_1 is the mass, in grams, of the sieved test portion (6.2);

m_2 is the mass, in grmas, of the test portion accodring to Section 6.4 or 6.5 respectively as the result of the last weighing.

Take as the result the arithmetic mean of the two individual determinations.

C.Determination of the Combustible Ingredients

SCOPE AND FIELD OF APPLICATION

1. This method defines the procedure for the determination of the combustible content of straight ammonium nitrate fertilisers containing more than 28% nitrogen by weight.

PRINCIPLE

2. The carbon dioxide produced by inorganic filters is removed in advance with an acid. The organic compounds are oxidised by means of a chromic acid/sulphuric acid mixture. Carbon dioxide formed is absorbed in a barium hydroxide solution. The precipitate is dissolved in a solution of hydrochloric acid and measured by back-titration with sodium hydroxide solution.

REAGENTS

3.—(3.1) Analytical-grade chromium VI oxide; Cr-(VI)-)3.

(3.2) Sulphuric acid diluted to 60% by volume:

pour 360 ml of water into a one-litre beaker and carefully add 640 ml of sulphuric acid, density at 20°C=1.83 g/ml.

(3.3) Silver nitrate: 0.1 M solution.

(3.4) Barium hydroxide:

weigh out 15 grams of barium hydroxide ($Ba(OH)_2.8H_2O$), and dissolve completely in hot water.

Allow to cool and transfer to a one-litre flask. Fill up to the mark and mix. Filter through a pleated filter paper.

(3.5) Hydrochloric acid : 0.1 M standard solution.

(3.6) Sodium hydroxide: 0.1 M standard solution.

(3.7) Bromophenol blue: solution of 0.4 grams per litre in water.

(3.8) Phenolphthalein: solution of 2 grams per litre in 60% by volume ethanol.

(3.9) Soda lime: particle dimensions, about 1.0 to 1.5 mm.

(3.10) Demineralised water, freshly boiled to remove carbon dioxide.

APPARATUS

4.—(4.1) Standard laboratory equipment, in particular:

— filter crucible with a plate of sintered glass and a capacity of 15 ml, plate diameter: 20 mm, total height : 50 mm, porosity 4 (pore diameter from 5 to 15µm);

— 600 ml beaker.

(4.2) Compressed nitrogen supply.

(4.3) Apparatus made up of the following parts and assembled, if possible, by means of spherical ground joints (see Figure 1).

(4.3.1) Absorption tube (A) about 200 mm long and 30 mm in diameter filled with soda lime (3.9) kept in place by fibreglass plugs.

(4.3.2) 500 ml reaction flask (B) with side arm and a round bottom.

(4.3.3) Vigreux fractionating column about 150 mm long (C').

(4.3.4) Double-surface condenser (C), 200 mm long.

(4.3.5) Drechsel bottle (D) acting as a trap for any excess acid which may distil over.

(4.3.6) Ice bath (E) to cool the Drechsel bottle.

(4.3.7) Two absorption vessels (F_1) and (F_2), 32 to 35 mm in diameter, the gas distributor of which comprises a 10 mm disc of low-porosity sintered glass.

(4.3.8) Suction pump and suction regulating device (G) comprising a T-shaped glass piece inserted into the circuit, the free arm of which is connected to a fine capillary tube by a short rubber tube fitted with a screw clamp.

Caution:

the use of boiling chromic acid solution in an apparatus under reduced pressure is a hazardous operation and requires appropriate precautions.

PROCEDURE

Sample for analysis

Sample for analysis

5.—(5.1) Weigh approximately 10 grams of ammonium nitrate to the nearest 0.001 grams.

Removal of carbonates

(5.2) Place the sample for analysis in the reaction flask (B). Add 100 ml of H_2So_4 (3.2). The prills dissolve in about 10 minutes at ambient temperature. Assemble the apparatus as indicated in the diagram: connect one end of the absorption tube (A) to the nitrogen source (4.2) via a non-return flow device containing 5 to 6 mm of mercury and the other end to the feed tube which enters the reaction flask. Place the Vigreux fractionating column (C') and the condenser (C) with coolinhg water supply in position. Adjust the nitrogen to provide a moderate flow through the solution, bring the solution to boiling point and heat for two minutes. At the end of this time there should be no more effervesence, if effervesence is seen, continue heating for 30 minutes. Allow solution to cool for at least 20 minutes with the nitrogen flowing through it.

Complete assembly of the apparatus as indicated in the diagram by connecting the condenser tube to the Drechsel bottle (D) and the bottle to the absorption vessels F_1 and F_2. The nitrogen must continue to pass through the solution during the assembly operation. Rapidly introduce 50 ml of barium hydroxide solution (3.4) into each of the absorption vessels (F_1 and F_2).

Bubble a stream of nitrogen through for about 10 minutes. The solution must remain clear in the absorbers. If this does not happen, the carbonate removal process must be *adjusted*.

Oxidation and absorption

(5.3) After withdrawing the nitrogen feed tube, rapidly introduce 20 grams of chromium trioxide (3.1) and 6 ml of silver nitrate solution (3.3) via the side arm of the reaction flask (B). Connect the apparatus to the suction pump and adjust the nitrogen flow so that a steady stream of gas bubbles passes through the sintered-glass absorbers (F_1) and (F_2).

Heat the reaction flask (B) until the liquid boils and keep it boiling for one-and-a-half hours(**1**). It may be necessary to adjust the suction-regulating valve (G) to control the nitrogen flow since it is possible that the barium carbonate precipitated during the test may block the sintered glass discs. The operation is satisfactory when the barium hydroxide solution in the absorber (F_2) remains clear. Otherwise repeat the test. Stop heating and dismantle the apparatus. Wash each of the distributors both inside and outside to remove barium hydroxide and collect the washings in the corresponding absorber. Place the distributors one after the other in a 600 ml beaker which will subsequently be used for the determination.

Rapidly filter under vacuum firstly the contents of absorber F_2 and then of absorber F_1 using the sintered glass crucible. Collect the precipitate by rinsing the absorbers with water (3.10) and

(**1**) A reaction time of one-and-a-half hours is sufficient in the case of most of the organic substances in the presence of silver nitrate catalyst.

wash the crucible with 50 ml of the same water. Place the crucible in the 600 ml beaker and add about 100 ml of boiled water (3.10). Introduce 50 ml of boiled water into each of the absorbers and pass nitrogen through the distributors for five minutes. Combine the water with that fro the beaker. Repeat the operation once to ensure that the distributors are rinsed thoroughly.

Measurement of the carbonates originating from organic material

(5.4) Add five drops of phenolphthalein (3.8) to the contents of the beaker. The solution becomes red in colour. Add hydrochloric acid (3.5) drop by drop until the pink colour just disappears. Stir the solution well in the crucible to check that the pink colour does not reappear. Add five drops of bromophenol blue and titrate with hydrochloric acid until the solution turns yellow. Add a further 10 ml of hydrochloric acid.

Heat the solution to boiling point and continue boiling for a maximum of one minute. Check carefully that no precipitate remains in the liquid.

Allow to cool and back titrate with the sodium hydroxide solution (3.6).

BLANK TEST

6. Carry out a blank test following the same procedure and using the same quantities of all reagents.

EXPRESSION OF RESULTS

7. The content of combustible ingredients (C), expressed as carbon, as a percentage by mass of the sample, is given by the formula:

$$C\% = 0.06 \times \frac{V_1 - V_2}{E}$$

where:

E = the mass in grams of the test portion;

V_1 = the total volume in ml of 0.1 M hydrochloric acid added after the change in colour of the phenolphthalein;

V_2 = the volume in ml of the 0.1 M sodium hydroxide solution used for back titration.

D.Determination of the pH value

SCOPE AND FIELD OF APPLICATION

1. This method defines the procedure for measuring the pH value of a solution of a straight ammonium nitrate fertiliser containing more than 28% nitrogen by weight.

PRINCIPLE

2. Measurement of the pH of an ammonium nitrate solution by means of a pH meter.

REAGENTS

3. Distilled or demineralised water, free from carbon dioxide.

Buffer solution, pH 6.88 at 20°C

(3.1) Dissolve 3.40±0.01 grams of potassium dihydrogen orthophosphate (KH_2PO_4) in approximately 400 ml of water. The dissolve 3.55±0.01 gram of disodium hydrogen orthophosphate

(Na_2HPO_4) in approximately 400 ml of water. Transfer the two solutions without loss into a 1,00 ml standard flask, make up to the mark and mix. Keep the solution in an airtight vessel.

Buffer solution, pH 4.00 at 20°C

(3.2) Dissolve 10.21±0.01 grams of potassium hydrogen phthalate ($KHC_8O_4H_4$) in water, transfer without loss into a 1,00 ml standard flask, make up to the mark and mix.

Keep this solution in an airtight vessel.

(3.3) Commercially available pH standard solutions may be used.

APPARATUS

4. pH meter, equipped with glass and calomel electrodes or equivalent, sensitivity 0.05 pH unit.

APPARATUS

Calibration of the pH meter

Calibration of the pH meter

5.—(5.1) Calibrate the pH meter (4) at a temperature of 20(±1)°C, using the buffer solutions (3.1), (3.2) or (3.3). Pass a slow stream of nitrogen onto the surface of the solution and maintain this throughout the test.

Determination

(5.2) Pour 100.0 ml of water onto 10 (±0.01) grams of the sample in a 250 ml beaker. Remove the insolubles by filtering, decanting or centrifuging the liquid.

Measure the pH value of the clear solution at a temperature of 20 (±1)°C according to the same procedure as for the calibration of the meter.

EXPRESSION OF RESULTS

6. Express the result in pH units, to the nearest 0.1 unit and state the temperature used.

E.Determination of the Particle Size

SCOPE AND FIELD OF APPLICATION

1. This method defines the procedure for the test sieving of straight ammonium nitrate fertilisers containing more than 28% nitrogen by weight.

PRINCIPLE

2. The test sample is sieved on a nest of three sieves, either by hand or by mechanical means. The mass retained on each sieve is recorded and the percentage of material passing the required sieves are calculated.

APPARATUS

3.—(3.1) 200 mm diameter woven-wire test sieves to BS 410 (1986) with apertures of 2.0 mm, 1.0 mm and 0.5 mm respectively of standard ranges. One lid and one receiver for these sieves.

(3.2) Balance to weigh to 0.1 gram.

(3.3) Mechanical sieve shaker (if available) capable of imparting both vertical and horizontal motion to the test sample.

PROCEDURE

4.—(4.1) The sample is divided representatively into portions of approximately 100 grams.

(4.2) Weigh one of these portions to the nearest 0.1 gram.

(4.3) Arrange the nest of sieves in ascending order; receiver 0.5 mm, 1 mm, 2 mm and place the weighed test portion on the top sieve. Fit the lid to the top of the nest of sieves.

(4.4) Shake by hand or machine, imparting both a vertical and horizontal motion and, if by hand, tapping occasionally. Continue this process for 10 minutes or until the quantity passing through each sieve in one minute is less than 0.1 gram.

(4.5) Remove the sieves from the nest in turn and collect the material retained, brush gently from the reverse side with a soft brush, if necessary.

(4.6) Weigh the material retained on each sieve and that collected in the receiver, to the nearest 0.1 gram.

EVALUATION OF RESULTS

5.—(5.1) Convert the fraction masses to a percentage of the total of the fraction masses (not of the original charge).

Calculate the percentage in the receiver (ie <0.5 mm): A%

Calculate the percentage retained on the 0.5 mm sieve: B%

Calculate the percentage passing 1.0 mm, ie (A + B)%.

The sum of the fraction masses should be within 2% of the initial mass taken.

(5.2) At least two seperate analyses should be carried out and the individual results for A should not differ by more than 1.0% absolute and for B by more than 1.5% absolute. Repeat the test if this is not the case.

EXPRESSION OF RESULTS

6. Report the mean of the two values for A on the one hand and for A + B on the other hand.
F.Determination of the Chlorine Content (as Chloride Ion)

SCOPE AND FIELD OF APPLICATION

1. This method defines the procedure for the determination of the chlorine content (as chloride ion) of straight ammonium nitrate fertilisers containing more than 28% nitrogen by weight.

PRINCIPLE

2. Chloride ions dissolved in water are determined by potentiometric titration with silver nitrate in an acidic medium.

REAGENTS

3. Distilled or demineralised water, free from chloride ions.

(3.1) Acetone AR.

(3.2) Concentrated nitric acid (density at 20°C = 1.40 g/ml).

(3.3) Silver nitrate 0.1 M standard solution. Store this solution in a brown glass bottle.

(3.4) Silver nitrate 0.004 M standard solution—prepare this solution at the time of use.

(3.5) Potassium chloride 0.1 M standard reference solution. Weigh, to the nearest 0.1 mg, 3.7276 grams of analytical-grade potassium chloride, previously dried for one hour in an oven at 130°C and cooled in a desiccator to ambient temperature. Dissolve in a little water, transfer the solution without loss into a 500 ml standard flask, dilute to the mark and mix.

(3.6) Potassium chloride 0.004 M standard reference solution—prepare this solution at the time of use.

APPARATUS

4.—(4.1) Potentiometer with silver indicating electrode and calomel reference electrode, sensitivity 2 mV, covering the range −500 to +500 mV, or with silver and mercury (1) sulphate electrodes.

(4.2) Bridge, containing a saturated potassium nitrate solution, connected to the calomel electrode (4.1), fitted at the ends with porous plugs. This bridge is not necessary if silver and mercury (1) sulphate electrodes are used.

(4.3) Magnetic stirrer, with a Teflon-coated rod.

(4.4) Microburette with a fine-pointed tip, graduated in 0.01 ml divisions.

PROCEDURE

Standardisation of the silver nitrate solution

Standardisation of the silver nitrate solution

5.—(5.1) Take 5.00 ml and 10.00 ml of the standard reference potassium chloride solution (3.6) and place in two low-form beakers of convenient capacity (for example 250 ml). Carry out the following titration of the contents of each beaker.

Add 5 ml of the nitric acid solution (3.2), 120 ml of the acetone (3.1) and sufficient water to bring the total volume to about 150 ml. Place the rod of the magnetic stirrer (4.3) in the beaker and set the stirrer in motion. Immerse the silver electrode (4.1) and the free end of the bridge (4.2) in the solution. Connect the elctrodes to the potentiometer (4.1) and, after verifying the zero of the apparatus, note the value of the starting potential.

Titrate, using the microburette (4.4), adding initially 4 or 9 ml respectively of the silver nitrate solution corresponding to the standard reference potassium chloride solution used. Continue the addition in 0.1 ml portions for the 0.004 M solutions and in 0.05 ml portions for the 0.1 M solutions. After each addition, await the stabilisation of the potential.

Record the volumes added and the corresponding values of the potential in the first two columns of a table.

In a third column of the table, record the successive increments ($\Delta_1 E$) of the potential E. In a fourth column, record the differences ($\Delta_2 E$) positive or negative, between the potential increments ($\Delta_1 E$). The end of the titration corresponds to the addition of the 0.1 or 0.05 ml portion (V_1) of the silver nitrate solution which gives the maximum value of ($\Delta_1 E$).

In order to calculate the exact volume (Veq) of the silver nitrate solution corresponding to the end of the reaction, use the formula:

$$V_{eq} = V_1 + (V_1 \times \frac{h}{B})$$

where:

V_0 is the total volume, in ml, of the silver nitrate solution immediately lower than the volume which gives the maximum increment of $\Delta_1 E$;

V_1 is the volume, in ml, of the last portion of the silver nitrate solution added (0.1 or 0.05 ml);

b is the last positive value of $\Delta_2 E$;

B is the sum of the absolute values of the last positive values of $\Delta_2 E$ and the first negative value of $\Delta_2 E$ (see example in Table 1).

Blank test

(5.2) Carry out a blank test and take account thereof when calculating the final result.

The result V_4 of the blank test and take account thereof when calculating the final result.

$$V_4 = 2V_3 - V_2$$

where:

V_2 is the value, in ml, of the exact volume (Veq) of the silver nitrate solution corresponding to the titration of 10 ml of the potassium chloride standard reference solution used;

V_3 is the value, in ml, of the exact volume (Veq) of the silver nitrate solution corresponding to the titration of 5 ml of the potassium chloride standard reference solution used.

Check test

(5.3) The blank test can at the same time serve as a check that the apparatus is functioning satisfactorily and that the test procedure is being implemented correctly.

Determination

(5.4) Take a portion of sample in the range of 10 to 20 grams and weigh to the nearest 0.01 gram. Transfer quantitatively to a 250 ml beaker. Add 20 ml of water, 5 ml of nitric acid solution (3.2), 120 ml of acetone (3. 1) and sufficient water to bring the total volume to about 150 ml.

Place the rod of the magnetic stirrer (4.3) in the beaker, place the beaker on the stirrer and set the stirrer in motion. Immerse the silver electrode (4.1) and the free end of the bridge (4.2) in the solution, connect the electrodes to the potentiometler (4. 1) and, after having verified the zero of the apparatus, note the value of the starting potential.

Titrate with the silver nitrate solution, by additions from the microburette (4.4) in increments of 0.1 ml. After each addition, await the stabilisation of the potential.

Continue the titration as specified in 5. 1, starting from the fourth paragraph: “Record the volumes added and the corresponding values of the potential in the first two columns of a table….”.

EXPRESSION OF RESULTS

6. Express the result of the analysis as the percentage of chlorine contained in the sample as received for analysis.

Calculate the percentage of chlorine (CI) content from the formula:

$$Cl\% = \frac{0.03545 \times T \times (V_5 - V_4) \times 100}{m}$$

where:

T is the molarity of silver nitrate solution used;

V_4 is the result, in ml, of the blank test (5.2);

V_5 is the value, in ml, of Veq corresponding to the determination (5.4);

m is the mass, in grams, of the test portion.

Table 1

EXAMPLE

Volume of the silver nitrate solution V ml	Potential E mv	$\Delta_1 E$	$\Delta_2 E$
4.80	176		
4.90	211	72	35
5.00	283	72	+37
5.10	306	23	−49
5.20	319	13	−10

$$V_{eq} = 4.9 + 0.1 \times \frac{37}{37 - 49} = 4.943$$

G.Determination of Copper

SCOPE AND FIELD OF APPLICATION

1. This method defines the procedure for the determination of copper content of straight ammonium nitrate fertilisers containing more than 28% nitrogen by weight.

PRINCIPLE

2. The sample is dissolved in dilute hydrochloric acid and the copper content is determined by atomic absorption spectrophotometry.

REAGENTS

3.—(3.1) Hydrochloric acid (density at 20°C=1.18 g/ml).

(3.2) Hydrochloric acid, 6 M solution.

(3.3) Hydrochloric acid, 0.5 M solution.

(3.4) Ammonium nitrate.

(3.5) Hydrogen peroxide, 30%

(3.6) Copper solution(**2**) (stock): weigh, to the nearest 0.001 gram, 1 gram of pure copper, dissolve in 25 ml 6 M hydrochloric acid solution (3.2), add 5 ml of hydrogen peroxide (3.5) in portions and dilute to I litre with water. 1 ml of this solution contains 1,000,µg of copper (Cu).

(3.6.1) Copper solution (dilute): dilute 10 ml of stock solution (3.6) to 100 ml with water and then dilute 10 ml of the resulting solution to 100 ml with water. 1 ml of the final dilution contains 10µg of copper (Cu).

Prepare this solution at the time of use.

APPARATUS

4. Atomic absorption spectrophotometer with a copper lamp (324.8 nm).

PROCEDURE

Preparation of the solution for analysis

Preparation of the solution for analysis

5.—(5.1) Weigh, to the nearest O.OO1 gram, 25 grams of the sample, place it in a 400 ml beaker, add carefully 20 ml of hydrochloric acid (3.1) (there may be a vigorous reaction due to carbon dioxide formation). Add more hydrochloric acid, if necessary. When effervescence has stopped, evaporate to dryness on a steam bath, stirring occasionally with a glass rod. Add 15 ml 6 M hydrochloric acid solution (3.2) and 120 ml of water. Stir with the glass rod, which should be left in the beaker and cover the beaker with a watch glass. Boil the solution gently until dissolution is complete and then cool.

Transfer the solution quantitatively into a 250 ml graduated flask, by washing the beaker with 5 ml 6 M hydrochloric acid (3.2), and twice with 5 ml of boiling water, make up to the mark with 0.5 M hydrochloric acid (3.3) and mix carefully.

Filter through a copper-free filter paper(**3**), discarding the first 50 ml.

Blank solution

(5.2) Prepare a blank solution from which only the sample has been omitted and allow for this in the calculation of the final result.

Determination

Preparation of sample and blank test solutions

(5.3.1) Dilute the sample solution (5.1) and the blank test solution (5.2) with 0.5 M hydrochloric acid solution (3.3) to a concentration of copper within the optimal measuring range of the spectrophotometer. Normally no dilution is needed.

Preparation of the calibration solutions

(5.3.2) By diluting the standard solution (3.6.1) with 0.5 M hydrochloric acid solution (3.3), prepare at least five standard solutions corresponding to the optimal measuring range of the spectrophotometer (0 to 5.0 µ/l Cu). Before making up to the mark, add to every solution ammonium nitrate (3.4) to give a final concentration of 100 mg per ml.

Measurement

(**2**) Commercially available standard copper solution may be used.
(**3**) Whatman 541 or equivalent.

(5.4) Set up the spectrophotometer (4) at a wavelength of 324.8 nm using an oxidising air-acetylene flame. Spray successively, in triplicate, the calibration solutions (5.3.2), the sample solution and the blank solution (5.3.1), washing the instrument through with distilled water between each spraying. Plot the calibration curve using the mean absorbances of every standard used as the ordinates and the corresponding concentrations of copper in μ/ml as the abscissae.

Determine the concentration of copper in the final sample and blank solutions by reference to the calibration curve.

EXPRESSION OF RESULTS

6. Calculate the copper content of the sample taking into account the weight of the test sample, the dilutions carried out in the course of the analysis and the value of the blank. Express the result as mg Cu/kg.