SCHEDULE 2

METHODS OF ANALYSIS

PART I

14f.

DETERMINATION OF THE CHLORINE CONTENT (AS CHLORIDE ION)

1 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.

2 PRINCIPLE

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

3 REAGENTS

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

3.1 Acetone AR.

3.2 Concentrated nitric acid (density at 20°C p=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.

4 APPARATUS

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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) sulfate 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) sulfate electrodes are used.

4.3 etic stirrer, with a Teflon-coated rod.

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

5 PROCEDURE

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Standardisation of the silver nitrate solution

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 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 electrodes 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 value of the potential in the first two columns of a table.

In a third column of the table, record the successive increments (Δ_1E) of the potential E. In a fourth column, record the differences (Δ_2E) positive or negative, between the potential increments (Δ_1E). 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 Δ_1E.

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

$$Veq=Vo+V1\times bB$$

where:

V_o is the total volume, in ml, of the silver nitrate solution immediately lower than the volume which gives the maximum increment of Δ_1E;

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 Δ_2E;

B is the sum of the absolute values of the last positive value of 2E and the first negative value of 2E (see example in Table 1).

Blank test

5.2 Calculate the blank value using the equation below and take account thereof when calculating the final result.

The result V_4 of the blank test on the reagents is given, in ml, by the formula:

$$V_4 = 2V_3 - V_2$$

where:

V_2 is the value, in ml, of the exact volume (V_{eq}) 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 (V_{eq}) of the silver nitrate solution corresponding to the titration of 5 ml of the potassium chloride standard reference solutions 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.

5.4 Determination

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 potentiometer (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…’

6 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 (Cl) content from the formula:

Cl%=0.03545×T×(V5V4)×100m

where:

T is the molarity of silver nitrate solution used;

V4 is the result, in ml, of the blank test (5.2);

V5 is the value, in ml, of V_{eq} 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		
		35	
4.90	211		+ 37
		72	
5.00	283		− 49

Volume of the silver nitrate solution V ml	*Potential E mv*	*$\Delta_1 E$*	*$\Delta_2 E$*
		23	
5.10	306		− 10
		13	
5.20	319		

Vea=4.9+0.1×3737+494.943