INTERNATIONAL STANDARD ISO 3695

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION • МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ • ORGANISATION INTERNATIONALE DE NORMALISATION

Ammonium nitrate for industrial use – Determination of chloride ions content – Potentiometric method

Nitrate d'ammonium à usage industriel – Dosage des ions chlorure – Méthode potentiométrique

First edition – 1977-12-15

UDC 661.525 : 546.132 : 543.257

Ref. No. ISO 3695-1977 (E)

Descriptors : ammonium nitrate, chemical analysis, determination of content, chlorides, potentiometric analysis.

Price based on 4 pages

FOREWORD

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 3695 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in January 1975.

It has been approved by the member bodies of the following countries :

- Austria
- Belgium
- Brazil
- Bulgaria
- France
- Germany
- Hungary
- India
- Ireland
- Israel
- Italy
- Netherlands
- New Zealand
- Poland
- Portugal
- Romania
- South Africa, Rep. of
- Spain
- Switzerland
- Turkey
- United Kingdom
- U.S.S.R.
- Yugoslavia

No member body expressed disapproval of the document.

Printed in Switzerland

Ammonium nitrate for industrial use — Determination of chloride ions content — Potentiometric method

1 SCOPE

This International Standard specifies a potentiometric method for the determination of the chloride ions content of ammonium nitrate for industrial use.

2 FIELD OF APPLICATION

The method is applicable to products having chloride ions contents, expressed as chloride (Cl^-), equal to or greater than 0,000 2 % (*m/m*).

3 PRINCIPLE

Potentiometric titration of the chloride ions with silver nitrate solution in a nitric acid-acetone-water medium, using a silver measurement electrode and a calomel reference electrode.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Acetone.

4.2 Nitric acid, ρ approximately 1,40 g/ml, about 68 % (*m/m*) solution.

4.3 Silver nitrate, approximately 0,1 N solution.

Dissolve 8,5 g of silver nitrate in water in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Store this solution in a brown glass bottle.

4.4 Silver nitrate, approximately 0,01 N solution.

Take 50 ml of the silver nitrate solution (4.3), place in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

4.5 Silver nitrate, approximately 0,004 N solution.

Take 20 ml of the silver nitrate solution (4.3), place in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

4.6 Silver nitrate, approximately 0,001 N solution.

Take 5 ml of the silver nitrate solution (4.3), place in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

4.7 Potassium chloride, 0,1 N standard reference solution.

Weigh, to the nearest 0,000 1 g, 3,727 6 g of potassium chloride, previously dried for 1 h at about 130 °C and cooled in a desiccator. Dissolve in a little water, transfer the solution quantitatively to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution fresh.

4.8 Potassium chloride, 0,01 N standard reference solution.

Take 50,0 ml of the standard reference potassium chloride solution (4.7), place in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution fresh.

4.9 Potassium chloride, 0,004 N standard reference solution.

Take 20,0 ml of the standard reference potassium chloride solution (4.7), place in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

4.10 Potassium chloride, 0,001 N standard reference solution.

Take 5,0 ml of the standard reference potassium chloride solution (4.7), place in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

Prepare this solution at the time of use.

5 APPARATUS

Ordinary laboratory apparatus and

5.1 Potentiometric titration apparatus, comprising

5.1.1 Potentiometer, sensitivity 2 mV, covering the range − 500 to + 500 mV.

5.1.2 Calomel electrode, fitted with a safety reservoir, filled with saturated potassium chloride solution.

5.1.3 Bridge, containing a saturated potassium nitrate solution, connected to the calomel electrode (5.1.2), fitted at the ends with porous plugs.

NOTE — This bridge is not necessary if silver and mercury(I) sulphate electrodes are used.

5.1.4 Silver electrode.

NOTE — For the determination of chloride ions contents below 0,001 % *(m/m)*, use a silver electrode coated with a layer of silver chloride instead of the ordinary silver electrode. Prepare this electrode as follows : electrolyse a 0,1 N hydrochloric acid solution for about 30 min at a current density of 0,1 mA/cm^2, using a silver electrode (5.1.4) immersed to a depth of about 5 cm as the anode and a platinum electrode as the cathode. Thoroughly wash the prepared electrode first under running water for at least 24 h then with distilled water.

5.2 Magnetic stirrer, with a polytetrafluoroethylene (PTFE)-coated rod.

5.3 Microburette, with fine-pointed tip, graduated in 0,01 ml divisions.

6 PROCEDURE

Select the reagent solutions and test portion according to the expected chloride ions content, as indicated in the following table.

Expected chloride ions content, expressed as Cl$^-$ % *(m/m)*	Silver nitrate solution	Standard reference potassium chloride solution	Mass of test portion
From 0,000 2 up to and including 0,001	0,001 N (4.6)	0,001 N (4.10)	50 g, weighed to the nearest 0,01 g
Above 0,001 up to and including 0,01	0,004 N (4.5)	0,004 N (4.9)	20 to 10 g, weighed to the nearest 0,01 g
Above 0,01 up to and including 0,1	0,01 N (4.4)	0,01 N (4.8)	10 to 1 g, weighed to the nearest 0,001 g
Above 0,1	0,1 N (4.3)	0,1 N (4.7)	3 to 1 g, weighed to the nearest 0,001 g

6.1 Standardization of the silver nitrate solution

6.1.1 *Titration*

Take 5,00 ml and 10,00 ml of the appropriate standard reference potassium chloride solution and place in two low-form beakers of convenient capacity (for example 250 ml). Carry out the following titration on the contents of each beaker.

Add 5 ml of the nitric acid solution (4.2), 120 ml of the acetone (4.1) and sufficient water to bring the total volume to about 150 ml. Place the rod of the magnetic stirrer (5.2) in the beaker, place the beaker on the stirrer and set the stirrer in motion. Immerse the silver electrode (5.1.4) and the free end of the bridge (5.1.3) in the solution, connect the electrodes to the potentiometer (5.1.1) and, after having verified the zero of the apparatus, note the value of the starting potential.

Titrate, using the microburette (5.3), 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 0,2 ml portions for the 0,001 N solutions, in 0,1 ml portions for the 0,004 N solutions and in 0,05 ml portions for the 0,01 N and 0,1 N solutions. After each addition, await the stabilization of the potential.

Note 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, note the successive increments ($\Delta_1 E$) of the potential E. In a fourth column, note 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 0,2 or 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 (V_{EQ}) of the silver nitrate solution corresponding to the end of the reaction, use the formula

$$V_{EQ} = V_0 + V_1 \times \frac{b}{B}$$

where

V_0 is the total volume, in millilitres, 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 millilitres, of the last portion of the silver nitrate solution added (0,2 or 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 value of $\Delta_2 E$ and the first negative value of $\Delta_2 E$ (see example in annex A).

6.1.2 *Calculation of concentration of the solution*

The concentration, T, of the silver nitrate solution, expressed as a normality, is given by the formula

$$T = T_0 \times \frac{5}{V_2 - V_3}$$

where

T_0 is the concentration, expressed as a normality, of the standard reference potassium chloride solution used;

V_2 is the value, in millilitres, of V_{EQ} corresponding to the titration of 10 ml of the standard reference potassium chloride solution used;

V_3 is the value, in millimetres, of V_{EQ} corresponding to the titration of 5 ml of the standard reference potassium chloride solution used;

5 is the difference, in millilitres, between the two volumes of the standard reference potassium chloride solution used.

6.1.3 *Calculation of the blank test result*

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

$$V_4 = 2V_3 - V_2$$

where V_2 and V_3 have the same meaning as in 6.1.2.

6.2 Determination

6.2.1 *Test portion*

Weigh the test portion indicated in the table in clause 6 and transfer quantitatively into a low-form beaker of convenient capacity (for example 250 ml).

6.2.2 *Titration*

Add to the test portion (6.2.1) in the beaker, 20 ml of water, 5 ml of the nitric acid solution (4.2), 120 ml of the acetone (4.1) and sufficient water to bring the total volume to about 150 ml.

NOTE — For test portions of 50 g, dissolve in 35 ml of water; the final volume of the solution is about 160 ml. It is therefore not necessary to add water. The ratio of acetone/water is still favourable and permits a satisfactory titration.

Place the rod of the magnetic stirrer (5.2) in the beaker, place the beaker on the stirrer and set the stirrer in motion. Immerse the silver electrode (5.1.4) and the free end of the bridge (5.1.3) in the solution, connect the electrodes to the potentiometer (5.1.1) and, after having verified the zero of the apparatus, note the value of the starting potential.

Titrate with the silver nitrate solution corresponding to the test portion taken, by addition, from the microburette (5.3), of 0,2 ml portions for the 0,001 N solutions, of 0,1 ml portions for the 0,004 N solutions, and 0,05 ml portions for the 0,01 and 0,1 N solutions. After each addition, await the stabilization of the potential.

Continue the titration as specified in 6.1.1, starting from the fourth paragraph : "Note the volumes added and the corresponding values of the potential in the first two columns of a table . . ."

NOTE — If the chloride ions content is very low and therefore the volume of the appropriate silver nitrate solution used for the titration is less than approximately 1 ml, add to the test solution a known volume, exactly measured (for example 5,00 ml), of the corresponding standard reference potassium chloride solution. Take this addition into account in the calculation of the result.

7 EXPRESSION OF RESULTS

The chloride ions content, expressed as a percentage by mass of chloride (Cl^-), is given by the formula

$$(V_5 - V_4) \times T \times 0{,}035\,45 \times \frac{100}{m}$$

$$= \frac{3{,}545\, T\,(V_5 - V_4)}{m}$$

where

T is the concentration, expressed as a normality, of the silver nitrate solution used, determined according to 6.1.2;

V_4 is the result, in millilitres, of the blank test (6.1.3);

V_5 is the value, in millilitres, of V_{EQ} corresponding to the determination (6.2.2);

m is the mass, in grams, of the test portion (6.2.1);

0,035 45 is the mass, in grams, of chloride ions corresponding to 1 ml of exactly 1 N silver nitrate solution.

8 TEST REPORT

The test report shall include the following particulars :

a) the reference of the method used;

b) the results and the method of expression used;

c) any unusual features noted during the determination;

d) any operation not included in this International Standard, or regarded as optional.

ANNEX A

EXAMPLE

Volume of 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
		23	
5,10	306		– 10
		13	
5,20	319		

$$V_{EQ} = 4{,}9 + 0{,}1 \times \frac{37}{37 + 49} = 4{,}943$$

ANNEX B

ISO PUBLICATIONS RELATING TO AMMONIUM NITRATE FOR INDUSTRIAL USE

ISO 2364 – Determination of free acidity – Volumetric method.

ISO 2365 – Measurement of pH value – Potentiometric method.

ISO 2995 – Determination of matter insoluble in water – Gravimetric method.

ISO 3329 – Determination of content of sulphur compounds – Method by reduction and titrimetry.

ISO 3330 – Determination of ammoniacal nitrogen content – Titrimetric method after distillation.

ISO 3331 – Determination of total nitrogen content – Titrimetric method after distillation.

ISO 3695 – Determination of chloride ions content – Potentiometric method.

ISO 5791 – Determination of water content – Karl Fischer method.