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# INTERNATIONAL STANDARD 3693

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## Nitric acid for industrial use – Determination of chloride ions content – Potentiometric method

*Acide nitrique à usage industriel – Dosage des ions chlorure – Méthode potentiométrique*

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## FOREWORD

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International Standard ISO 3693 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in January 1975.

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# Nitric acid 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 nitric acid for industrial use.

## 2 FIELD OF APPLICATION

The method is applicable to products having chloride ions contents, expressed as chloride ( $\text{Cl}^-$ ), 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**,  $\rho$  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 the at 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) and 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 0,4 mA/cm<sup>2</sup>, 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 <sup>-</sup> % (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 millilitres, 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

$$V_4 = 2 V_3 - V_2$$

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 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, 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 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.

Introduce the rod of the magnetic stirrer (5.2) into 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 N 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 ( $\text{Cl}^-$ ), is given by the formula

$$\frac{(V_5 - V_4) \times T \times 0,035\,45 \times \frac{100}{m}}{3,545\,7} = \frac{3,545\,7 (V_5 - V_4)}{m}$$

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 :

- the reference of the method used;
- the results and the method of expression used;
- any unusual features noted during the determination;
- any operation not included in this International Standard, or regarded as optional.

## ANNEX A

## EXAMPLE

Volume of silver nitrate solution $V$	Potential $E$	$\Delta_1 E$	$\Delta_2 E$
ml	mV		
4,80	176		
4,90	211	35	+ 37
5,00	283	72	- 49
5,10	306	23	- 10
5,20	319	13	

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

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## ANNEX B

ISO 3693:1977  
**ISO PUBLICATIONS RELATING TO NITRIC ACID FOR INDUSTRIAL USE**  
<https://standards.iteh.ai/catalog/standards/sist/15c6556c-c461-4712-ad0b-d921d0224faa/iso-3693-1977>

- ISO 1980 – Determination of total acidity – Titrimetric method.
- ISO 1981 – Determination of nitrous compounds – Titrimetric method.
- ISO/R 1982 – Determination of iron content – 2,2'-Bipyridyl photometric method.
- ISO 1983 – Determination of sulphated residue on ignition – Gravimetric method.
- ISO 2990 – Evaluation of the nitric acid concentration by measurement of density.
- ISO 2991 – Determination of ammoniacal nitrogen content – Spectrophotometric method.
- ISO 3328 – Determination of sulphate content – Method by reduction and titrimetry.
- ISO 3693 – Determination of chloride ions content – Potentiometric method.

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