International Standard 6227

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

Chemical products for industrial use — General method for determination of chloride ions — Potentiometric method

Produits chimiques à usage industriel — Méthode générale de dosage des ions chlorure — Méthode potentiométrique

First edition — 1982-09-01

UDC 661 : 543.257.1 : 546.131 **Ref. No. ISO 6227-1982 (E)**

Descriptors : chemical compounds, chemical analysis, determination, ions, chlorine, potentiometric analysis, industrial products.

Price based on 8 pages

Foreword

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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 6227 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in August 1981.

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

Austria
Belgium
China
Egypt, Arab Rep. of
France
Germany, F. R.
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Korea, Rep. of
Netherlands
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Romania
South Africa, Rep. of
Switzerland
Thailand
United Kingdom
USSR

No member body expressed disapproval of the document.

Printed in Switzerland

Chemical products for industrial use — General method for determination of chloride ions — Potentiometric method

1 Scope

This International Standard specifies a general potentiometric method for the determination of chloride ions in solutions prepared from chemical products for industrial use.

The preparation of the test solution and any modifications to the general procedure should be dealt with in the specific International Standard for the chemical product to which the method is to be applied.

2 Field of application

The method is applicable to test solutions having chloride ion concentrations, expressed in milligrams per litre, of between 1 and 1 500. The method may be used to determine the total chlorine contained in chemical products after transforming it, if necessary, into chloride ions by a suitable process. The method has an absolute error, expressed as milligrams of chlorine, of 0,1 to 1 mg, according to the concentration of the standard volumetric solution used.

Under certain conditions, it is possible to determine bromide and iodide ions either simultaneously or separately. If chloride only is to be determined, bromide and iodide may be eliminated by the method described in annex C.

Cyanides, sulphides, thiocyanates, ammonium and iron(III) salts affect the determination; it is therefore necessary to eliminate them by suitable processes (see annex C).

3 Principle

Potentiometric titration of the chloride (Cl^-) ions with standard volumetric silver nitrate solution in an acid medium and in the presence of acetone, using a silver electrode or a chloride or silver ion-selective electrode (measuring electrode) and a calomel or a mercury(I) sulphate electrode (reference electrode). Other electrode pairs have been recommended (for example silver-platinum, calomel-platinum) but tests have shown that better potential increments are obtained with the electrode pairs indicated above.

NOTE — A manual procedure has been described, but automatic devices can obviously be used.

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 Potassium nitrate, solution saturated at room temperature.

4.4 Silver nitrate, solution, $c(AgNO_3) = 0{,}1$ mol/l approximately.

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

Store the solution in a dark glass bottle.

4.5 Silver nitrate, solution, $c(AgNO_3) = 0{,}01$ or 0,004 mol/l approximately.

Select the appropriate solution according to the information in the table relating to 6.1.

Prepare the selected solution at the time of use from the silver nitrate solution (4.4), diluting when required in a one-mark volumetric flask.

NOTE — If solution 4.4 is used directly, as indicated in the table relating to 6.1, it should be standardized according to the procedure specified in 6.2. If the solutions prepared from that specified in 4.4 are used (see 4.5), the calibration of solution 4.4 is not necessary. It is sufficient to standardize the solution selected in 4.5, in all cases according to the procedure specified in 6.2.

4.6 Potassium chloride, standard reference solution, $c(KCl) = 0{,}1$ mol/l exactly.

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 and transfer the solution quantitatively into a 500 ml one-mark volumetric flask. Dilute to the mark and mix.

This solution shall not be kept for more than one month.

4.7 Potassium chloride, standard reference solution $c(\mathrm{KCl}) = 0{,}01$ or 0,004 mol/l exactly.

Use the solution of concentration corresponding to that of the silver nitrate solution selected for the titration.

Prepare this solution at the time of use from the standard reference potassium chloride solution (4.6), diluting when required in a one-mark volumetric flask.

5 Apparatus

Ordinary laboratory apparatus and

5.1 Potentiometric titration apparatus, comprising :

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

5.1.2 Reference electrodes.

5.1.2.1 Calomel electrode, fitted with a reservoir filled with saturated potassium chloride solution, or

5.1.2.2 Mercury(I) sulphate electrode.

5.1.3 Bridge, containing some of the saturated potassium nitrate solution (4.3), connected to the calomel electrode (5.1.2.1) and fitted with porous diaphragms at the ends, to be used only if a calomel electrode is used.

5.1.4 Measuring electrodes.

5.1.4.1 Silver electrode, or

5.1.4.2 Chloride or **silver ion-selective electrode.**

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

5.3 Burettes with a fine-pointed tip, graduated in 0,02 or 0,01 ml divisions.

6 Procedure

6.1 Test portion and preparation of the test solution

Weigh a mass of the test sample and prepare the test solution following the procedure specified in the International Standard relating to the product to which the method is to be applied, taking care that the chloride ion concentration in the test solution, expressed in milligrams per litre, is between 1 and 1 500.

According to the expected chloride ion content, use either all the test solution or a suitable aliquot portion and, for the titration, a silver nitrate solution of appropriate concentration as indicated, for example only, in the table below.

6.2 Determination of the blank test and standardization of the selected silver nitrate solution

6.2.1 Preparation of the blank test solution

At the same time as the determination (6.3), carry out a blank test using the same quantities of all the reagents used for the preparation of the test solution but omitting the test portion. Adjust the volume of the solution to the same as that of the test solution.

NOTE — If all the test solution is taken for the determination, prepare the blank test solution in duplicate in order to carry out the two titrations envisaged in 6.2.2 and 6.2.3.

6.2.2 Preparation of the solution to be standardized

Place the blank test solution (6.2.1) or an aliquot portion of volume equal to that used for the determination (see the table relating to 6.1) in a beaker of suitable capacity. Add, using one of the burettes (5.3), 5,00 ml of the appropriate standard reference potassium chloride solution (4.6 or 4.7).

If the resulting solution is alkaline, neutralize it using the nitric acid solution (4.2), cooling if necessary, and then add an excess of 2 ml of this acid.

Table

Expected $\mathrm{Cl^-}$ concentration in test solution	Aliquot portion to be used		Concentration of solution $c(\mathrm{AgNO_3})$
	Volume	Corresponding mass of $\mathrm{Cl^-}$	
mg/l	ml	mg	mol/l
1 to 20	50*	0,05 to 1	0,004
20 to 50	20	0,4 to 1	
50 to 250	20	1 to 5	0,01
250 to 1 500	50	12,5 to 75	0,1

* Use the method of controlled additions (see the note in 6.3.1).

Add to the beaker such a quantity of the acetone (4.1) as will give a ratio of acetone to aqueous solution preferably equal to 80/10 (V/V) but, in any case, not lower than 50/50 (V/V). However, if the concentration of the silver nitrate solution to be used is greater than $c(AgNO_3) = 0{,}01$ mol/l, the acetone can be omitted.

NOTE — The solution to be titrated should have a volume of at least 50 ml to avoid attack of the silver electrode by the nitric acid solution.

6.2.3 Titration

Introduce into the beaker a magnetic stirrer rod (5.2), place the beaker on the stirrer and set it in motion. Introduce in the solution the measuring electrode (5.1.4) and the reference electrode (5.1.2). If, however, a calomel electrode (5.1.2.1) is to be used, introduce one end of the bridge (5.1.3) instead of the reference electrode and immerse the other end in a beaker of water containing the calomel electrode. Connect the electrodes to the potentiometer (5.1.1) and note the initial value of the potential, after having checked the zero setting of the instrument.

Titrate, using a second burette (5.3), adding the silver nitrate solution — corresponding to the same concentration of the standard reference potassium chloride solution used — in 0,1 ml increments for the 0,004 mol/l solution and in 0,05 ml increments for 0,01 and 0,1 mol/l solutions. After each addition, wait for the potential to reach a steady value.

Note, in the first two columns of a table, the successive volumes added and the corresponding potentials.

In a third column, 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 ml, 0,1 ml or 0,05 ml (V_1) of the silver nitrate solution, which gives the maximum value of $\Delta_1 E$.

The exact volume (V_{EQ}) of the silver nitrate solution corresponding to the end of the reaction is given by the formula

$$V_{EQ} = V_0 + \left(V_1 \times \frac{b}{B}\right)$$

where

V_0 is the volume, in millitres, of the silver nitrate solution which had been added before addition of the increment which gave the maximum value of $\Delta_1 E$;

V_1 is the volume, in millilitres, of the silver nitrate solution corresponding to the last increment added (0,2 or 0,1 or 0,05 ml, according to the solution used);

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 the example in annex A).

Repeat the operations specified in 6.2.2 and 6.2.3, this time using 10,00 ml instead of 5,00 ml, of the standard reference potassium chloride solution.

NOTE — If the expected titration is known approximately, most of the titrant can be added as one increment. Thus, in the particular case, for the 5,00 ml of the standard reference potassium chloride solution, 4 ml and for the 10,00 ml, 9 ml of the titrant can be added immediately.

6.2.4 Calculation of concentration of the solution

The concentration of the silver nitrate solution, expressed as moles of AgNO$_3$ per litre, is given by the formula

$$c(AgNO_3) = c(KCl) \times \frac{5}{V_2 - V_3}$$

where

$c(KCl)$ is the concentration, in moles of KCl per litre, 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, in the presence of the blank test solution;

V_3 is the value, in millilitres, of V_{EQ} corresponding to the titration of 5 ml of the standard reference potassium chloride solution, in the presence of the blank test solution;

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

6.2.5 Calculation of value of blank test

The value of the reagent blank test, V_4, is given, in millilitres, by the formula

$$V_4 = 2\,V_3 - V_2$$

where V_2 and V_3 are as defined in 6.2.4.

6.3 Determination

6.3.1 Preparation of the solution to be titrated

Introduce a suitable amount of the test solution (see the table in 6.1) in a beaker. Further proceed as specified in 6.2.2, starting from the second paragraph ("If the resulting solution is alkaline . . .").

NOTE — If the chloride ion content is very low, that is if the volume of the silver nitrate solution of suitable normality intended for the determination is less than about 1 ml, add to the solution to be titrated a known and exactly measured volume (for example 5,0 ml) of the standard reference potassium chloride solution of the same normality. Take this addition into account in the calculation of the results.

The addition, as an example, of 5,00 ml of the standard reference solution enables the titration already carried out in 6.2.3 in the presence of the blank test solution as indicated in 6.2.2 to be used.

6.3.2 Titration

Titrate the solution obtained in 6.3.1 with the standard volumetric silver nitrate solution of appropriate concentration (see, for example, the table concerning 6.1), following the procedure specified in 6.2.3.

This volume is designated V_5.

7 Expression of results

The mass, in grams, of chloride, expressed as chlorine (Cl), in the test solution, is given by the formula

$$(V_5 - V_4) \times c \times 0{,}035\,45 \times r_D$$

where

V_5 is the volume, in millilitres, of V_{EQ} corresponding to the determination (6.3.2);

V_4 is the value, in millilitres, of the blank test on the reagents (6.2.5);

c is the actual concentration, in moles per litre, of the silver nitrate solution used for the determination (6.2.4);

r_D is the ratio between the volume of the test solution and the volume of the aliquot portion taken for the determination;

0,035 45 is the mass, in grams, of chlorine (Cl) corresponding to 1 ml of the silver nitrate solution, c = 1 mol/l exactly.

NOTE — In the case of the method by addition (see note to 6.3.1), by using an addition of 5,00 ml of the standard reference potassium chloride solution the formula becomes

$$(V_5 - V_3) \times c \times 0{,}035\,45 \times r_D$$

where

V_5, c, 0,035 45 and r_D have the same values as in the formula above, and

V_3 is the volume, in millilitres, defined in 6.2.4.

The International Standard relating to the product in question will give the formula to be applied for the calculation.

8 Test Report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the general method used and to the International Standard relating to the product being analysed (see annex D);

c) the results and the method of expression used;

d) any unusual features noted during the determination;

e) any operation not included in this International Standard or in the International Standard relating to the product being analysed, or regarded as optional.

Annex A

Example

(Electrode pair : silver-calomel)

Volume of silver nitrate solution $c(AgNO_3) = 0{,}01$ mol/l V	Potential E	$\Delta_1 E$	$\Delta_2 E$
ml	mV	mV	mV
4,80	140		
		8	
4,85	148		+ 5
		13	
4,90	161		+ 6
		19	
4,95	180		+40
		59	
5,00	239		−19
		40	
5,05	279		−16
		24	
5,10	303		

$$V_{EQ} = 4{,}95 + \left(0{,}05 \times \frac{40}{40 + 19}\right) = 4{,}984$$

Annex B

Methods of mineralization of organic products for the determination of total chlorine

B.0 This annex is not comprehensive. The following methods may be suitable for preparing test solutions for the determination of total chloride in organic chemicals.

B.1 Preliminary hydrolysis in an aqueous solution, in an alkaline medium.

The method is applicable to aliphatic hydrocarbons.

B.2 Combustion in a Grote apparatus, which comprises a silica tube fitted with two fritted silica discs and a third pierced plate. The end of the tube is connected to an absorbent flask with a porous plate. Combustion is carried out in a current of air or oxygen.

The method is applicable to all organic products, especially liquids and gaseous compounds.

B.3 Combustion in the Wickbold apparatus, which comprises a silica tube fitted with a condenser and an absorber. The apparatus shall be fitted with a safety device to prevent flashback and with three flowmeters for the oxygen and hydrogen.

The method is applicable to volatile liquid and gaseous products.

B.4 Combustion in the Berthelot-Mahler-Krœcker bomb calorimeter, under pressurized oxygen.

The method is applicable to liquid and solid products.

B.5 Fusion of the test portion with anhydrous sodium carbonate in a platinum crucible or dish.

This method is applicable to non-volatile compounds.

B.6 Prolonged boiling with anhydrous propan-2-ol and metallic sodium, according to Stepanow.

B.7 Combustion in a bomb with sodium peroxide (the Parr bomb or its equivalent). In this method, the test portion is limited to about 200 to 300 mg.

B.8 Fusion of the test portion with Eschka mixture.

The method is applicable to non-volatile products.

B.9 Combustion in an oxygen medium in a Schœniger flask. In this method, the mass of the test portion is very limited.

Which method is chosen depends on the nature of the organic products to be analysed and of their physical state (solid, liquid or gaseous). Furthermore, the mass of the test portion to be mineralized depends on the expected chlorine content of the sample.

Annex C

Interferences

C.0 Introduction

This annex is not comprehensive. A check for possible interferences should always be carried out. Furthermore, the treatments in clauses C.1 to C.4 may not cover all possible cases.

C.1 Other halogens

All halogens (except for fluorine) may be determined at the same time. If their contents are all of the same order, iodide, bromide and chloride can be determined simultaneously, taking advantage of the different potential end-points. The order of titration is : iodide, bromide and finally chloride.

NOTE — Because of the possible formation of mixed crystals the separation chloride/bromide is not an exact stoichiometric one.

If only the chloride has to be titrated, the bromides and iodides may be eliminated beforehand by oxidation (for example with hydrogen peroxide) in a dilute nitric acid medium, followed by extraction with a suitable solvent.

C.2 Oxidizing agents

Oxidizing agents may oxidize the silver electrode. They can be destroyed by treatment with sodium sulphite, with ascorbic acid solution or with other reducing agents that do not affect the determination.

C.3 Ammonium and iron(III) salts

If present in large quantities, these salts can reduce the difference in potential $\Delta_1 E$ approaching the equivalence point. The influence of these salts may be eliminated by boiling in sodium hydroxide medium in presence of hydrogen peroxide, filtration of the precipitated iron(III) hydroxide, redissolution of the precipitate in a small quantity of nitric acid and second precipitation of iron(III) under the same conditions. After filtration, the precipitate is discarded and the combined filtrate acidified with nitric acid solution.

Interference by iron(III), if present in small quantities, can also be eliminated by complexing, for example, with EDTA.

C.4 Cyanides, thiocyanates and sulphides

These ions interfere by competing for silver in the titration. They can be eliminated by oxidation in sodium hydroxide medium with hydrogen peroxide and prolonged boiling.