International Standard 5790

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Inorganic chemical products for industrial use — General method for determination of chloride content — Mercurimetric method

Produits chimiques inorganiques à usage industriel — Méthode générale de dosage des chlorures — Méthode mercurimétrique

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Foreword

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Inorganic chemical products for industrial use — General method for determination of chloride content — Mercurimetric method

1 Scope

This International Standard specifies a general mercurimetric method for the determination of chloride content.

2 Field of application

The method is applicable to inorganic chemical products for industrial use. It enables quantities of chloride (Cl^-) exceeding 1 mg in the test portion to be determined with an absolute error of 0,2 to 0,5 mg, according to the concentration of the standard volumetric solution used.

The determination is not affected by the elements or compounds listed in annex A when they are present in quantities up to the specified limits.

In certain cases, this annex contains instructions for the treatment to be applied to reduce or eliminate interferences.

3 Principle

Conversion of Cl^- ions into weakly ionized mercury(II) chloride, using highly ionized standard volumehric mercury(II) nitrate solution. Detection of the end-point by reaction of the excess of mercury(II) nitrate with 1,5-diphenylcarbazone used as an indicator, by the appearance of a violet colour.

4 Reagents

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

4.1 Nitric acid, $\varrho \approx 1{,}40$ g/ml, approximately 68 % (*m*/*m*) solution, of which the chloride content, expressed as chlorine (Cl), is not greater than 0,5 mg/kg.

4.2 Nitric acid, approximately 126 g/l solution, prepared by dilution of the nitric acid solution (4.1).

4.3 Sodium hydroxide, approximately 80 g/l solution of which the chloride content, expressed as chlorine (Cl) is not greater than 5 mg/kg.

4.4 Sodium chloride, standard reference solution, $c(\mathrm{NaCl}) = 0{,}1$ mol/l[1].

Weigh, to the nearest 0,000 1 g, 5,844 2 g of sodium chloride, previously dried for 1 h at approximately 500 °C and cooled in a desiccator, and dissolve in water. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

4.5 Sodium chloride, standard reference solution, $c(\mathrm{NaCl}) = 0{,}05$ mol/l[2].

Place 100,0 ml of the standard reference solution (4.4) in a 200 ml one-mark volumetric flask, dilute to the mark and mix.

4.6 Sodium chloride, standard reference solution, $c(\mathrm{NaCl}) = 0{,}02$ mol/l[3].

Place 100,0 ml of the standard reference solution (4.4) in a 500 ml one-mark volumetric flask, dilute to the mark and mix.

4.7 Standard end-point matching solution.

Prepare this solution at the time of use. Do not use the solution for more than 30 min after preparation.

Place the same volume of water as in the test solution (6.2.1) in a 500 ml conical flask, add 3 drops of the bromophenol blue solution (4.11) and the nitric acid solution (4.2), drop by drop, until the colour changes from blue to yellow. Add an excess of 3 drops of this acid, 0,5 to 1,0 ml of the diphenylcarbazone solution (4.12) and, from the burette (5.1), the minimum volume of the standard volumetric mercury(II) nitrate solution (4.8, 4.9 or 4.10) necessary to change the colour of the solution from yellow to mauve.

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[1] Previously 0,1 N

[2] Previously 0,05 N

[3] Previously 0,02 N

4.8 **Mercury(II) nitrate,** standard volumetric solution, $c[1/2\ Hg(NO_3)_2.H_2O] = 0{,}1$ mol/l[1].

Use this solution to determine quantities greater than 20 mg of chloride (Cl^-) in the test portion.

4.8.1 Preparation of the solution

Weigh 10,85 ± 0,01 g of mercury(II) oxide (HgO) and dissolve in 10 ml of the nitric acid solution (4.1). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

NOTE — This solution may also be prepared by dissolution of a mass of 17,13 g of mercury(II) nitrate monohydrate $[Hg(NO_3)_2.H_2O]$ in water acidified with 1 ml of the nitric acid solution (4.1).

Standardize this solution following the procedure specified in 4.8.2 and adjust it, if necessary, to exactly 0,1 mol/l.

4.8.2 Standardization of the solution

Place 40,0 ml of the standard reference sodium chloride solution (4.4), 160 ml of water and 3 drops of the bromophenol blue solution (4.11) in a 500 ml conical flask. Add the nitric acid solution (4.2), drop by drop, until the colour of the indicator changes from blue to yellow and then add an excess of 3 drops of this acid and the volume of the diphenylcarbazone solution (4.12) added for the standard end-point matching solution (4.7). Titrate (see note in 6.2.2) with the mercury(II) nitrate solution (4.8.1) to be standardized until the colour matches the mauve of the standard end-point matching solution and deduct the volume of the mercury(II) nitrate solution (4.8.1) added during the preparation of this standard end-point matching solution (generally 1 drop).

The volume corresponding to exactly 0,1 mol/l is 40,0 ml.

NOTE — Store the residual solution obtained from the titration and treat it as specified in annex B, so as to avoid the pollution of waste water by the mercury.

4.9 **Mercury(II) nitrate,** standard volumetric solution, $c[1/2\ Hg(NO_3)_2.H_2O] = 0{,}05$ mol/l[2].

Use this solution to determine quantities between 1 and 20 mg of chloride (Cl^-) in the test portion.

4.9.1 Preparation of the solution

Use one of the two following methods :

- dilute 100 ml of the solution (4.8.1) to the mark in a 200 ml one-mark volumetric flask and mix, or
- weigh 5,43 ± 0,01 g of mercury(II) oxide (HgO) and dissolve in 10 ml of the nitric acid solution (4.1). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix. [See note in 4.8.1 for the use of 8,565 g of mercury(II) nitrate monohydrate.]

Standardize this solution following the procedure specified in 4.9.2 and adjust it, if necessary, to exactly 0,05 mol/l.

4.9.2 Standardization of the solution

Place 10,0 ml of the standard reference sodium chloride solution (4.5), 190 ml of water and 3 drops of the bromophenol blue solution (4.11) in a 500 ml conical flask. Add the nitric acid solution (4.2), drop by drop, until the colour of the indicator changes from blue to yellow and then add an excess of 3 drops of this acid and the volume of the diphenylcarbazone solution (4.12) added for the standard end-point matching solution (4.7). Titrate (see note in 6.2.2) with the mercury(II) nitrate solution (4.9.1) to be standardized until the colour matches the mauve of the standard end-point matching solution and deduct the volume of the mercury(II) nitrate solution (4.9.1) added during the preparation of this standard end-point matching solution (generally 2 drops).

The volume corresponding to exactly 0,05 mol/l is 10,00 ml.

4.10 **Mercury(II) nitrate,** standard volumetric solution, $c(1/2\ Hg(NO_3)_2.H_2O] = 0{,}02$ mol/l[3].

Analysts who can easily detect the diphenylcarbazone colour change can take advantage of this solution to determine quantities between 1 and 5 mg of chloride (Cl^-) in the test portion.

4.10.1 Preparation of the solution

Use one of the two following methods :

- dilute 100 ml of the solution (4.8.1) to the mark in a 500 ml one-mark volumetric flask and mix, or
- weigh 2,18 ± 0,01 g of mercury(II) oxide (HgO) and dissolve in 10 ml of the nitric acid solution (4.1). Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix. [See note in 4.8.1 for the use of 3,43 g of mercury(II) nitrate monohydrate.]

Standardize this solution following the procedure specified in 4.10.2 and adjust it, if necessary, to exactly 0,02 mol/l.

4.10.2 Standardization of the solution

Place 5,00 ml of the standard reference sodium chloride solution (4.6), 195 ml of water and 3 drops of the bromophenol blue solution (4.11) in a 500 ml conical flask. Add the nitric acid solution (4.2), drop by drop, until the colour changes from blue to yellow and then add an excess of 3 drops of this acid and the volume of the diphenylcarbazone solution (4.12) added for the standard end-point matching solutuon (4.7). Titrate (see note in 6.2.2) with the mercury(II) nitrate solution to be standardized

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[1] Previously 0,1 N

[2] Previously 0,05 N

[3] Previously 0,02 N

(4.10.1) until the colour matches the mauve of the standard ent-point matching solution and deduct the volume of the mercury(II) nitrate solution (4.10.1) added during the preparation of this standard end-point matching solution.

The volume corresponding to exactly 0,02 mol/l is 5,00 ml.

4.11 Bromophenol blue, 1 g/l solution in 95 % (*V*/*V*) ethanol.

4.12 1,5-Diphenylcarbazone, 5 g/l solution in 95 % (*V*/*V*) ethanol.

Store this solution in a refrigerator and replace it when it no longer gives a sharp colour change.

5 Apparatus

Ordinary laboratory apparatus, and

5.1 Burette, of capacity 50 ml, complying with the requirements of class A of ISO/R 385, having a fine point enabling 30 drops per millilitre to be delivered.

6 Procedure

6.1 Test portion

Weigh a quantity of the test sample not exceeding 10 g, containing between 1 and 175 mg of chloride (Cl^-) and not containing more than one of the interferences listed in annex A, clause A.1, or all of the interferences listed in annex A, clause A.2.

6.2 Determination

6.2.1 Preparation of the test solution

Transfer the test portion (6.1) to a 500 ml conical flask and, according to the solubility of the sample, add between 50 and 350 ml of water. Neutralize it with care using the nitric acid solution (4.1) or the sodium hydroxide solution (4.3). Dilute, if necessary, to obtain in the conical flask a volume between 200 and 350 ml, cool to room temperature, add 3 drops of the bromophenol blue solution (4.11) and then add successively :

- the nitric acid solution (4.2), if necessary, until the colour changes to yellow;
- the sodium hydroxide solution (4.3), drop by drop, until the colour changes to blue;
- the nitric acid solution (4.2) until the colour changes to yellow;
- an excess of 3 drops of this acid (4.2).

6.2.2 Titration of the test solution

Add to the test solution (6.2.1) the volume of the diphenylcarbazone solution (4.12) added for the standard end-point matching solution (4.7) and titrate with the appropriate standard volumetric mercury(II) nitrate solution (4.8, 4.9 or 4.10) until the colour matches the mauve of the standard end-point matching solution.

NOTE — Stir gently during the titration so as to avoid the formation of foam which may absorb the indicator and thereby obscure the colour change.

Add the standard volumetric solution slowly and reduce the speed of flow sharply towards the end of the titration so as to enable the last traces of chloride to react with the mercury(II) nitrate solution.

Store the residual solutions obtained from the titration and treat them as specified in annex B, so as to avoid the pollution of waste water by the mercury.

7 Expression of results

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

$$(V_0 - V_1) \times c \times 0{,}035\,453 \times \frac{100}{m}$$

$$= \frac{3{,}545\,3\,(V_0 - V_1)\,c}{m}$$

where

V_0 is the volume, in millilitres, of the standard volumetric mercury(II) nitrate solution (4.8, 4.9 or 4.10) used for the determination;

V_1 is the volume, in millilitres, of the standard volumetric mercury(II) nitrate solution (4.8, 4.9 or 4.10) used for the preparation of the standard end-point matching solution (4.7);

c is the concentration, expressed in moles per litre, of the standard volumetric mercury(II) nitrate solution used (see 4.8.2, 4.9.2 or 4.10.2);

m is the mass, in grams, of the test portion (6.1);

0,035 453 is the mass, in grams, of chlorine corresponding to 1 ml of mercury(II) nitrate solution $c[1/2\ Hg(NO_3)_2.H_2O]$ = 1 mol/l[1] exactly.

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[1] Previously 1 N

8 Test report

The test report shall include the following particulars :

a) an identification of the sample;

b) the reference of the method used;

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 regarded as optional.

Annex A

Table of interferences

A.1 Interferences present separately

Element or compound		Limit of non-interference	Reason for the limit and possible remedy
$NaNO_3$		100 g/l	
KNO_3		100 g/l	
NO_3^-		70 g/l	
SO_4^{2-}		70 g/l	Slight buffer effect (see A.3.1)
SO_3^{2-}	1)	1,5 mg/l	Complexes with Hg
	2)	3 g/l	After oxidation by HNO_3 or by H_2O_2 (see A.3.2)
S^{2-}	1)	1 mg/l	Precipitation of HgS
	2)	2 g/l	After oxidation by H_2O_2 (see A.3.3)
SiO_2		1 g/l	Inhibits formation of $HgCl_2$
CO_2		70 g/l	Neutralized carbonates release CO_2 the presence of which does not interfere
CH_3COONa		2 g/l	Colour change less sharp, even with controlled pH
CrO_4^{2-}	1)	1 mg/l	Diphenylcarbazone oxidized
	2)	50 mg/l	If titration is carried out immediately (see A.3.4)
F^-	1)	100 mg/l	Progressive colour change by intermediate formation of HgF_2
	2)	1 g/l	After precipitation of AlF_3 (excess of Al : max. 1 g/l)
Br^-		< 1 mg/l	Titrated as Cl^-
I^-		< 1 mg/l	Titrated as Cl^-
H^+		pH between 2,5 and 3,0	At pH < 2,5 : high results At pH > 3,0 : low results
Na^+		30 g/l	
K^+		40 g/l	
Fe^{2+}	1)	100 mg/l	Formation of insoluble hydroxide
	2)	1 g/l	After redissolution of the insoluble matter (see A.3.5)
Fe^{3+}	1)	10 mg/l	Formation of insoluble coloured hydroxide
	2)	100 mg/l	In the presence of 5 g of $Na_4P_2O_7 . 10H_2O$ per litre
Ca^{2+}		100 g/l	
Mg^{2+}		40 g/l	Saturation

A.1 (*concluded*)

Element or compound	Limit of non-interference	Reason for the limit and possible remedy
Al^{3+}	1 g/l	Precipitation of $Al(OH)_3$, adsorbing the indicator
Zn^{2+}	100 g/l	
Pb^{2+}	100 g/l	
Ni^{2+}	2,5 g/l	Own coloration
Cr^{3+}	200 mg/l	Own coloration (see A.3.6)
Cu^{2+}	200 mg/l	Colour reaction with the diphenylcarbazone
Mn^{2+}	500 mg/l	Precipitation of $Mn(OH)_2$ and $MnO_2.H_2O$
Co^{2+}	1 g/l	Own coloration
Hg^{2+}	0,5 mg/l	Complexes Cl^-
Ag^+	0,5 mg/l	Precipitation of AgCl
PO_4^{3-} 1)	3,5 g/l	Buffer effect
2)	> 10 g/l	After adjustment of pH between 2,5 and 3
NH_4^+ 1)	300 mg/l	Complexes Hg^{2+}
2)	> 1 g/l	After boiling in presence of NaOH

A.2 Interferences present together

Element or compound	Limit of non-interference	Reason for limit	Remedy
SiO_2	1 g/l	Adsorbent precipitate	Addition of 5 g of $Na_4P_2O_7.10H_2O$ per litre. In these conditions, slight cloudiness remains which causes only slight interference (accuracy of colour change reduced by half).
Al^{3+}	1 g/l	Adsorbent precipitate	
Zn^{2+}	1 g/l	Adsorbent precipitate	
Mg^{2+}	1 g/l	Adsorbent precipitate	
Fe^{3+}	0,05 g/l		
Mn^{2+}	0,05 g/l		
Cu^{2+}	0,02 g/l		
Ni^{2+}	0,02 g/l		
Cr^{3+}	0,02 g/l		
Co^{2+}	0,02 g/l		

A.3 Remedy for interferences

A.3.1 Sulphate ion (SO_4^{2-}) interference

Neutralization is difficult owing to a buffer effect. To change from blue to colourless, 2 drops of the nitric acid solution (4.2) are sufficient, but a further 10 to 15 drops are required to change from colourless to pale yellow.

A.3.2 Sulphite ion (SO_3^{2+}) interference

A.3.2.1 Oxidation by nitric acid (HNO_3)

Neutralize with the nitric acid solution (4.1) and add 5 ml in excess. Boil for 5 min, cool and neutralize. Carry out a blank test under the same conditions.

A.3.2.2 Oxidation by hydrogen peroxide (H_2O_2)

Neutralize, add 1 ml of the sodium hydroxide solution (4.3), 10 ml of a 30 % (*m*/*m*) hydrogen peroxide solution and 2 ml of a 0,5 g/l solution of cobalt dinitrate hexahydrate [$Co(NO_3)_2.6H_2O$]. Heat gently to initiate decomposition and, when complete, add several glass beads, boil for 5 min, cool and neutralize with the nitric acid solution (4.2). Carry out a blank test under the same conditions.

A.3.3 Sulphide ion (S^{2-}) interference

See A.3.2.2.

A.3.4 Chromate ion (CrO_4^{2-}) interference

Titrate within 2 min of adding the diphenylcarbazone solution (4.12) or add the indicator immediately prior to titration.

The pink colour does not affect detection of the colour change by an alert analyst.

A.3.5 Iron(II) ion (Fe^{2+}) interference

Up to a level of 1 g/l, a precipitate appears on neutralization but re-dissolves after the addition of 2 drops of the nitric acid solution (4.2).

The slight yellow colour does not affect detection of the colour change.

A.3.6 Chromium(III) ion (Cr^{3+}) interference

Up to a level of 200 mg/l, the neutralization, which is not possible in the presence of bromophenol blue, may be carried out by adding the sodium hydroxide solution (4.3) until green-yellow and then the nitric acid solution (4.2) until grey-blue, followed by an excess of 3 drops of this acid.

Annex B

Removal of mercury from residual solutions obtained from mercurimetric titrations

B.1 Scope and field of application

This annex specifies a method for removing mercury from solutions obtained by the use of the mercurimetric method for the determination of chloride content, in order to prevent pollution of waste water.

This procedure is recommended principally if titrations using the mercury(II) nitrate solution (4.8) have been carried out.

B.2 Principle

Collection of the residual solutions in a container of sufficient capacity (for example 50 litres).

Precipitation of mercury in an alkaline medium with excess sodium sulphide.

Oxidation of this excess by hydrogen peroxide to prevent the mercury from re-dissolving in the form of polysulphides.

Decantation and filtration of the mercury-free solution before disposal to waste.

Transfer of the insoluble residues to a storage container with a view to subsequent recovery of the mercury by specialist firms.

B.3 Reagents

Use reagents of technical quality.

B.3.1 ***Di*****sodium sulphide nonahydrate,** ($Na_2S.9H_2O$).

B.3.2 Hydrogen peroxide, approximately 30 % (*m/m*) solution.

B.3.3 Sodium hydroxide, approximately 400 g/l solution.

B.4 Apparatus

B.4.1 Polyethylene container, of sufficient capacity (approximately 50 litres).

B.4.2 Small laboratory pump or water pump, with a suction tube the end of which is fitted with a sintered glass disc of porosity P16 (pore size diameter 4 to 16 µm) or a funnel containing cotton wool.

B.5 Procedure

Pour into the container (B.4.1) the residual solutions obtained from the mercurimetric titrations and having a mercury content sufficiently high to pollute the drain water.

When the volume collected has reached approximately 40 litres, add successively, mixing by means of compressed air, 400 ml of the sodium hydroxide solution (B.3.3), 100 g of the sodium sulphide (B.3.1) and, after 10 min, slowly, 400 ml of the hydrogen peroxide solution (B.3.2).

Allow to stand for 24 h, then draw off the clear liquid using the pump (B.4.2) and discard as drain water.

Rinse the container several times with a quantity of water sufficient to transfer the insoluble substances into another container into which the insoluble substances obtained from subsequent operations are collected.

Bibliography

MIMA, Margaret J., Safe and Simple Method for the Disposal of Mercury-Containing Wastes from Kjeldahl Analyses, 2250 *Analytical Chemistry*, vol. 46, No. 14, December 1974.

Annex C

Other publications of ISO/TC 47 relating to determination of chloride content by mercurimetry

ISO 742 — Sodium carbonate for industrial use.

ISO 981 — Sodium hydroxide for industrial use.

ISO 992 — Potassium hydroxide for industrial use.

ISO 2201 — Sodium hydrogen carbonate for industrial use.

ISO 2463 — Sodium chlorate for industrial use.

ISO 2481 — Sodium chloride for industrial use.

ISO 3121 — Boric acid, boric oxide and disodium tetraborates for industrial use.

ISO 3236 — Sodium sulphate for industrial use.