INTERNATIONAL STANDARD 4323

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Soaps — Determination of chloride content — Potentiometric method

Savons — Dosage des chlorures — Méthode potentiométrique

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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 4323 was developed by Technical Committee ISO/TC 91, *Surface active agents*, and was circulated to the member bodies in August 1975.

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

Australia	India	South Africa, Rep. of
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Spain

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Soaps — Determination of chloride content — Potentiometric method

1 SCOPE AND FIELD OF APPLICATION

This International Standard specifies a potentiometric method for the determination of the chloride content of commercial soaps, containing or not containing other surface active agents, and also of compounded products.

2 REFERENCE

ISO . . ., *Soaps — Sampling.*[1)]

3 PRINCIPLE

Potentiometric titration of the chloride (Cl^-) ions with standard volumetric silver nitrate solution in a nitric acid medium, using a silver-silver chloride 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 Potassium nitrate, solution saturated at 20 °C.

4.2 Nitric acid, approximately 6 N solution.

4.3 Silver nitrate, approximately 0,1 N standard volumetric 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 dark amber-coloured flask.

4.4 Silver nitrate, approximately 0,01 N solution.

Prepare this solution immediately before use by appropriate dilution of the standard volumetric silver nitrate solution (4.3).

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

Weigh, to the nearest 0,001 g, 3,728 g of potassium chloride, previously dried for 2 h at 105 °C and cooled in a desiccator. Dissolve in a small quantity of water and transfer quantitatively to a 500 ml one-mark volumetric flask. Dilute to the mark and mix.

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

Prepare this solution immediately before use by appropriate dilution of the standard reference potassium chloride solution (4.5).

4.7 Methyl orange, 1 g/l solution.

5 APPARATUS

Ordinary laboratory apparatus, and

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

5.2 Electrodes.

5.2.1 Calomel electrode — KCl saturated.

5.2.2 Silver-silver chloride electrode.

5.2.3 Bridge, containing the saturated potassium nitrate solution (4.1), connected to the calomel electrode (5.2.1).

5.3 Combined electrode, as an alternative to the calomel electrode (5.2.1) and the silver electrode (5.2.2).

5.4 Electromagnetic stirrer.

5.5 Burette, capacity 50 ml, complying with the requirements of ISO/R 385, Class A.

1) In preparation.

6 SAMPLING

The laboratory sample of soap shall be prepared and stored according to the procedure specified in ISO . . .

7 PROCEDURE

7.1 Measurement temperature

In order to reduce the effects of thermal and electric hysteresis, take care that the temperatures of the electrodes, the water used for washings, the standard solutions and the test solution are as close to each other as possible. The temperatures of the standard solutions and the test solution shall not differ by more than 1 °C. The measurement temperature should be 20 °C whenever possible.

7.2 Test portion and preparation of test solution

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

Expected chloride content expressed as NaCl % (*m/m*)	Silver nitrate solution	Standard reference potassium chloride solution	Mass of test portion
Below 0,1	0,01 N (4.4)	0,01 N (4.6)	1 to 10 g
Above 0,1	0,1 N (4.3)	0,1 N (4.5)	1 to 3 g

Weigh, to the nearest 0,001 g, the appropriate test portion and dissolve in 50 to 100 ml of hot water. Add 2 drops of the methyl orange solution (4.7), acidify with the nitric acid solution (4.2) and add several drops in excess. Filter through a wet filter paper and wash the fatty acids with small portions of hot water. Cool the filtrate, i.e. the test solution for titration, to 20 °C.

7.3 Calibration of the silver nitrate solution

7.3.1 *Preparation of the apparatus*

Assemble the apparatus and switch it on. Allow it to operate, according to the manufacturer's instructions, for a sufficient time to obtain a good electric stabilization before beginning the measurements. Take care that the interior liquid of the KCl-saturated calomel electrode (5.2.1) is in equilibrium with the atmospheric pressure, in order that its outflow across the bridge (5.2.3) is not obstructed.

Note the temperature of the standard reference solutions, make the corresponding adjustments in the circuit for correction of temperatures, and verify the zero of the apparatus. Do not alter the settings during the measurements.

7.3.2 *Titration*

Take 5,00 ml and 10,00 ml respectively of the appropriate standard reference potassium chloride solution (4.5 or 4.6) and place in two clean, dry vessels of convenient capacity (for example 150 ml). Carry out the following titration on the contents of each vessel.

After acidification by the nitric acid solution (4.2), add sufficient water to bring the total volume to about 100 ml.

Stir the resultant solution and immerse the combined electrode (5.3) or the silver-silver chloride electrode (5.2.2) and the free end of the bridge (5.2.3) in the solution, connect the electrode to the potentiometer (5.1) and, after having verified the zero of the apparatus, note the value of the starting potential.

Add, from the burette (5.5), in 1 ml portions, the silver nitrate solution (4.3 or 4.4) having the same normality as that of the standard reference potassium chloride solution (4.5 or 4.6) used. After each addition, await the stabilization of the potential.

Record the volumes added and the corresponding values of the potential in the first two columns of a table.

When approaching the end-point, continue the addition of the silver nitrate solution in portions of 0,1 ml for the 0,01 N solution or 0,05 ml for the 0,1 N solution.

In a third column of the table, record the successive increments $\Delta_1 E$ of the potential E. In a fourth column, record 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 0,1 ml or 0,05 ml portion 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 volume, in millilitres, of the silver nitrate solution (4.3 or 4.4), immediately lower than the volume which gives the maximum increment of $\Delta_1 E$;

V_1 is the volume, in millilitres, of the final portion of silver nitrate solution (4.3 or 4.4) added (0,05 or 0,1 ml respectively);

b is the last value of $\Delta_2 E$ which is positive;

B is the sum of the absolute values of the final positive value of $\Delta_2 E$ and the first negative value of $\Delta_2 E$ (see example in annex).

7.3.3 *Calculation of normality of solution*

The normality T of the silver nitrate solution is given by the formula

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

where

T_0 is the normality of the standard reference potassium chloride solution (4.5 or 4.6);

V_2 is the value, in millilitres, of V_{EQ}, corresponding to the titration of 10 ml of the standard reference potassium chloride solution (4.5 or 4.6);

V_3 is the value, in millilitres, of V_{EQ}, corresponding to the titration of 5 ml of the standard reference potassium chloride solution (4.5 or 4.6);

5 is the difference, in millilitres, between the two volumes of standard reference potassium chloride solution (4.5 or 4.6) used.

7.4 Blank test

Carry out a blank test without the test portion.

The value 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 are as defined in 7.3.3.

7.5 Determination

Titrate the test solution (7.2) with the silver nitrate solution (4.3 or 4.4) corresponding to the expected chloride content and note the end-point of the reaction in accordance with the instructions given in 7.3.

8 EXPRESSION OF RESULTS

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

$$(V_5 - V_4) \times T \times 0{,}058\,5 \times \frac{100}{m} = \frac{5{,}85\,T\,(V_5 - V_4)}{m}$$

where

T is the normality of the silver nitrate solution, calculated in accordance with 7.3.3;

V_4 is the volume, in millilitres, corresponding to the blank test (7.4);

V_5 is the value, in millilitres, of V_{EQ}, corresponding to the determination (7.5);

m is the mass, in grams, of the test portion (see 7.2).

9 TEST REPORT

The test report shall include the following particulars :

a) all information necessary for the complete identification of the sample;

b) the reference of method used (reference to this International Standard);

c) the results and the method of expression used;

d) the test conditions;

e) any operational details not specified in this International Standard or the International Standard to which reference is made, or regarded as optional, as well as all incidents likely to have affected the results.

ANNEX

EXAMPLE

Volume of silver nitrate solution (4.4) V	Potential E	$\Delta_1 E$	$\Delta_2 E$
ml	mV		
0,80	176		
		35	
0,90	211		+ 37
		72	
1,00	283		− 49
		23	
1,10	306		− 10
		13	
1,20	319		
$V_{EQ} = 0{,}9 + 0{,}1 \times \frac{37}{37 + 49} = 0{,}943$			

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