INTERNATIONAL STANDARD ISO 894

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

Surface active agents — Technical sodium primary alkylsulphates — Methods of analysis

Agents de surface — prim. Alkylsulfates de sodium techniques — Méthode d'analyse

First edition — 1977-11-01

UDC 661.185 : 543

Ref. No. ISO 894-1977 (E)

Descriptors : surfactants, sodium primary alkylsulphate, chemical analysis, determination of content, water, pH, alkalinity, acidity, sodium sulphates, sodium chloride.

Price based on 8 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 894 was developed by Technical Committee ISO/TC 91, *Surface active agents*, and was circulated to the member bodies in October 1975.

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

Australia
Belgium
Brazil
Canada
France
Germany
Hungary
India

Iran
Japan
Mexico
Netherlands
New Zealand
Poland
Portugal
Romania

South Africa, Rep. of
Spain
Switzerland
Turkey
United Kingdom
U.S.A.
U.S.S.R.

No member body expressed disapproval of the document.

This International Standard cancels and replaces ISO Recommendation R 894-1968, of which it constitutes a technical revision.

Printed in Switzerland

Surface active agents — Technical sodium primary alkylsulphates — Methods of analysis

0 INTRODUCTION

The word "primary" preceding the generic name for the products in the title is intended to distinguish these products from those which, in accordance with current scientific usage, could be designated as technical sodium secondary alkylsulphates. As shown in the general formula given below, the former are derived from primary alcohols, whereas the latter may be considered as derived from secondary alcohols.

It is therefore the former which are the subject of this International Standard. They are commonly known today as technical sulphates of primary fatty alcohols.

In order to simplify the text of this International Standard and avoid unecessary repetition, the word "primary" has been omitted from the term "sodium alkylsulphates", but it should be understood that only "sodium primary alkylsulphates" are covered.

The general formula of the products which are the subject of this International Standard is

$R - CH_2 - O - SO_3Na$

where **R** is an aliphatic radical.

1 SCOPE

This International Standard specifies methods of analysis of technical sodium alkylsulphates. It covers the following determinations :

- Measurement of pH.
- Determination of water content.
- Determination of free alkalinity or free acidity.
- Determination of total alkalinity.
- Determination of matter extractable by light petroleum.
- Determination of matter extractable by diethyl ether after acid hydrolysis (combined technical fatty alcohols).
- Determination of sodium sulphate content.
- Determination of sodium chloride content.

It also sets out, in an annex, a general scheme of analysis.

2 FIELD OF APPLICATION

This International Standard is applicable only to technical sodium alkylsulphates in powder, paste or liquid form (aqueous solutions), free from any product extraneous to their manufacture.

3 REFERENCES

ISO 607, *Surface active agents — Detergents — Methods of sample division.*[1]

ISO 2877, *Sulphuric acid for industrial use — Determination of chlorides content — Potentiometric method.*

ISO 4314, *Surface active agents — Determination of free alkalinity or free acidity — Titrimetric method.*

ISO 4315, *Surface active agents — Determination of alkalinity — Titrimetric method.*

ISO 4316, *Surface active agents — Determination of the pH of aqueous solutions — Potentiometric method.*

ISO 4317, *Surface active agents — Determination of water content — Karl Fischer method.*

ISO 4318, *Surface active agents and soaps — Determination of water content — Azeotropic distillation method.*

ISO . . ., *Surface active agents — Determination of sodium sulphate content — Titrimetric method.*[2]

4 SAMPLING

Prepare and store a laboratory sample of approximately 300 g according to the instructions given in ISO 607.

5 GENERAL PRINCIPLE[3]

Preparation of an aqueous alcoholic solution of a test portion, from which are isolated the products extractable by light petroleum.

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1) In preparation. (Revision of ISO/R 607.)

2) In preparation.

3) See the general scheme of analysis in the annex.

Evaporation to dryness of the residual aqueous alcoholic liquor in the presence of ethanol. Hot acid hydrolysis of the dry residue and isolation from the acid reaction liquor of all products extractable by diethyl ether (combined technical fatty alcohols).

On separate test portions :

- measurement of pH;
- determination of water content;
- determination of free alkalinity or free acidity;
- determination of total alkalinity;
- determination of sodium sulphate content;
- determination of sodium chloride content.

6 METHODS OF ANALYSIS

6.1 Measurement of pH

Carry out the measurement of pH by the method specified in ISO 4316, on a 10 % (*m/m*) solution of the laboratory sample.

NOTE — If the pH is below 7,0, the sample and the batch it represents will be unstable; therefore, the results for most of the tests will change with time. In these cases, the batch is usually rejected without further analysis.

6.2 Determination of water content

Depending on the amount of water in the product, carry out the determination according to one of the two following methods :

a) the Karl Fischer method, applicable to products having less than 10 % (*m/m*) of water;

b) the azeotropic distillation method, applicable only to products containing more than 5 % (*m/m*) of water.

6.2.1 *Karl Fischer method*

Carry out the determination of water content by the method specified in ISO 4317.

6.2.2 *Azeotropic distillation method*

Carry out the determination of water content by the method specified in ISO 4318.

6.3 Determination of free alkalinity or free acidity

Carry out the determination of free alkalinity or free acidity by the method specified in ISO 4314.

6.4 Determination of total alkalinity

It may happen that, on measuring the pH in accordance with 6.1, a pH that is significantly greater than 7 is observed and that, on determining the alkalinity in accordance with 6.3, an alkali value significantly greater than 0,3 is obtained. In such cases, it is advisable to carry out the determination of the total alkalinity by the method specified in ISO 4315.

6.5 Determination of matter extractable by light petroleum

6.5.1 *Introduction*

Matter extractable by light petroleum consists of sulphur-free products as well as products containing sulphur which, when present, do not ionize in aqueous solution.

6.5.2 *Principle*

Extraction with light petroleum of the products specified in 6.5.1, from an aqueous alcoholic solution of the test portion, taking into consideration the volatility of the products in question.

6.5.3 *Reagents*

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

6.5.3.1 Sodium sulphate, anhydrous.

6.5.3.2 Ethanol, 96 % (*V/V*) solution.

6.5.3.3 Ethanol, 50 % (*V/V*) solution.

6.5.3.4 Light petroleum, boiling between 40 and 60 °C. The residue after evaporation shall not be greater than 0,002 % (*m/m*).

6.5.3.5 Sodium hydroxide, approximately 0,1 N solution.

6.5.3.6 Phenolphthalein, 1 g/l solution in ethanol.

6.5.4 *Apparatus*

Ordinary laboratory apparatus and

6.5.4.1 Round-bottomed flask, of capacity 250 ml, with ground glass neck.

6.5.4.2 Fractionating column, of length 20 cm and inside diameter approximately 10 mm, with a ground glass cone at its lower end to fit into the neck of the flask (6.5.4.1).

6.5.4.3 Glass condenser, of nominal (jacket) length 160 mm, complying with the requirements of ISO 4799.

6.5.4.4 Three separating funnels, of capacity 500 ml, with ground glass stoppers, complying with the requirements of ISO 4800.

6.5.4.5 Conical flask, of capacity 250 ml, complying with the requirements of ISO 1773.

6.5.5 *Procedure*

6.5.5.1 TEST PORTION

Weigh, to the nearest 0,01 g, a mass of the laboratory sample containing approximately 4 g of sodium alkylsulphates, into a 100 ml beaker.

6.5.5.2 DETERMINATION

Dissolve or, if necessary, dilute the test portion (6.5.5.1) in 50 ml of hot water (approximately 70 °C), stirring with a glass rod, and add 50 ml of the ethanol solution (6.5.3.2) while continuing to stir. Place the liquid obtained into one of the 500 ml separating funnels (6.5.4.4) (A). Wash the beaker alternately with small equal portions of hot water and of the ethanol solution (6.5.3.2) until the final volume is approximately 300 ml.

Check that the liquid is slightly alkaline to the phenolphthalein solution (6.5.3.6) and, if necessary, render it alkaline with the sodium hydroxide solution (6.5.3.5) until a pale pink colour is obtained with the indicator.

Shake to render the mixture homogeneous. Allow to cool.

Add 50 ml of the light petroleum (6.5.3.4).

Shake vigorously for approximately 30 s and allow to separate. Add the minimum quantity of the ethanol solution (6.5.3.2) necessary to break any emulsion that may be formed.

Transfer the lower layer into the second separating funnel (6.5.4.4) (B). Extract with another 50 ml portion of the light petroleum. Collect the lower layer in the third separating funnel (6.5.4.4) (C) and transfer the upper layer into the first separating funnel (A).

Extract the aqueous alcoholic phase three more times, each time using 50 ml of the light petroleum.

Combine the hydrocarbon phases in separating funnel (A) and transfer the aqueous alcoholic phase into a 400 ml beaker after the last extraction. Wash the separating funnels (B) and (C) three times, each time using 10 ml of the ethanol solution (6.5.3.3).

Add the washings to the aqueous alcoholic phase in the beaker.

Wash the hydrocarbon extract with successive portions of the ethanol solution (6.5.3.3) until the washings are no longer alkaline; add the washings to the aqueous alcoholic phase.

This solution, L_1, is used for the determination of the combined technical fatty alcohols content.

Transfer the hydrocarbon layer quantitatively to the conical flask (6.5.4.5) containing about 10 g of the sodium sulphate (6.5.3.1). Shake, and allow to stand for 30 min, then filter through filter paper into the previously tared flask (6.5.4.1) containing a few glass beads. Wash the conical flask, the sodium sulphate and the filter five times, each time using 10 ml of the light petroleum. Pay particular attention to the edges of the filter paper, which should not show any greasy marks.

Fit the fractionating column (6.5.4.2) and condenser (6.5.4.3) to the flask, place the assembly on a hot-plate or in a water bath and distil until almost all the solvent has passed over. Remove the fractionating column, cool to about 30 °C and eliminate the last traces of solvent by a gentle current of dry, cold air. To do this, maintain the current of air and rotate the flask by hand, in an inclined position, away from the hot-plate or water bath. In this way, the liquid in the flask is spread over the interior in a thin film, facilitating the removal of the last traces of solvent.

It is advisable to bear in mind that lower alcohols, such as lauric alcohol for example, are fairly volatile, particularly in the presence of traces of moisture which, in some circumstances, may cause quite considerable losses. Therefore, particular care is necessary in evaporating the solvent, especially while passing the current of air. For this purpose, first weigh the flask, cooled to room temperature and carefully dried, while there is still a detectable odour of solvent. Note the mass, then reheat the flask to approximately 30 °C so as to liquefy the contents and pass a current of air over them for a further 1 min. After cooling and drying the flask, weigh it again and note the mass.

By repeating these operations and plotting successive weighings on a graph, it will be noted that, after a rapid drop, the curve reaches a practically horizontal minimum. The second weighing on the horizontal part is regarded as the end of the operation and the mass noted is recorded as that of the final dry residue. Any difference between the last two weighings should be apparent only in the third significant figure.

6.5.6 *Expression of results*

6.5.6.1 METHOD OF CALCULATION

The content of matter extractable by light petroleum is given, as a percentage by mass, by the formula

$$m_1 \times \frac{100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion (6.5.5.1);

m_1 is the mass, in grams, of the residue obtained.

6.5.6.2 REPRODUCIBILITY

The difference between results obtained on the same sample, in two different laboratories, should not exceed 1 %.

6.6 Determination of matter extractable by diethyl ether after acid hydrolysis (combined technical fatty alcohols)

6.6.1 *Principle*

Evaporation of the aqueous alcoholic liquid (L_1) resulting from the previous determination (see 6.5.5.2) to one-fifth of its volume, and addition of ethanol, evaporation to dryness.

Dissolution of the dry residue in water and, after the addition of hydrochloric acid, acid hydrolysis at boiling point. When the hydrolysis is complete, cold extraction by diethyl ether of all the fatty substances released.

These fatty substances consist almost entirely of combined fatty alcohols but they may, in some cases, contain sulphonic derivatives (true sulphonates) and fatty acids, generally in very small proportions.

NOTE — It is very important that the solution remains alkaline throughout this determination.

6.6.2 *Reagents*

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

6.6.2.1 Sodium sulphate, anhydrous.

6.6.2.2 Ethanol, 96 % (*V/V*) solution, rendered slightly alkaline with a 0,1 N sodium hydroxide solution in the presence of phenolphthalein as indicator.

6.6.2.3 Diethyl ether.

6.6.2.4 Hydrochloric acid, ρ_{20} 1,19 g/ml, sulphate-free solution.

6.6.2.5 Hydrochloric acid, approximately 1 N solution.

6.6.3 *Apparatus*

Ordinary laboratory apparatus and

6.6.3.1 Saponification flask, of capacity 250 ml.

6.6.3.2 Three separating funnels, of capacity 500 ml, complying with the requirements of ISO 4800.

6.6.3.3 Round-bottomed flask, of capacity 250 ml, with ground glass neck.

6.6.3.4 Fractionating column, 20 cm long, inside diameter approximately 10 mm, with a ground glass cone at its lower end to fil into the neck of the flask (6.6.3.3).

6.6.3.5 Glass condenser, of nominal (jacket) length 160 mm, complying with the requirements of ISO 4799.

6.6.4 *Procedure*

6.6.4.1 TEST PORTION

Use the aqueous alcoholic solution L_1 resulting from the determination of matter extractable by light petroleum (see 6.5).

6.6.4.2 DETERMINATION

Reduce the test portion (6.6.4.1) to approximately one-fifth of its volume by evaporation on a water bath, using a current of air. Add 20 ml of the ethanol solution (6.6.2.2) and evaporate to dryness.

Dissolve, heating if necessary, in 50 ml of water and transfer quantitatively to the saponification flask (6.6.3.1) by means of water, bringing the final volume to approximately 100 ml. Add two glass beads and then, very carefully, 35 ml of the hydrochloric acid solution (6.6.2.4). (Care is necessary to avoid losses from the flask due to overflow of the foam resulting from decomposition of any carbonates formed during the evaporation to dryness.)

Attach the condenser (6.6.3.5) and reflux for at least 4 h. Cool and transfer quantitatively to one of the separating funnels (6.6.3.2) (A). Wash the condenser and flask carefully and quantitatively with the diethyl ether (6.6.2.3) and water, and add the washings to the liquid in the separating funnel.

Shake in order to homogenize thoroughly.

Add 30 ml of the diethyl ether (6.6.2.3). Shake vigorously and allow to settle.

Transfer the lower layer to the second separating funnel (6.6.3.2) (B). Extract once again with 30 ml of the diethyl ether. Collect the lower layer in the third separating funnel (C) and transfer the upper layer to the first separating funnel (A).

Extract the aqueous phase three more times, each time using 30 ml of the diethyl ether.

Combine the ethereal phases in separating funnel (A) and wash the ethereal extract three times, each time using 15 ml of the hydrochloric acid solution (6.6.2.5).

Transfer the ethereal extract quantitatively to a 250 ml conical flask containing about 10 g of the sodium sulphate (6.6.2.1). Shake, allow to stand for 30 min, and filter through a filter paper into the previously tared flask (6.6.3.3) containing a few glass beads. Wash the conical flask, the sodium sulphate and the filter five times, each time using 10 ml of the diethyl ether. Pay particular attention to the edges of the filter paper, which should not show any greasy marks.

Fit the fractionating column (6.6.3.4) and condenser (6.6.3.5) to the flask, place the assembly on a water bath and distil until almost all the solvent has passed over. Remove the fractionating column and eliminate the last traces of solvent by a gentle current of dry, cold air. To do this, maintain the current of air, and rotate the flask by hand, in an inclined position, away from the water bath. In this way, the liquid in the flask is spread over the interior in a thin film, facilitating the removal of the last traces of solvent.

It is advisable to bear in mind that lower alcohols, such as lauric alcohol for example, are fairly volatile, particularly in the presence of traces of moisture which, in some circumstances, may cause quite considerable losses. Therefore, particular care is necessary in evaporating the solvent, especially while passing the current of air. For this purpose, first weigh the flask, cooled to room temperature and carefully dried, while there is still a detectable odour of solvent. Note the mass, then reheat the flask to approximately 30 °C so as to liquefy the contents and pass a current of air over them for a further 1 min. After cooling and drying the flask, weigh it again and note the mass.

By repeating these operations and plotting successive weighings on a graph, it will be noted that, after a rapid drop, the curve reaches a practically horizontal minimum. The second weighing on the horizontal part is regarded as the end of the operation and the mass noted is recorded as that of the final dry residue. Any difference between the last two weighings should be apparent only in the third significant figure.

6.6.5 *Expression of results*

6.6.5.1 METHOD OF CALCULATION

The content of matter extractable by diethyl ether after acid hydrolysis is given, as a percentage by mass, by the formula

$$m_1 \times \frac{100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion (6.5.5.1);

m_1 is the mass, in grams, of the residue obtained.

6.6.5.2 REPRODUCIBILITY

The difference between results obtained on the same sample, in two different laboratories, should not exceed 1 %.

NOTES

1 The determination of the alkali value and the acid value should be carried out on the combined technical fatty alcohols, isolated according to ISO 4314.

2 The acid value should be less than, or at most equal to, 2.

6.7 Determination of sodium sulphate content

Carry out the determination of sodium sulphate content by the method specified in ISO . . .

6.8 Determination of sodium chloride content

6.8.1 *Principle*

Potentiometric titration of the chloride (Cl^-) ions with standard volumetric silver nitrate solution, in a nitric acid medium, using a silver measurement electrode and a mercury-mercury(I) sulphate reference electrode.

6.8.2 *Reagents*

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

6.8.2.1 Nitric acid, ρ_{20} 1,33 g/ml.

6.8.2.2 Nitric acid, approximately 6 N solution.

6.8.2.3 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 brown glass bottle.

6.8.2.4 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 little water, transfer quantitatively to a 500 ml one-mark volumetric flask, dilute to the mark and mix.

6.8.2.5 Methyl orange, 1 g/l solution.

6.8.3 *Apparatus*

Ordinary laboratory apparatus and

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

6.8.3.2 Silver electrode.

6.8.3.3 Mercury-mercury(I) sulphate electrode (with potassium sulphate solution as bridge).

NOTE — If a reference electrode of this type is not available, a calomel electrode may be used instead, but it should be connected by a potassium nitrate-agar bridge to the beaker in which the titration is carried out and into which the silver measurement electrode is immersed.

A bridge of this kind can easily be made as follows : saturate 100 ml of water with approximately 32 g of potassium nitrate and then add 4 g of agar. Heat at 70 °C until dissolution is complete. Fill a U-shaped capillary tube of internal diameter 2 to 3 mm, length of legs 8 to 10 cm, distance between legs about 6 cm, at about 70 °C, with the above solution and allow to cool. During cooling, keep the open ends of the legs in the solution.

6.8.3.4 Electromagnetic stirrer.

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

6.8.4 *Procedure*

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 standard solutions shall not differ by more than 1 °C. The recommended measurement temperature shall, whenever possible, be 20 °C.

NOTE — The method of determination is similar to that specified in ISO 2877 and also to the general method of determination of chlorides by potentiometry established by Technical Committee ISO/TC 47.

6.8.4.1 TEST PORTION

Weigh, to the nearest 0,001 g, approximately 2 g of the laboratory sample into a 250 ml beaker.

6.8.4.2 STANDARDIZATION OF THE SILVER NITRATE SOLUTION

6.8.4.2.1 *Preparation of the apparatus*

Make the necessary connections and switch on the apparatus. Let it operate, according to the manufacturer's instructions, for an appropriate length of time to ensure good electric stabilization before the beginning of measurement.

Note the temperature of the standard reference solution, make the corresponding adjustments to the circuit for correction of temperatures and verify the zero of the apparatus. Do not alter the settings.

6.8.4.2.2 *Titration*

Take 5,00 ml and 10,00 ml respectively of the standard reference potassium chloride solution (6.8.2.4) and place in two clean, dry beakers of convenient capacity (for example 150 ml). Carry out the following titration on the contents of each beaker.

After acidification with the nitric acid solution (6.8.2.2), add sufficient water to bring the total volume to about 100 ml.

Stir the solution obtained and immerse the silver electrode (6.8.3.2) and the free end of the bridge in the solution, connect the electrodes to the potentiometer (6.8.3.1) and, after having verified the zero of the apparatus, note the value of the starting potential.

Add the silver nitrate solution (6.8.2.3) from the burette (6.8.3.5) in 1 ml portions, awaiting the stabilization of the potential after each addition.

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 0,05 ml portions.

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 0,05 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

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

where

V_0 is the volume, in millilitres, of the silver nitrate solution (6.8.2.3), 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 (6.8.2.3) added (here 0,05 ml);

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 $\Delta_2 E$.

6.8.4.2.3 *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 (6.8.2.4);

V_2 is the value, in millilitres, of V_{EQ}, corresponding to the titration of 10 ml of the standard reference potassium chloride solution (6.8.2.4),

V_3 is the value, in millilitres, of V_{EQ}, corresponding to the titration of 5 ml of the standard reference potassium chloride solution (6.8.2.4);

5 is the difference, in millilitres, between the two volumes of standard reference potassium chloride solution (6.8.2.4) used.

6.8.4.3 DETERMINATION

Dissolve or, where applicable, dilute the test portion (6.8.4.1) with 100 ml of water. Add 10 ml of the nitric acid solution (6.8.2.1) and carry out the measurement according to the instructions given in 6.8.4.2.1 and 6.8.4.2.2.

6.8.4 *Procedure*

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 standard solutions shall not differ by more than 1 °C. The recommended measurement temperature shall, whenever possible, be 20 °C.

NOTE — The method of determination is similar to that specified in ISO 2877 and also to the general method of determination of chlorides by potentiometry established by Technical Committee ISO/TC 47.

6.8.4.1 TEST PORTION

Weigh, to the nearest 0,001 g, approximately 2 g of the laboratory sample into a 250 ml beaker.

6.8.4.2 STANDARDIZATION OF THE SILVER NITRATE SOLUTION

6.8.4.2.1 *Preparation of the apparatus*

Make the necessary connections and switch on the apparatus. Let it operate, according to the manufacturer's instructions, for an appropriate length of time to ensure good electric stabilization before the beginning of measurement.

Note the temperature of the standard reference solution, make the corresponding adjustments to the circuit for correction of temperatures and verify the zero of the apparatus. Do not alter the settings.

6.8.4.2.2 *Titration*

Take 5,00 ml and 10,00 ml respectively of the standard reference potassium chloride solution (6.8.2.4) and place in two clean, dry beakers of convenient capacity (for example 150 ml). Carry out the following titration on the contents of each beaker.

After acidification with the nitric acid solution (6.8.2.2), add sufficient water to bring the total volume to about 100 ml.

Stir the solution obtained and immerse the silver electrode (6.8.3.2) and the free end of the bridge in the solution, connect the electrodes to the potentiometer (6.8.3.1) and, after having verified the zero of the apparatus, note the value of the starting potential.

Add the silver nitrate solution (6.8.2.3) from the burette (6.8.3.5) in 1 ml portions, awaiting the stabilization of the potential after each addition.

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 0,05 ml portions.

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 0,05 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

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

where

V_0 is the volume, in millilitres, of the silver nitrate solution (6.8.2.3), 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 (6.8.2.3) added (here 0,05 ml);

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 $\Delta_2 E$.

6.8.4.2.3 *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 (6.8.2.4);

V_2 is the value, in millilitres, of V_{EQ}, corresponding to the titration of 10 ml of the standard reference potassium chloride solution (6.8.2.4),

V_3 is the value, in millilitres, of V_{EQ}, corresponding to the titration of 5 ml of the standard reference potassium chloride solution (6.8.2.4);

5 is the difference, in millilitres, between the two volumes of standard reference potassium chloride solution (6.8.2.4) used.

6.8.4.3 DETERMINATION

Dissolve or, where applicable, dilute the test portion (6.8.4.1) with 100 ml of water. Add 10 ml of the nitric acid solution (6.8.2.1) and carry out the measurement according to the instructions given in 6.8.4.2.1 and 6.8.4.2.2.