International Standard 754

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Acetic anhydride for industrial use — Methods of test

Anhydride acétique à usage industriel — Méthodes d'essai

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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 754 was developed by Technical Committee ISO/TC 47, *Chemistry*. It results from the combination into one single document of draft International Standard ISO/DIS 754 parts 1 to 10, which were submitted to member bodies in January 1981.

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

Australia*	Germany, F. R.	Poland
Austria	Hungary	Portugal
Belgium	India	Romania
Brazil	Italy	South Africa, Rep. of
China	Korea, Dem. P. Rep. of	Switzerland
Czechoslovakia	Korea, Rep. of***	Thailand
Egypt, Arab Rep. of	Mexico	United Kingdom
France**	Philippines	USSR

This International Standard has also been approved by the International Union of Pure and Applied Chemistry (IUPAC).

It cancels and replaces ISO Recommendation R 754-1968, of which it constitutes a technical revision.

* Australia disapproved clauses 9 and 13 (formerly parts 2 and 6).

** France disapproved clause 9 (formerly part 2).

*** The Republic of Korea did not vote on clause 16 (formerly part 9).

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INTERNATIONAL STANDARD ISO 754-1982 (E)

Acetic anhydride for industrial use — Methods of test

WARNING — Acetic anhydride is a flammable liquid which causes burns; the vapour is toxic and irritant. Avoid breathing the vapour. Prevent contact with eyes and skin. In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

1 Scope and field of application

This International Standard gives general instructions and specifies methods of test for the analysis of acetic anhydride for industrial use.

The methods of test relating to acetic anhydride for industrial use are the following :

— Determination of distillation yield

— Determination of bromine number

— Measurement of colour

— Determination of arsenic content

— Determination of acetic anhydride content — Titrimetric method

— Determination of ash — Gravimetric method

— Determination of phosphate content — Molybdovanadate spectrometric method

— Determination of permanganate index

— Determination of dichromate index

— Visual limit test for inorganic chlorides

— Visual limit test for inorganic sulphates

— Visual limit test for heavy metals (including iron)

— Sulphuric acid colour test

NOTE — 1,10-Phenanthroline spectrometric methods for the determination of the iron content will be added later.

2 References

ISO 761, *Acetic anhydride and butan-1-ol for industrial use — Determination of bromine number.*

ISO 918, *Liquid chemical products for industrial use — Determination of distillation properties — General method.*[1]

ISO 2211, *Liquid chemical products — Measurement of colour in Hazen units (platinum-cobalt scale).*

ISO 2590, *General method for the determination of arsenic — Silver diethyldithiocarbamate photometric method.*

General instructions

3 Sampling[2]

Place the laboratory sample in a clean, dry and airtight, ground glass stoppered bottle or a screw-capped bottle fitted with an inert plastics cone insert of such capacity that it is almost entirely filled by the sample. If it is necessary to seal the bottle, care shall be taken to avoid contaminating the contents in any way.

NOTE — A sample of not less than 750 ml is necessary for performing all the tests specified for the product.

4 Test report

The test report, for each determination, shall contain 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 in the International Standards to which reference is made, or regarded as optional.

1) At present at the stage of draft. (Revision of ISO/R 918.)

2) The sampling of liquid chemical products for industrial use will form the subject of a future International Standard.

Methods of test

5 Determination of distillation yield

Use the method specified in ISO 918, subject to the following details appropriate for acetic anhydride.

5.1 Thermometer, complying with the requirements of ISO 918, sub-clause 5.1.2, and of table 1.

Table 1 — Requirements for the thermometer

Thermometer range	Graduations	Maximum error	Maximum error in an interval of 10 °C
°C	°C	°C	°C
98 to 152	0,2	0,4	0,4

5.2 Corrections to be applied to temperatures

If the corrected barometric pressure deviates from 1 013 mbar[1], apply a correction to the observed temperature by subtracting 0,038 °C for every millibar above, or adding 0,038 °C for every millibar below, 1 013 mbar (see ISO 918, clause 9).

5.3 Distillation

Adjust the rate of heating so that the first drop of the distillate falls from the end of the condenser in 12 to 17 min (see ISO 918, sub-clause 7.2).

6 Determination of bromine number

Use the method specified in ISO 761.

7 Measurement of colour

Use the method specified in ISO 2211.

8 Determination of arsenic content

Use the method specified in ISO 2590, subject to the following details appropriate for acetic anhydride.

8.1 Reagents

Use the reagents specified in clause 4 of ISO 2590 together with the following :

8.1.1 Hydrogen peroxide, 100 g/l solution.

8.1.2 Sulphuric acid, ϱ approximately 1,84 g/ml solution about 96 % (m/m) solution.

8.1.3 Sulphuric acid, approximately 200 g/l solution.

8.2 Test portion and preparation of test solution (see ISO 2590, sub-clause 6.1)

WARNING — Carry out all operations for the preparation of the test solution in a well-ventilated fume cupboard.

Transfer a quantity of the test sample containing 1 to 20 µg of arsenic (usually about 50 g) into a 100 ml conical flask fitted with a ground glass stopper and weigh the flask contents to the nearest 0,1 g. Transfer most of the contents of the flask, 1 to 2 ml at a time, into a 250 ml borosilicate glass beaker containing 50 ml of hot water (temperature about 50 °C), ensuring that each increment is completely dissolved before making the next addition. Weigh the flask to the nearest 0,1 g and determine the mass of the test portion by difference.

Add 5 ml of hydrogen peroxide solution (8.1.1) to the beaker and evaporate the solution almost to dryness on, for example, a sand bath. Allow the solution to cool and carefully add 5 ml of the sulphuric acid solution (8.1.2). Evaporate the solution until white fumes are evolved. Allow to cool and dissolve the residue in about 5 ml of water.

Transfer the solution quantitatively to the conical flask (5.1.1) of the apparatus (see ISO 2590, sub-clause 5.1), using the sulphuric acid solution (8.1.3) to effect the transfer. Make up to about 40 ml with the same acid solution.

Proceed as in ISO 2590, sub-clause 6.1.

8.3 Expression of results (see ISO 2590, clause 7)

The arsenic content, expressed in milligrams of arsenic (As) per kilogramme, is given by the formula

$$\frac{m_1 - m_2}{m_0}$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in micrograms, of As found in the test solution;

m_2 is the mass, in micrograms, of As found in the blank test solution.

1) 1 bar = 10^5 Pa

9 Determination of acetic anhydride content — Titrimetric method

9.1 Principle

Hydrolysis of a test portion with an excess of standard volumetric sodium hydroxide solution. Back-titration with standard volumetric hydrochloric acid solution to determine the amount of sodium hydroxide consumed.

Reaction of the acetic anhydride in a similar test portion with aniline, giving acetic acid. Addition of an excess of the same sodium hydroxide solution and back-titration with the same hydrochloric acid solution to determine the amount of sodium hydroxide consumed by the acetic acid.

Calculation of the acetic anhydride content from the difference between the amounts of sodium hydroxide consumed respectively in the hydrolysis reaction and by the acetic acid formed from the reaction with aniline.

9.2 Reactions

$$(CH_3CO)_2O + 2NaOH \rightarrow 2\,(CH_3COONa) + H_2O \quad ...(1)$$

$$(CH_3CO)_2O + C_6H_5NH_2 \rightarrow C_6H_5NHCOCH_3 + CH_3COOH \quad ...(2)$$

9.3 Reagents

WARNING — Attention is drawn to the dangers involved in the use of aniline and cyclohexane (see the notes to clauses 9.3.1 and 9.3.2).

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

9.3.1 Aniline ($C_6H_5NH_2$), dry, freshly distilled.

NOTE — Toxic in contact with skin. Avoid breathing vapour. Avoid contact with skin and eyes.

9.3.2 Cyclohexane (C_6H_{12}), dry, freshly distilled.

NOTE — Highly flammable. Irritant. Avoid breathing vapour. Avoid contact with skin and eyes.

9.3.3 Methanol (CH_3OH).

9.3.4 Sodium hydroxide, standard volumetric solution c(NaOH) = 1 mol/l.

9.3.5 Hydrochloric acid, standard volumetric solution c(HCl) = 1 mol/l.

9.3.6 Phenolphthalein, 5 g/l ethanolic solution.

Dissolve 0,5 g of phenolphthalein in 100 ml of 95 % (V/V) ethanol and make faintly pink by the addition of the dilute sodium hydroxide solution (9.3.4).

9.4 Apparatus

Ordinary laboratory apparatus and

9.4.1 Weighing pipette, of capacity approximately 5 ml.

9.4.2 Conical flasks, of borosilicate glass, of capacity 500 ml, provided with ground glass stoppers.

9.4.3 Burette, of capacity 50 ml, complying with the requirements of ISO 385, class A.

9.4.4 Pipette, of capacity 50 ml, complying with the requirements of ISO 684, class A.

NOTE — To improve accuracy, the same pipette and burette should be used in each of the three titrations.

9.5 Procedure

9.5.1 Test portion and first titration

Using the pipette (9.4.1), introduce 50,0 ml of the sodium hydroxide solution (9.3.4) into one of the conical flasks (9.4.2). Then introduce, by means of the weighing pipette (9.4.1), approximately 2 g of the laboratory sample, weighed to the nearest 0,000 1 g. Stopper the flask and allow to stand for 1 h. Add 40 ml of the cyclohexane (9.3.2), 10 ml of the aniline (9.3.1) and 100 ml of the methanol (9.3.3). Add 0,5 ml of the phenolphthalein solution (9.3.6), and, using the burette (9.4.3), titrate the excess sodium hydroxide with the hydrochloric acid solution (9.3.5) until the pink colour is just discharged.

9.5.2 Test portion and second titration

Using the weighing pipette (9.4.1), weigh by difference, to the nearest 0,000 1 g, approximately 2 g of the laboratory sample and transfer to another flask (9.4.2), containing 20 ml of the cyclohexane (9.3.2). Stopper the flask, cool it in ice, and add an ice cold solution of 10 ml of the aniline (9.3.1) in 20 ml of the cyclohexane. Allow the flask to stand in ice for 1 h. Add 100 ml of the methanol (9.3.3) and 50,0 ml of the sodium hydroxide solution (9.3.4). Add 0,5 ml of the phenolphthalein solution (9.3.6), and, using the burette (9.4.3), titrate the excess sodium hydroxide with the hydrochloric acid solution (9.3.5) until the pink colour is just discharged.

9.5.3 Blank test

Carry out a blank test at the same time as the second titration following the same procedure as specified in 9.5.2, and using the same reagents as used for the determination, but omitting the test portion.

It is essential to take into account corrections arising from calibration of the burette and to correct the volumes of the standard volumetric solutions used, for any deviation of temperature from that at which these solutions were standardized.

9.6 Expression of results

The anhydride content, expressed as a percentage by mass of acetic anhydride [$(CH_3CO)_2O$], is given by the formula

$$\left[\frac{(V_0 - V_1)}{m_0} - \frac{(V_0 - V_2)}{m_1}\right] \times 0{,}102\ 1 \times 100$$

$$= 10{,}21\left[\frac{(V_0 - V_1)}{m_0} - \frac{(V_0 - V_2)}{m_1}\right]$$

where

V_0 is the volume, in millilitres, of the hydrochloric acid solution (9.3.5) used for the blank test (9.5.3);

V_1 is the volume, in millilitres, of the hyrochloric acid solution (9.3.5) used for the first titration (9.5.1);

V_2 is the volume, in millilitres, of the hydrochloric acid solution (9.3.5) used for the second titration (9.5.2);

m_0 is the mass, in grams, of the test portion taken in 9.5.1;

m_1 is the mass, in grams, of the test portion taken in 9.5.2;

0,102 1 is the mass, in grams, of acetic anhydride corresponding to 1,00 ml of hydrochloric acid solution, c(HCl) = 1,000 mol/l.

NOTE — If the concentration of the standard volumetric solutions used is not exactly as specified in the list of reagents, an appropriate correction should be made.

10 Determination of ash — Gravimetric method

10.1 Principle

Evaporation to dryness of a test portion and heating at 600 ± 30 °C to constant mass.

10.2 Apparatus

Ordinary laboratory apparatus and

10.2.1 Weighing pipette, of capacity approximately 120 ml.

10.2.2 Platinum or silica dish, of capacity approximately 150 ml.

10.2.3 Electric furnace, capable of being controlled at approximately 200 °C and at 600 ± 30 °C.

10.3 Procedure

10.3.1 Test portion

Using the weighing pipette (10.2.1), weigh by difference, to the nearest 0,01 g, 100 g of the laboratory sample, depending on the expected ash.

10.3.2 Determination

Place the test portion (10.3.1) in the dish (10.2.2), previously heated for about 30 min in the electric furnace (10.2.3), controlled at 600 ± 30 °C, cooled in a desiccator and weighed to the nearest 0,000 1 g.

Gently evaporate the contents of the dish to dryness on a steam bath or electric-hot plate in a well-ventilated fume cupboard, taking care to avoid splashing.

Transfer the dish and its contents to the electric furnace, maintained at approximately 200 °C, and raise the temperature progressively to 600 ± 30 °C. Keep the dish at this temperature during 1 h (disappearance of carbonaceous matter). Transfer the dish from the furnace to a desiccator and allow it to cool to ambient temperature. Weigh the dish to the nearest 0,000 1 g.

If required, use the residue for the determination of iron content by means of the method specified in ISO 754/11[1].

10.4 Expression of results

The ash is given, as a percentage by mass, by the formula

$$(m_2 - m_1) \times \frac{100}{m_0}$$

where

m_0 is the mass, in grams, of the test portion (10.3.1);

m_1 is the mass, in grams, of the dish (10.2.2);

m_2 is the mass, in grams, of the dish and ash.

11 Determination of phosphate content — Molybdovanadate spectrometric method

11.1 Applicability

The method is applicable to products having phosphates contents, expressed as P_2O_5, in the range 0,005 to 0,05 % (m/m).

11.2 Principle

Hydrolysis of a test portion with water, addition of nitric acid solution and evaporation to dryness. Dissolution of the residue in nitric and hydrochloric acid solution. Formation of the yellow molybdovanadate and spectrometric measurement at a wavelength of approximately 420 nm.

1) Under study. (Revision of ISO/R 754, clause 11.)

11.3 Reagents

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

11.3.1 Nitric acid, ϱ approximately 1,40 g/ml, about 68 % (m/m) solution.

11.3.2 Hydrochloric acid, ϱ approximately 1,19 g/ml, about 38 % (m/m) solution.

11.3.3 Ammonium molybdovanadate, nitric solution.

Dissolve 20 g of ammonium molybdate tetrahydrate [$(NH_4)_2MoO_4.4H_2O$] in approximately 500 ml of water, with heating. When dissolution is complete, add 1 g of ammonium metavanadate (NH_4VO_3) and allow to dissolve. Cool the solution and add, in small quantities with stirring, 150 ml of the nitric acid solution (11.3.1). Cool the solution. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark with water and mix.

11.3.4 Phosphate, standard solution corresponding to 1,0 g of P_2O_5 per litre.

Weigh, to the nearest 0,001 g, 1,92 g of potassium dihydrogen phosphate (KH_2PO_4) and dissolve in water. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 1,0 mg of P_2O_5.

11.3.5 Phosphate, standard solution corresponding to 0,10 g of P_2O_5 per litre.

Immediately before use, transfer 10,0 ml of this solution to a 100 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,10 mg of P_2O_5.

Prepare this solution at the time of use.

11.4 Apparatus

Ordinary laboratory apparatus and

11.4.1 Conical flask, of capacity 50 ml, fitted with a ground glass stopper.

11.4.2 Platinum dish, of capacity approximately 100 ml.

11.4.3 Spectrometer with a radiation selector for continuous variation, fitted with cells of optical path lengths 4 or 5 cm and 1 cm, or

11.4.4 Spectrometer with a radiation selector for discontinuous variation, fitted with filters providing maximum transmission at a wavelength of about 420 nm.

11.5 Procedure

11.5.1 Test portion

Transfer approximately 20 g of the laboratory sample to the conical flask (11.4.1) and weigh to the nearest 0,001 g. Transfer the contents, 1 to 2 ml at a time, into the platinum dish (11.4.2), containing 50 ml of water at a temperature of about 50 °C, until approximately 10 ml are added, ensuring that each increment is dissolved before the addition of the next. Weigh the flask and contents to the nearest 0,001 g and determine the mass of the test portion by difference.

11.5.2 Preparation of the test solution

Add to the test portion (11.5.1) in the dish (11.4.2) 15 ml of the nitric acid solution (11.3.1) and evaporate to dryness on a boiling water bath. Take up the residue with 10 ml of the nitric acid solution and 5 ml of water and heat gently. Transfer quantitatively the solution and insoluble matter, if any, to a beaker of suitable capacity (100 ml for example). Add 10 ml of the hydrochloric acid solution (11.3.2) and heat for 15 min. Allow to cool to ambient temperature and add 50 ml of water. Transfer the solution quantitatively to a 250 ml one-mark volumetric flask, first filtering, if necessary, to remove any insoluble residue. Dilute to the mark and mix.

11.5.3 Blank test

Carry out a blank test at the same time as the determination, following the same procedure and using the same quantities of all the reagents as used for the determination, but omitting the test portion.

11.5.4 Preparation of calibration graph

11.5.4.1 Preparation of standard matching solution for spectrometric measurements carried out with cells of optical path lengths 4 or 5 cm, and 1 cm

Depending on the expected phosphate content, introduce into a series of 12 100 ml one-mark volumetric flasks, the volumes of the standard phosphate solution (11.3.5) given in table 2.

Table 2 — Test conditions

Expected phosphate content, % (m/m) of P_2O_5			
0,005 to 0,025		0,025 to 0,05	
Standard phosphate solution (11.3.5)	Corresponding mass of P_2O_5	Standard phosphate solution (11.3.5)	Corresponding mass of P_2O_5
ml	mg	ml	mg
0*	0	0*	0
1,0	0,10	6,0	0,60
2,0	0,20	7,0	0,70
3,0	0,30	8,0	0,80
4,0	0,40	9,0	0,90
5,0	0,50	10,0	1,00
Optical path length of cells, cm			
4 or 5		1	

* Blank test on the reagents for calibration.

Treat the contents of each flask as follows. Dilute to approximately 50 ml with water, add 2 ml of the hydrochloric acid solution (11.3.2) and 2 ml of the nitric acid solution (11.3.1). Finally, add 25 ml of the ammonium molybdovanadate solution (11.3.3) and mix. Dilute to the mark, mix and allow to stand for at least 10 min.

11.5.4.2 Spectrometric measurements

Carry out the spectrometric measurements using either the spectrometer (11.4.3), at a wavelength of maximum absorption (about 420 nm), or the spectrometer (11.4.4), fitted with suitable filters, after having adjusted the apparatus to zero absorbance against water.

11.5.4.3 Plotting the graphs

Deduct the absorbance of the solution of the blank test on the reagents for calibration from that of each of the standard matching solutions. Plot graphs having, for example, the number of milligrams of P_2O_5 contained in 100 ml of standard matching solution as abscissae, and the corresponding values of absorbance as ordinates.

11.5.5 Determination

11.5.5.1 Colour development

Place 50,0 ml of the test solution (11.5.2) in a 100 ml one-mark volumetric flask, add 25 ml of the ammonium molybdovanadate solution (11.3.3), dilute to the mark, mix and allow to stand for at least 10 min.

11.5.5.2 Spectrometric measurements

Carry out the spectrometric measurements on the test solution and on the blank test solution (11.5.3), after colour development, as specified in 11.5.4.2.

11.6 Expression of results

By means of the calibration graph (11.5.4.3), determine the masses of P_2O_5 corresponding to the absorbances.

The phosphates content, expressed as a percentage by mass of P_2O_5, is given by the formula

$$\frac{m_1 - m_2}{1\,000\ m_0} \times 100 \times \frac{250}{50}$$

$$= \frac{m_1 - m_2}{2\ m_0}$$

where

m_0 is the mass, in grams, of the test portion (11.5.1);

m_1 is the mass, in milligrams, of P_2O_5 found in the aliquot portion of the test solution taken for the colour development;

m_2 is the mass, in milligrams, of P_2O_5 found in the corresponding aliquot portion of the blank test solution.

12 Determination of permanganate index

12.1 Definition

For the purpose of this International Standard, the following definition applies.

permanganate index : The number of milligrams of potassium permanganate reduced by 100 ml of the laboratory sample under the conditions specified.

12.2 Principle

Reaction of a test portion, under specified conditions, with an excess of potassium permanganate solution in the presence of dilute sulphuric acid solution. Iodometric titration of the residual potassium permanganate.

12.3 Reagents

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

12.3.1 Sulphuric acid, 50 g/l solution.

12.3.2 Potassium permanganate, 1 g/l solution.

12.3.3 Potassium iodide, 100 g/l solution.

12.3.4 Sodium thiosulphate, standard volumetric solution $c(Na_2S_2O_3) = 0{,}033$ mol/l.

12.3.5 Starch solution.

Triturate 1,0 g of soluble starch with 5 ml of water and, whilst stirring, pour the mixture into 100 ml of boiling water. Boil for a few minutes and cool.

Discard the solution after 2 weeks.

12.4 Apparatus

Ordinary laboratory apparatus and

12.4.1 Two conical flasks, of capacity 250 ml, of borosilicate glass, provided with ground glass stoppers.

12.4.2 Water bath, capable of being controlled at 20 ± 0,5 °C.

12.4.3 Burettes, of capacity 10 ml, complying with the requirements of ISO 385/2, class A.

12.5 Procedure

12.5.1 Test portion

Take 5,0 ml of the laboratory sample, place in one of the conical flasks (12.4.1) containing 50 ml of the sulphuric acid solution (12.3.1) and shake gently until dissolved (5 to 10 min).

12.5.2 Blank test

Carry out a blank test at the same time as the determination, using the second conical flask (12.4.1), following the same procedure and using the same quantities of all the reagents except the sodium thiosulphate (12.3.4) as used for the determination, but omitting the test portion.

12.5.3 Determination

Immerse the flask containing the test portion (12.5.1) in the water bath (12.4.2), controlled at 20 ± 0,5 °C, and add potassium permanganate solution (12.3.2) from one of the burettes (12.4.3) until a permanent red colour is established. Then add a further 10 ml of the potassium permanganate solution and note the total volume of this solution used.

Leave in the dark for 40 min in the water bath (12.4.2), controlled at 20 ± 0,5 °C.

Determine the excess of potassium permanganate iodometrically by adding 10 ml of the potassium iodide solution (12.3.3) and titrating the liberated iodine with the sodium thiosulphate solution from one of the burettes. When the solution becomes pale yellow, add 0,5 ml of the starch solution (12.3.5) and continue the titration until the blue colour is discharged.

12.6 Expression of results

The permanganate index is given by the formula

$$1{,}07 \times (V_0 - V_1) \times \frac{100}{5}$$

$$= 21{,}4\,(V_0 - V_1)$$

where

V_0 is the volume, in millilitres, of the sodium thiosulphate solution (12.3.4) used for the blank test;

V_1 is the volume, in millilitres, of the sodium thiosulphate solution (12.3.4) used for the determination;

1,07 is the mass, in milligrams, of potassium permanganate corresponding to 1 ml of sodium thiosulphate solution, $c(Na_2S_2O_3) = 0{,}033$ mol/l.

NOTE — If the concentration of the standard volumetric solution used is not exactly as specified in the list of reagents, an appropriate correction should be applied.

13 Determination of dichromate index

13.1 Definition

For the purpose of this International Standard, the following definition applies.

dichromate index : The number of millilitres of standard volumetric potassium dichromate solution, $c(1/6\ K_2Cr_2O_7) = 0{,}1$ mol/l, that are reduced by 1,0 ml of the laboratory sample under the specified conditions.

13.2 Principle

Heating of a test portion with an excess of potassium dichromate solution in the presence of sulphuric acid. Iodometric titration of the residual potassium dichromate.

13.3 Reagents

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

13.3.1 Potassium iodide, 100 g/l solution.

13.3.2 Potassium dichromate, acidified standard volumetric solution, $c(1/6\ K_2Cr_2O_7) = 0{,}1$ mol/l, in dilute sulphuric acid.

Weigh, to the nearest 0,01 g, 4,90 g of potassium dichromate and dissolve in approximately 500 ml of water. Add slowly and carefully, while cooling, 400 ml of sulphuric acid, ϱ 1,84 g/ml. Transfer the solution quantitatively to a 1 000 ml one-mark volumetric flask, allow to cool to ambient temperature, dilute to the mark with water and mix.

13.3.3 Sodium thiosulphate, standard volumetric solution $c(Na_2S_2O_3) = 0{,}1$ mol/l.

13.3.4 Starch solution.

Triturate 1,0 g of soluble starch with 5 ml of water and, whilst stirring, pour the mixture into 100 ml of boiling water. Boil for a few minutes and cool.

Discard the solution after 2 weeks.

13.4 Apparatus

Clean all glassware prior to use by heating with a chromic/sulphuric acid mixture, taking the usual precautions, and then by rinsing first with running water and finally with distilled water.

Ordinary laboratory apparatus and

13.4.1 Two conical flasks, of capacity 500 ml, of borosilicate glass, fitted with ground glass stoppers.

13.4.2 Water bath, capable of being controlled at 50 ± 2 °C.

13.4.3 Burette, of capacity 10 ml, graduated in 0,02 ml.

13.4.4 Pipette, of capacity 50 ml, complying with the requirements of ISO 684, class A.

NOTE — Use the same pipette (13.4.4) for taking the potassium dichromate solution for the determination and for the blank test.

13.5 Procedure

13.5.1 Test portion

Add 5,0 ml of the laboratory sample, drop by drop, to one of the conical flasks (13.4.1) cooled in ice and containing 50,0 ml of the potassium dichromate solution (13.3.2), measured by means of the pipette (13.4.4).

13.5.2 Blank test

Carry out a blank test at the same time as the determination, using the second conical flask (13.4.1), following the same procedure and using the same reagents [except the sodium thiosulphate solution (13.3.3)] as used for the determination, but omitting the test portion.

13.5.3 Determination

Loosely stopper the flask containing the test portion (13.5.1) and heat on the water bath (13.4.2), controlled at 50 ± 2 °C, for 60 min.

Allow the flask to cool, add 100 ml of water and 10 ml of the potassium iodide solution (13.3.1). Titrate the mixture with the sodium thiosulphate solution (13.3.3) from the burette (13.4.3). When the solution becomes yellowish-green, add 0,5 ml of the starch solution (13.3.4) and continue the titration until the blue colour is discharged.

13.6 Expression of results

The dichromate index is given by the formula

$$(V_0 - V_1) \times \frac{1}{5}$$

$$= 0{,}2\,(V_0 - V_1)$$

where

V_0 is the volume, in millilitres, of the sodium thiosulphate solution (13.3.3) used for the blank test;

V_1 is the volume, in millilitres, of the sodium thiosulphate solution (13.3.3) used for the determination.

NOTE — If the concentration of the standard volumetric solution used is not exactly as specified in the list of reagents, an appropriate correction should be made.

14 Visual limit test for inorganic chlorides

14.1 Applicability

Using a test portion of 50 g, the method is applicable directly to products having inorganic chloride contents, expressed as Cl^-, in the range 0,000 5 to 0,05 % (m/m), but this range can be extended by adjusting the mass of the test portion (14.5.1).

14.2 Principle

Hydrolysis of a test portion in water. Visual comparison of the turbidity obtained by adding a silver nitrate solution to a solution of a test portion acidified with nitric acid, with that similarly obtained from a chloride solution of known concentration.

14.3 Reagents

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

14.3.1 Nitric acid, 315 g/l solution.

14.3.2 Silver nitrate, 50 g/l solution.

14.3.3 Chloride, standard solution corresponding to 0,1 g of Cl^- per litre.

Transfer 28,2 ml of a standard volumetric hydrochloric acid solution, c(HCl) = 0,1 mol/l, to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of Cl^-.

14.4 Apparatus

Ordinary laboratory apparatus and

14.4.1 Filter paper, chloride-free.

14.4.2 Weighing bottle, tall form, of capacity approximately 70 ml.

14.4.3 Two matched Nessler cylinders, of capacity 100 ml.

14.5 Procedure

14.5.1 Test portion

If the expected inorganic chlorides content lies within the range 0,000 5 to 0,05 % (m/m), weigh 50 ± 0,5 g of the laboratory sample into the weighing bottle (14.4.2). If the content is outside this range, weigh an appropriately reduced or increased mass, and adjust the volume of the aliquot portion, $0{,}05/x$ ml, taken in sub-clause 14.5.4, accordingly.

14.5.2 Preparation of the test solution

Transfer the test portion (14.5.1) quantitatively, 2 to 3 ml at a time, to a porcelain dish containing 100 ml of water at a temperature of about 50 °C, ensuring that each increment is dissolved before adding the next. Allow the solution to cool to ambient temperature, transfer quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

If the solution is cloudy, filter it through one of the filter papers (14.4.1) to remove turbidity due to aluminium.

14.5.3 Preparation of standard turbidimetric solution

Transfer 1,0 ml of the standard chloride solution (14.3.3) to one of the Nessler cylinders (14.4.3), dilute to the 100 ml mark with water, add 2 ml of the nitric acid solution (14.3.1) and mix.

14.5.4 Test

For a sample required to contain not more than x % (m/m) of inorganic chlorides, expressed as Cl^-, transfer to the other Nessler cylinder (14.4.3) an aliquot portion, (0,05/x) ml, of the test solution (14.5.2), dilute to the 100 ml with water, add 2 ml of the nitric acid solution (14.3.1) and mix.

Add to each Nessler cylinder 1 ml of the silver nitrate solution (14.3.2) and mix. Allow the cylinders to stand in the dark for 5 min, and then compare the turbidity produced by the aliquot portion of the test solution with that produced by the standard turbidimetric solution (14.5.3).

14.6 Expression of results

The inorganic chlorides content does not exceed x % (m/m) of Cl^- if the turbidity produced by the test solution does not exceed that produced by the standard turbidimetric solution.

15 Visual limit test for inorganic sulphates

15.1 Applicability

Using a test portion of 100 g, the method is applicable directly to products having inorganic sulphate contents, expressed as SO_4^{2-}, in the range 0,001 to 0,1 % (m/m), but this range can be extended by adjusting the mass of the test portion (see 15.5.1).

15.2 Principle

Hydrolysis of a test portion in water. Visual comparison of the turbidity obtained by adding a barium chloride solution to a solution of a test portion acidified with hydrochloric acid, with that similarly obtained from a sulphate solution of known concentration.

15.3 Reagents

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

15.3.1 Sodium carbonate, 53 g/l solution.

15.3.2 Hydrochloric acid, 36,5 g/l solution.

15.3.3 Barium chloride dihydrate, 100 g/l solution.

15.3.4 Sulphate, standard solution corresponding to 0,1 g of SO_4^{2-} per litre.

Transfer 20,8 ml of a standard volumetric sulphuric acid solution, $c(1/2H_2SO_4)$ = 0,1 mol/l, to a 1 000 ml one-mark volumetric flask. Dilute to the mark with water and mix.

1 ml of this standard solution contains 0,1 mg of SO_4^{2-}.

15.4 Apparatus

Ordinary laboratory apparatus and

15.4.1 Filter papers, sulphate-free.

15.4.2 Weighing bottle, tall form, of capacity approximately 120 ml.

15.4.3 Two matched Nessler cylinders, of capacity 100 ml.

15.5 Procedure

15.5.1 Test portion

If the expected inorganic sulphates content lies within the range 0,001 to 0,1 % (m/m), weigh 100 ± 1 g of the laboratory sample. If the content is outside this range, weigh an appropriately reduced or increased mass and adjust the volume of the aliquot portion, (0,1/x) ml, taken in sub-clause 15.5.4, accordingly.

15.5.2 Preparation of the test solution

Transfer the test portion (15.5.1) quantitatively, 2 to 3 ml at a time, to a porcelain dish containing 150 ml of water at a temperature of about 50 °C, ensuring that each increment is dissolved before adding the next. Add 0,2 ml of the sodium carbonate solution (15.3.1) and evaporate to dryness on a boiling water bath in a fume cupboard. Dissolve the residue in water containing 1 ml of the hydrochloric acid solution (15.3.2), transfer the solution quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

If the solution is cloudy, filter it through one of the filter papers (15.4.1) to remove turbidity due to aluminium.

15.5.3 Preparation of standard turbidimetric solution

Transfer 4,0 ml of the standard sulphate solution (15.3.4) to one of the Nessler cylinders (15.4.3), dilute to the mark with water, add 2 ml of the hydrochloric acid solution (15.3.2) and mix.

15.5.4 Test

For a sample required to contain not more than x % (m/m) of inorganic sulphates, expressed as SO_4^{2-}, transfer to the other Nessler cylinder (15.4.3) an aliquot portion (0,1/x) ml, of the test solution (15.5.2), dilute to the 100 ml with water, add 2 ml of the hydrochloric acid solution (15.3.2) and mix.

Add to each Nessler cylinder 2 ml of the barium chloride solution (15.3.3) and mix. Allow the cylinders to stand for 5 min, mix again and compare the turbidity produced by the aliquot portion of the test solution with that produced by the standard turbidimetric solution (15.5.3).

15.6 Expression of results

The inorganic sulphates content does not exceed x % (m/m) of SO_4^{2-} if the turbidity produced by the test solution does not exceed that produced by the standard turbidimetric solution.

16 Visual limit test for heavy metals (including iron)

16.1 Applicability

Using a test portion of 25 g, the method is applicable directly to products having heavy metal content, expressed as Pb, in the range 0,000 44 to 0,04 % (m/m), but this range can be extended by adjusting the mass of the test portion (see 16.5.1).

The method detects only the heavy metals present in non-complex form and is not specific for any one heavy metal.

16.2 Principle

Hydrolysis of a test portion in water. Conversion of heavy metals, such as lead, copper and iron, to their sulphides by treatment with sodium sulphide in ammoniacal solution, and visual comparison of the colour produced with that given by a standard lead solution similarly treated with sodium sulphide in the same way.

16.3 Reagents

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

16.3.1 Ammonia solution, ϱ 0,88 g/ml, approximately 34,3 % (m/m) solution.

16.3.2 Sodium sulphide nonahydrate ($Na_2S.9H_2O$), 100 g/l solution.

16.3.3 Lead, standard solution corresponding to 0,010 g of Pb per litre.

Weigh, to the nearest 0,000 1 g, 0,016 0 g of lead nitrate [$Pb(NO_3)_2$], dissolve in water, transfer the solution to a 1 000 ml one-mark volumetric flask, dilute to the mark and mix.

1 ml of this standard solution contains 0,010 mg of Pb.

Prepare this solution on the day of use.

16.3.4 Litmus paper, (pH range 5 to 8).

16.4 Apparatus

Ordinary laboratory apparatus and

16.4.1 Weighing bottle, tall form, of capacity approximately 50 ml.

16.4.2 Two matched Nessler cylinders, of capacity 50 ml.

16.5 Procedure

16.5.1 Test portion

If the expected heavy metals content lies within the range 0,000 44 to 0,04 % (m/m), weigh 25 ± 0,1 g of the laboratory sample in the weighing bottle (16.4.1). If the content is outside this range, weigh an appropriately reduced or increased mass and adjust the volume of the aliquot portion (0,02/x) ml, taken in 16.5.4 accordingly.

16.5.2 Preparation of the test solution

Transfer the test portion (16.5.1) quantitatively, 2 to 3 ml at a time, to a porcelain dish containing 100 ml of water at a temperature of about 50 °C, ensuring that each increment is dissolved before adding the next. Allow the solution to cool to ambient temperature, transfer quantitatively to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

If the solution is cloudy, filter it to remove turbidity due to aluminium.

16.5.3 Preparation of standard matching solution

Add to 30 ml of water in one of the Nessler cylinders (16.4.2), 2,0 ml of the standard lead solution (16.3.3) and 1 ml of the ammonia solution (16.3.1). Dilute to the 50 ml mark with water and mix. Then add 0,1 ml (2 drops) of the sodium sulphide solution (16.3.2) and mix again.

16.5.4 Test

For a sample required to contain not more than x % (m/m) of heavy metals, expressed as Pb, transfer to the other Nessler cylinder an aliquot portion (0,02/x) ml of the test solution, not exceeding 45 ml. Add the ammonia solution (16.3.1) until the solution is alkaline to the litmus paper (16.3.4) (blue colour), dilute to the 50 ml mark with water and mix. Then add 0,1 ml (2 drops) of the sodium sulphide solution (16.3.2) and mix again.

Compare the depth of colour of this solution with that of the standard matching solution (16.5.3).

16.6 Expression of results

The heavy metals content does not exceed x % (m/m), expressed as Pb, if the depth of colour of the test solution does not exceed that of the standard matching solution.

17 Sulphuric acid colour test

17.1 Principle

Treatment of a test portion with a solution of sulphuric acid, under specified conditions, and visual comparison of the colour developed with that of the same volume of an agreed colour standard.

NOTE — The colour developed may be measured in Hazen units (platinum-cobalt scale), in which case the method specified in ISO 2211 should be used.

17.2 Reagents

During the test, use only reagents of recognized analytical reagent grade.

17.2.1 Sulphuric acid, ϱ 1,84 g/ml, about 96 % (m/m) solution.

NOTE — Take care to control the density.

17.3 Apparatus

Ordinary laboratory apparatus and

17.3.1 Cold-water bath, controlled at approximately 10 °C.

17.3.2 Water bath, capable of being controlled at 35 ± 1 °C.

17.3.3 Two matched Nessler cylinders, of capacity 50 ml.

17.3.4 Burette, of capacity 10 ml, complying with the requirements of ISO 385/2, class A.

17.4 Procedure

17.4.1 Cleaning of the apparatus

Carefully clean the conical flask and the Nessler cylinders (17.3.3) with the sulphuric acid solution (17.2.1), then rinse in running water and finally with distilled water. Eliminate the distilled water by rinsing with ethanol 95 % (V/V). Drain well and leave to dry in the air.

NOTE — Do not grease the ground glass joints or the taps.

17.4.2 Test portion

Take 5,0 ml of the laboratory sample.

17.4.3 Preparation of colour standard

Prepare the agreed colour standard.

NOTE — If it has been agreed to measure the colour developed in Hazen units, prepare the standard colorimetric solutions in accordance with ISO 2211, clause 6.

17.4.4 Test

Transfer the test portion (17.4.2) to a cleaned dry conical flask of capacity 50 ml and immerse the flask in the cold-water bath (17.3.1) controlled at approximately 10 °C. Add, drop by drop, from the burette (17.3.4), 5,0 ml of the sulphuric acid (17.2.1), swirling during the whole of addition. During the addition of the acid, take care that the temperature of the liquid in the flask does not rise above 30 °C.

Remove the flask from the cold water bath and place it in the water bath (17.3.2) controlled at 35 ± 1 °C ensuring that the level of the test mixture in the flask is lower than that of the water in the bath and allow to stand for 60 min. Cool the test mixture to ambient temperature by placing the flask in the cold-water bath.

Transfer the test mixture to one of the Nessler cylinders (17.3.3), and compare its colour with that of an equivalent volume of the agreed colour standard (17.4.3) in the other Nessler cylinder.

NOTE — If it has been agreed to measure the colour developed in Hazen units, use the procedure specified in ISO 2211, clause 7, to compare the colours.

17.5 Expression of results

Report whether the colour developed in the test portion is darker, equal to or less than that of the agreed colour standard, or express it in Hazen units.