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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 754

ACETIC ANHYDRIDE FOR INDUSTRIAL USE

METHODS OF TEST

1st EDITION
June 1968

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BRIEF HISTORY

The ISO Recommendation R 754, *Acetic anhydride for industrial use – Methods of test*, was drawn up by Technical Committee ISO/TC 47, *Chemistry*, the Secretariat of which is held by the Ente Nazionale Italiano di Unificazione (UNI).

Work on this question by the Technical Committee began in 1956 and led, in 1962, to the adoption of a Draft ISO Recommendation.

In November 1963, this Draft ISO Recommendation (No. 653) was circulated to all the ISO Member Bodies for enquiry. It was approved, subject to a few modifications of an editorial nature, by the following Member Bodies :

Australia	Hungary	Romania
Austria	India	Spain
Belgium	Israel	Switzerland
Chile	Italy	U.A.R.
Colombia	Korea, Rep. of	United Kingdom
Czechoslovakia	Netherlands	U.S.A.
France	Poland	U.S.S.R.
Germany	Portugal	Yugoslavia

Two Member Bodies opposed the approval of the Draft :

Japan
New Zealand

The Draft ISO Recommendation was then submitted by correspondence to the ISO Council, which decided, in June 1968, to accept it as an ISO RECOMMENDATION.

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* Not included in this ISO Recommendation as these determinations are still under study.

ISO Recommendation R 754 June 1968

ACETIC ANHYDRIDE FOR INDUSTRIAL USE

METHODS OF TEST

1. SCOPE

This ISO Recommendation describes methods of test for acetic anhydride for industrial use, and is divided into two parts, namely :

Part I – Methods of test for general use

Part II – Methods of test for special purposes

2. SAMPLE

Take a volume of sample that is sufficient for all analyses to be carried out so that it is representative of the bulk.

Place the sample in a clean, dry and air-tight glass stoppered bottle of such a size that it is nearly filled by the sample.

When it is necessary to seal the container, care should be taken to avoid the risk of contaminating the sample in any way.

PART I – METHODS OF TEST FOR GENERAL USE

3. DETERMINATION OF DISTILLATION YIELD

3.1 Use the method described in ISO Recommendation R 918, *Test method for distillation (Distillation yield and distillation range).*

3.2 The following details, not given in the above ISO Recommendation, apply to acetic anhydride :

Thermometer, (see clause 3.2 of ISO Recommendation R 918) should also comply with the following requirements :

Values in degrees Celsius

Thermometer range	Graduations	Maximum error	Maximum error in an interval of 10 degrees Celsius
98 to 152	0.2	0.4	0.4

A correction of 0.050 (p - 760) degrees Celsius where p is the barometric pressure in standard millimetres of mercury, is added to the specified distillation temperatures (see clause 5.1 of ISO Recommendation R 918). The interval before the first drop of distillate falls from the end of the condenser should be 12 to 17 minutes (see clause 6.1 of ISO Recommendation R 918).

4. DETERMINATION OF ASH CONTENT

4.1 Apparatus

Ordinary laboratory apparatus.

4.2 Procedure

4.2.1 Evaporate to dryness a known mass (between 10 and 100 g depending on the ash content expected) of the sample in a weighed platinum or silica dish of capacity 50 ml, and gently ignite the residue until all carbonaceous matter has disappeared.

4.2.2 Cool the dish and its contents to atmospheric temperature in a desiccator containing anhydrous calcium chloride, and weigh.

4.3 Expression of results

$$\text{Ash, \% (m/m)} = \frac{100 \times M_1}{M_2}$$

where

M_1 is the mass, in grammes, of the residue,

M_2 is the mass, in grammes, of the test portion.

5. LIMIT TEST FOR INORGANIC CHLORIDES

This method is applicable when the chloride content, expressed as Cl, is not greater than 0.05 and not less than 0.0005 %. If the chloride content lies outside that range, the mass of test portion taken (5.4.1) should be reduced or increased and an appropriate adjustment made to the expression of $\frac{0.05}{x}$ ml in clause 5.4.4.

5.1 Principle

Comparison of the turbidity, obtained by the addition of silver nitrate to a solution prepared from the sample in presence of nitric acid, with that similarly obtained from a chloride solution of known concentration.

5.2 Reagents

Distilled water or water of equivalent purity should be used in the test. All reagents and filter paper should be chloride free.

5.2.1 *Nitric acid,* approximately 5 N solution.

5.2.2 *Standard chloride solution* (0.1 mg Cl/ml). Dilute 28.2 ml of 0.1 N hydrochloric acid solution to 1000 ml with water.

5.2.3 *Silver nitrate,* 50 g/l solution.

5.3 Apparatus

Ordinary laboratory apparatus.

5.4 Procedure

5.4.1 Weigh 50 ± 0.5 g of the test sample, dissolve in water, transfer to a 250 ml one-mark volumetric flask, dilute to the mark with water and mix.

5.4.2 If the solution is not clear, pass it through a filter paper. This should remove turbidity due to aluminium. If any turbidity remains in the filtrate due to contamination with wax, remove it by shaking with a suitable solvent, for example, light petroleum.

5.4.3 To prepare the chloride solution of known concentration, add to a 100 ml Nessler cylinder 1.0 ml of the standard chloride solution (5.2.2), dilute to the mark with water, add 2 ml of nitric acid solution (5.2.1) and mix.

5.4.4 For a sample required to contain not more than x % of chloride, expressed as Cl, transfer to a 100 ml Nessler cylinder an aliquot, $\frac{0.05}{x}$ ml, of the solution prepared from the test sample (5.4.1), dilute to the mark with water, add 2 ml of nitric acid solution (5.2.1), and mix.

5.4.5 Add to each Nessler cylinder 1 ml of silver nitrate solution (5.2.3) and mix. Allow the cylinders to stand in the dark for 5 minutes then compare the turbidity produced by the test sample with that produced by the chloride solution of known concentration.

5.5 Expression of results

A sample required to contain not more than x % of Cl does so if the turbidity produced from its solution (5.4.4) is equal to or less than that produced from the chloride solution of known concentration (5.4.3).

6. LIMIT TEST FOR INORGANIC SULPHATES

This method is applicable when the sulphate content, expressed as SO_4, is not greater than 0.1 % and not less than 0.001 %. If the sulphate content lies outside that range the mass of test portion taken (6.4.1) should be reduced or increased and an appropriate adjustment made to the expression $\frac{0.1}{x}$ ml in clause 6.4.4.

6.1 Principle

Comparison of the turbidity, obtained by the addition of barium chloride to a solution prepared from the sample in the presence of hydrochloric acid, with that similarly obtained from a sulphate solution of known concentration.

6.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

6.2.1 *Sodium carbonate*, N solution.

6.2.2 *Hydrochloric acid*, N solution.

6.2.3 *Barium chloride*, $BaCl_2.2H_2O$, 100 g/l solution.

6.2.4 *Standard sulphate solution* (0.1 mg SO_4/ml). Dilute 20.8 ml of 0.1 N standard volumetric solution of sulphuric acid to 1000 ml with water and mix thoroughly.

6.3 Apparatus

Ordinary laboratory apparatus.

6.4 Procedure

6.4.1 Weigh 100 ± 1 g of the test sample, dissolve it in water, add 0.2 ml of sodium carbonate solution (6.2.1) and evaporate to dryness in an evaporating basin on a boiling water bath. Dissolve the residue in water containing 1 ml of hydrochloric acid solution (6.2.2), transfer to a 250 ml one-mark volumetric flask, dilute to the mark with water, and mix.

6.4.2 If the solution is not clear, pass it through a filter paper. This should remove turbidity due to aluminium. If any turbidity remains in the filtrate due to contamination with wax, remove it by shaking with a suitable solvent, for example, light petroleum.

6.4.3 To prepare the sulphate solution of known concentration, add to a 100 ml Nessler cylinder 4.0 ml of the standard sulphate solution (6.2.4), dilute to the mark with water, add 2 ml of hydrochloric acid solution (6.2.2) and mix.

6.4.4 For a sample required to contain not more than x % of SO_4, transfer to a 100 ml Nessler cylinder an aliquot, $\frac{0.1}{x}$ ml, of the solution prepared from the test sample (6.4.1). Dilute to the mark with water, add 2 ml of hydrochloric acid solution (6.2.2) and mix.

6.4.5 Add to each Nessler cylinder 2 ml of barium chloride solution (6.2.3) and mix. Allow the cylinders to stand for 5 minutes, mix again, and compare the turbidity produced by the test sample with that produced by the sulphate solution of known concentration.

6.5 Expression of results

A sample required to contain not more than x % of SO_4 does so if the turbidity produced from its solution (6.4.4) is equal to or less than that produced from the sulphate solution of known concentration (6.4.3).

7. DETERMINATION OF ANHYDRIDE CONTENT

7.1 Principle

Hydrolysis of a given amount of the sample by means of a standard volumetric solution of sodium hydroxide, and determination of the alkali consumed, by back titration of the excess of sodium hydroxide with standard volumetric solution of hydrochloric acid.

Reaction with aniline of an equivalent quantity of sample in accordance with the reaction

$$(CH_3CO)_2O + C_6H_5NH_2 \longrightarrow C_6H_5NHCOCH_3 + CH_3COOH$$

and titration of the acetic acid formed using a standard volumetric solution of sodium hydroxide.

Calculation of the acetic anhydride content from the difference between the volumes of sodium hydroxide solution consumed respectively in the hydrolysis of the sample and in the titration of the acetic acid formed in its reaction with aniline.

7.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

7.2.1 *Sodium hydroxide*, N standard volumetric solution.

7.2.2 *Hydrochloric acid*, N standard volumetric solution.

7.2.3 *Benzene*, dry, freshly distilled.

7.2.4 *Aniline*, dry, freshly distilled.

7.2.5 *Methanol.*

7.2.6 *Phenolphthalein*, 5 g/l ethanolic solution. Dissolve 0.5 g of phenolphthalein in 100 ml of 95 % (v/v) ethanol and make it faintly pink by the addition of dilute sodium hydroxide solution.

7.3 **Apparatus**

Ordinary laboratory apparatus, and

7.3.1 *Weighing pipette,* capacity about 5 ml.

7.3.2 *Two flasks,* ground glass stoppered, capacity 500 ml.

7.4 **Procedure**

7.4.1 Dissolve about 2 g of the test sample, accurately weighed by means of the weighing pipette (7.3.1), in 50.0 ml of the sodium hydroxide solution (7.2.1) contained in a stoppered flask (7.3.2), and allow to stand for 1 hour. Add 40 ml of benzene (7.2.3), 10 ml of aniline (7.2.4) and 250 ml of methanol (7.2.5), and titrate the excess of alkali with the hydrochloric acid solution (7.2.2), using 0.5 ml of the phenolphthalein solution (7.2.6).

7.4.2 Dissolve about 2 g of the test sample, accurately weighed by means of the weighing pipette (7.3.1), in 20 ml of the benzene (7.2.3) in a stoppered flask (7.3.2), cool in ice and add a cold solution of 10 ml of the anline (7.2.4) in 20 ml of the benzene (7.2.3). Allow the mixture to stand for 1 hour in ice. Add 250 ml of methanol (7.2.5) and 50.0 ml of the sodium hydroxyde solution (7.2.1). Titrate the excess of alkali with the hydrochloric acid solution (7.2.2) using 0.5 ml of phenolphthalein solution (7.2.6).

7.5 **Expression of results**

$$\text{Acetic anhydride}[(CH_3CO)_2O],\ \% \text{ (m/m)} = 10.21 \times \left[\frac{50 - V_1}{M_1} - \frac{50 - V_2}{M_2}\right]$$

where

V_1 is the volume, in millilitres, of N hydrochloric acid solution (7.2.2) used in clause 7.4.1,

V_2 is the volume, in millilitres, of N hydrochloric acid solution (7.2.2) used in clause 7.4.2,

M_1 is the mass, in grammes, of the test portion taken in clause 7.4.2,

M_2 is the mass, in grammes, of the test portion taken in clause 7.4.2.

8. DETERMINATION OF BROMINE INDEX

Use the method described in ISO Recommendation R 761, *Method for the determination of bromine index.*

9. DETERMINATION OF PERMANGANATE INDEX

9.1 **Definition**

The permanganate index is defined as the number of milligrammes of potassium permanganate reduced by 100 ml of the sample under the conditions of the test.

9.2 **Principle**

Reaction of the sample under controlled conditions with an excess of potassium permanganate in the presence of dilute sulphuric acid. Iodometric determination of the quantity of permaganate left unreduced, and subtraction of this quantity from the amount taken.

9.3 Reagents

Distilled water or water of equivalent purity should be used in the test.

9.3.1 *Sulphuric acid,* 50 g/l solution.

9.3.2 *Potassium permanganate,* 1 g/l solution.

9.3.3 *Sodium thiosulphate,* M/30 standard volumetric solution.

9.3.4 *Potassium iodide,* 100 g/l solution.

9.3.5 *Starch,* 10 g/l solution, freshly prepared.

9.4 Apparatus

Ordinary laboratory apparatus and

9.4.1 *Two conical flasks,* ground glass stoppered, capacity 250 ml.

9.4.2 *Two microburettes,* 10 ml graduated in 0.02 ml divisions.

9.4.3 *Water bath,* controlled at 20 ± 0.5 °C.

9.5 Procedure

9.5.1 To 50 ml of the dilute sulphuric acid solution (9.3.1) contained in one of the stoppered 250 ml flasks (9.4.1), add 5.0 ml of the test sample, shaking gently until dissolved (5 to 10 minutes).

9.5.2 Add, at 20 ± 0.5 °C, potassium permanganate solution (9.3.2) from a microburette (9.4.2) until a permanent red colour is established and then add a further 10 ml. Note the total amount added. Leave in the dark to react for 40 minutes at 20 ± 0.5 °C.

9.5.3 Determine the excess of potassium permanganate iodometrically by adding an excess of potassium iodide solution (9.3.4) and titrating from the second microburette (9.4.2) with the sodium thiosulphate solution (9.3.3), adding 0.5 ml of starch solution (9.3.5) just before the end point is reached.

9.5.4 Carry out simultaneously a blank determination, in the second conical flask (9.4.1), using the above procedure and adding the same total volume of potassium permanganate solution (9.3.2) as that added in clause 9.5.2.

9.6 Expression of results

$$\text{Permanganate index} = 21\,(V_2 - V_1)$$

where

V_2 is the volume, in millilitres, of M/30 sodium thiosulphate solution used in clause 9.5.4,

V_1 is the volume, in millilitres, of M/30 sodium thiosulphate solution used in clause 9.5.3.

PART II – METHODS OF TEST FOR SPECIAL PURPOSES

In case where the acetic anhydride is required for special purposes, for example, pharmaceutical, the following additional test may be required.

10. LIMIT TEST FOR HEAVY METALS (INCLUDING IRON)

10.1 Principle

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

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

10.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

10.2.1 *Aqueous ammonia*, $d = 0.88$.

10.2.2 *Sodium sulphide*, 100 g/l solution.

10.2.3 *Standard lead solution* (10 µg Pb/ml), freshly prepared. Dissolve 0.0160 g of lead nitrate in water and make up to 1000 ml.

10.3 Apparatus

Ordinary laboratory apparatus.

10.4 Procedure

10.4.1 Pipette 25 ml of the test sample into a 250 ml one-mark volumetric flask, add 150 ml of water, shake over a period of 10 minutes (until the sample is completely dissolved) and then dilute to the mark with water. Mix well.

10.4.2 Transfer a 10 ml aliquot to a Nessler cylinder. Add the aqueous ammonia (10.2.1) until the solution is alkaline to litmus paper, and dilute to 50 ml with water. Add 0.1 ml (two drops) of sodium sulphide solution (10.2.2) and mix well.

10.4.3 Preparation of agreed standard matching solution. To 40 ml of water contained in a second Nessler cylinder, add the agreed quantity of the standard lead solution (10.2.3) and 1 ml of the aqueous ammonia (10.2.1). Dilute to 50 ml with water and mix well. Add 0.1 ml (two drops) of sodium sulphide solution (10.2.2) and again mix well.

10.4.4 Compare the darkening of the test solution (10.4.2) with that of the agreed standard matching solution (10.4.3).

10.5 Expression of results

Report the darkening of the test solution as greater than, equal to, or less than that of the agreed standard matching solution, mentioning the lead content of the latter.

11. DETERMINATION OF IRON CONTENT

11.1 Principle

Conversion of any iron present in the sample into the sulphate by evaporation to dryness in the presence of sulphuric acid, and colorimetric determination of the iron using 2,2'bipyridyl.

NOTE. – Although this method specifies the use of spectrophotometre or photometer, it is permissible to employ as an alternative procedure a visual method comparing the test solution with a series of standard matching solutions (see clause 11.5.5).

11.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

11.2.1 *Sulphuric acid*, $d = 1.84$, diluted 1 + 6 by volume.

11.2.2 *Nitric acid*, $d = 1.4$, diluted 1 + 3 by volume.

11.2.3 *Urea solution.* Dissolve 100 g of urea in 100 ml of water.

11.2.4 *Hydroxylammonium chloride*, 100 g/l solution.

11.2.5 *Ammonium acetate* 500 g/l solution.

11.2.6 *2,2'-bipyridyl*, 5 g/l hydrochloric acid solution. Dissolve 0.5 g of 2,2'-bipyridyl in 100 ml of N hydrochloric acid.

11.2.7 *Standard iron solution* (10 µg Fe/ml). Dissolve 0.7022 g of pure iron (II) – ammonium sulphate hexahydrate [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$] in 50 ml of the sulphuric acid solution (11.2.1) and dilute to 1000 ml with water. Dilute 100 ml solution thus obtained to 1000 ml with water.

11.3 Apparatus

Ordinary laboratory apparatus, and

11.3.1 *Spectrophotometer* or *photometer.*

11.4 Calibration charts

11.4.1 Place in 100 ml one-mark volumetric flasks the following quantities of standard iron solution (11.2.7)

0 – 2.0 – 4.0 – 7.0 – 10.0 – 15.0 – 20.0 ml

To each add 20 ml of the nitric acid solution (11.2.2), 2 ml of the urea solution (11.2.3) and 2 ml of the hydroxylammonium chloride solution (11.2.4). Mix and allow to stand for 2 minutes. Then add 30 ml of the ammonium acetate solution (11.2.5) and 5 ml of the 2,2'-bipyridyl solution (11.2.6) and dilute to the mark with water.

11.4.2 Measure the optical densities of the solutions in the spectrophotometer or photometer (11.3.1), determining the optical density at a wave length between 510 and 520 nm.

11.4.3 Draw a graph plotting optical densities as a function of the quantities of iron (in microgrammes) in 100 ml of the solution.

11.5 Procedure

11.5.1 Weigh 100 g of the test sample in a platinum basin of capacity about 150 ml and evaporate to dryness on a water bath under a hood having a good draught. Allow to cool and add 10 ml of sulphuric acid solution (11.2.1). Evaporate first on a water bath and finally on a sand bath until white fumes are just evolved.

11.5.2 Allow to cool, add a few drops of the dilute nitric acid (11.2.2) and re-evaporate until white fumes just cease to be evolved. If tarry products remain, add a few further drops of the nitric acid (11.2.2) and again evaporate on the sand bath.

11.5.3 Take up the residue with 20 ml of the nitric acid solution (11.2.2), warming to assist solution of salts. Transfer the solution quantitatively to a 100 ml one-mark volumetric flask, rinsing the platinum basin. Add 2 ml of the urea solution (11.2.3), stir and add 2 ml of the hydroxylammonium chloride solution (11.2.4), mix and allow to stand for 2 minutes. Then add 30 ml of the ammonium acetate solution (11.2.5) and 5 ml of the 2,2'-bipyridyl solution (11.2.6) and dilute to the mark with water.

11.5.4 Measure the optical density of the solution in the spectrophotometer or photometer (11.3.1) at a wave length between 510 and 520 nm using a cell with the same optical path length as those used in the preparation of the calibration chart, and by reference to the calibration chart prepared as indicated in clause 11.4, read the iron content (in microgrammes of iron in 100 ml) corresponding to this optical density.

11.5.5 As an alternative to measurement of optical density using a spectrophotometer or photometer, the test solution prepared as in clause 11.5.3 may be compared visually with a series of standard matching solutions prepared under similar conditions, and its iron content (in microgrammes of iron in 100 ml) deduced.

11.6 Expression of results

Express the iron content of the sample in parts per million by mass calculated by dividing by 100 the iron content determined according to clause 11.5.4 or clause 11.5.5.

12. DETERMINATION OF PHOSPHATE CONTENT

12.1 Principle

Evaporation to dryness of the sample in the presence of nitric acid solution and treatment of the residue with a solution of ammonium molybdate and ammonium vanadate. Measurement of the colour of the resulting solution and determination of the phosphate content by reference to calibration charts.

12.2 Reagents

Distilled water or water of equivalent purity should be used in the test.

12.2.1 *Nitric acid*, $d = 1.4$.

12.2.2 *Sulphuric acid*, $d = 1.84$ diluted 1 + 6 by volume.

12.2.3 *Ammonium molybdate and ammonium vanadate solution.* Dissolve 20 g of ammonium molybdate in 400 ml of water and 1 g of ammonium vanadate in 300 ml of warm water. Add slowly to the cooled vanadate solution 140 ml of the nitric acid solution (12.2.1). Mix the solutions. Dilute with water to 1000 ml and again mix thoroughly.

12.2.4 *Standard phosphate solution.* . Dissolve 3.835 g of potassium dihydrogen orthophosphate (KH_2PO_4) in water and dilute to 1000 ml, and immediately before use dilute one volume to twenty volumes. 1 ml of this solution is equivalent to 0.1 mg of P_2O_5.

12.3 Apparatus

Ordinary laboratory apparatus, and

12.3.1 *Spectrophotometer* or *photometer.*

12.3.2 *Two graduated pipettes,* 10 ml with 0.1 ml divisions.

12.4 Calibration charts

12.4.1 Place in 100 ml one-mark volumetric flasks from a graduated pipette (12.3.2), the following quantities of dilute standard phosphate solution (12.2.4)

1.0 – 3.0 – 5.0 – 7.0 – 10.0 ml

Add with a pipette 25 ml of ammonium molybdate and ammonium vanadate solution (12.2.3) to each flask, dilute to 100 ml with water and mix well. Allow to stand for 10 ± 2 minutes.

12.4.2 Measure the optical densities of the solutions as described in clause 12.5.4.

12.4.3 Draw a graph plotting optical densities as a function of the quantities of P_2O_5 (in milligrammes) in 100 ml of the solution.

NOTE. – This graph is not quite linear.

12.5 Procedure

12.5.1 Mix 2 ml of the test sample from a graduated pipette (12.3.2) (for low phosphate contents take a larger sample) with 5 ml of water in a platinum basin of capacity about 30 ml. When the sample has dissolved add 3 ml of nitric acid solution (12.2.1) and evaporate to dryness on a boiling water bath.

12.5.2 Dissolve the residue in 1 ml of sulphuric acid solution (12.2.2), add 50 ml of water and transfer quantitatively to a 100 ml one-mark volumetric flask. Add, from a pipette, 25 ml of ammonium molybdate-ammonium vanadate solution (12.2.3) to the flask, dilute to 100 ml with water and mix well. Allow to stand for 10 ± 2 minutes.

12.5.3 At the same time prepare a blank in exactly the same way, but omitting the sample.

12.5.4 Measure the optical density at a wave length between 460 and 470 nm of the solution prepared in clause 12.5.2 using a 4 cm cell in the spectrophotometer or photometer (12.3.1). Use the blank solution (12.5.3) in a 4 cm reference cell.

12.6 Expression of results

By reference to the calibration chart prepared as indicated in clause 12.4, calculate the P_2O_5 content as a percentage, by mass in the test sample, using the formula

$$P_2O_5, \% \text{ (m/m)} = \frac{0.10 \times D}{V \times \rho}$$

where

D is the P_2O_5 content (in milligrammes in 100 ml) shown on the calibration chart corresponding to the optical density determined in clause 12.5.4,

ρ is the density, in grammes, per millilitre of the test sample at 20 °C.

V is the volume, in millilitres, of the test portion.

NOTE. – An approximate determination of density is necessary.

13. DETERMINATION OF ARSENIC CONTENT

13.1 Principle

Reduction of the arsenic in the sample to arsenic trihydride which, in contact with a mercuric bromide paper, gives a coloured stain which varies from yellow to orange or brown according to the quantity of arsenic present. Colorimetric determination by a comparison with a series of stains obtained under the same conditions, from solutions containing known quantities of arsenic.

13.2 Reagents

Distilled water or water of equivalent purity should be used in the test. The reagents used should be free from arsenic.

13.2.1 *Lead acetate cotton wool pellets.* Soak pellets of absorbent cotton wool of a diameter of 5 to 6 mm in a 50 g/l neutral solution of lead acetate, then drain and lightly press.

13.2.2 *Lead acetate paper.* Immerse strips of filter paper 8 mm × 50 mm in size in a 10 g/l neutral aqueous solution of lead acetate, drain, remove surplus liquid by pressing them lightly between two or three sheets of filter paper.

13.2.3 *Sulphuric acid, d* = 1.84.

13.2.4 *Sodium chloride,* acid solution. Mix one volume of sulphuric acid (13.2.3) with four volumes of water. Then dissolve 100 g of pure sodium chloride in 1000 ml of the approximately 300 g/l sulphuric acid thus obtained.

13.2.5 *Iron (III) – ammonium sulphate,* acid solution. Dissolve in water 84 g of iron (III) – ammonium sulphate [$(NH_4)_2SO_4 . Fe_2(SO_4)_3 . 24\ H_2O$], add 10 ml of the sodium chloride solution (13.2.4) and make up to 1000 ml with water.

13.2.6 *Stannous chloride,* acid solution. Dissolve 22.6 g of stannous chloride, $SnCl_2.2H_2O$, in water. Add 56 ml of the sodium chloride solution (13.2.4) and make up to 1000 ml with water. Keep the solution in a bottle of yellow glass in the presence of a few pieces of pure tin.

13.2.7 *Pure granulated zinc,* in pieces of 4 to 5 mm diameter. The zinc weighed for the experiment should be washed at the time of use with the sodium chloride solution (13.2.4) and then with water.

13.2.8 *Sensitized mercuric bromide paper.* Immerse sheets of consistent, fine grained filter paper for 1 hour in a 50 g/l ethanolic solution of mercuric bromide. Then dry the well drained and pressed paper, preferably in dust free air, or more rapidly in an oven at 90 °C. Cut from the dried sheets, strips exactly 3 mm × 120 mm. Keep these in a dark blue, ground glass stoppered, container.

13.2.9 *Standard arsenic solution.* Dissolve 0.132 g of very pure arsenious oxide in 20 ml of 350 g/l sodium hydroxide solution. Dilute with a little boiled and cooled water and then add slowly 10 ml of sulphuric acid (13.2.3). Make the solution up to 1000 ml with boiled and cooled water. 1 ml of this solution contains 0.1 mg of arsenic. Take 10 ml (equivalent to 1 mg of arsenic) and make up to 1000 ml again with boiled and cooled water. 1 ml of the resulting solution contains 1.0 μg of arsenic.

13.2.10 *Hydrogen peroxide,* 100 g/l solution (30 volumes).

13.3 **Apparatus**

Ordinary laboratory apparatus, and

13.3.1 *Assembly* (see Fig. 1), consisting of

13.3.1.1 *Conical flask,* 100 ml of borosilicate glass, to which are connected, by means of ground joints, the following components in series.

13.3.1.2 *Tube for removal of hydrogen sulphide,* with an internal diameter of 12 mm and a height of 70 mm above a bulb of 20 mm diameter. In the bottom of the bulb is placed a thin layer of dry glass wool, mixed to the extent of one third, with lead acetate cotton wool pellets (13.2.1), followed by another light layer of glass wool, and lastly, strips of damp lead acetate paper (13.2.2).

13.3.1.3 *Glass tube,* with an internal diameter of 3 mm and 120 mm in length, above a slight constriction at the bottom end. In this tube is placed a sensitized mercuric bromide paper (13.2.8).

13.3.2 *Conical flask,* capacity 200 ml, with ground glass stopper.

13.3.3 *Graduated pipette,* 10 ml, graduated in 0.1 ml divisions.

13.4 **Procedure**

13.4.1 *Preparation of a standard colorimetric series of stains on filter paper.* Prepare a standard colorimetric series of stains corresponding respectively to 0.001 – 0.002 – 0.004 – 0.006 – 0.008 – 0.010 mg of arsenic, as described in clauses 13.4.1.1 and 13.4.1.2 below.

13.4.1.1 Into the flask (13.3.1.1) place 1 ml of the standard arsenic solution (13.2.9) using the graduated pipette (13.3.3), 30 ml of acid sodium chloride solution (13.2.4), 10 ml of iron (III) – ammonium sulphate solution (13.2.5) and 20 ml of stannous chloride solution (13.2.6).

Heat to boiling, cool immediately to about 20 °C by placing the flask into cold water, then place in the flask 10 g of granulated zinc (13.2.7) and connect quickly to the neck of the hydrogen sulphide removal tube (13.3.1.2) provided with the tube (13.3.1.3) containing the sensitized paper. Plunge the flask into water at 20 to 25 °C, allow the reaction to proceed for 1 hour then extract the paper and preserve it in darkness in a cardboard box, where the colour obtained can be preserved for several months.

13.4.1.2 Repeat the above procedure using, instead of 1 ml, respectively 2, 4, 6, 8 and 10 ml of the standard arsenic solution (13.2.9).

13.4.2 *Determination of the arsenic content of the sample*

13.4.2.1 Place about 50 ml of the test sample in the flask (13.3.2) and weigh. Transfer this in small increments of 1 to 2 ml to 50 ml of hot water contained in a 250 ml borosilicate glass beaker making sure that each increment is hydrolysed before the addition of the next.

Reweigh the flask to obtain the mass of test portion taken by difference from the previous weighing. Add 5 ml of the hydrogen peroxide solution (13.2.10). Evaporate almost to dryness on a sand bath.

Add 5 ml of sulphuric acid solution (13.2.3) and evaporate down to white fumes. Dissolve carefully in a little water, and transfer to a 100 ml one-mark volumetric flask. Add the washings of the beaker, dilute and mix. Cool, dilute with water up to the graduation mark. Mix well (Solution *X*).

13.4.2.2 Using 10 ml of solution X instead of the standard arsenic solution, proceed as in clause 13.4.1.1 above, then compare the stain thus obtained with the standard colorimetric series. If the stain is within the colour range, deduce from its position the arsenic content of the sample.

13.4.2.3 If, however, this stain is outside the limits of the standard colorimetric series, use this first test for the purpose only of a simple estimation of the arsenic content, and for choosing a correspondingly larger or smaller volume of solution X for a further test in which the colour stain produced will this time have an intensity within the standard series, thus permitting a more accurate estimation of the arsenic content. Conduct this second test accordingly and the comparison, noting the value of arsenic which corresponds in the scale to the stain obtained from the test.

13.5 Expression of results

$$\text{Arsenic content, parts per million (m/m)} = \frac{100\,M_2}{V \times M_1}$$

where

M_2 is the mass, in microgrammes, of arsenic in the solution yielding the standard stain matching the stain produced in the final test,

V is the volume, in millilitres, of sample solution X used in the final test,

M_1 is the mass, in grammes, of the test portion.

14. DETERMINATION OF WATER CONTENT

Use one of the methods described in ISO Recommendation R 760, *Determination of water by the Karl Fischer method,* but cooling the solution to be titrated in melting ice and keeping it cold throughout the whole of the titration.

15. DETERMINATION OF TOTAL HALOGEN CONTENT*

16. DETERMINATION OF TOTAL SULPHUR CONTENT*

17. DETERMINATION OF DICHROMATE INDEX

17.1 Definition

The dichromate index is defined as the number of millilitres of 0.1 N potassium dichromate solution that are reduced by 1 ml of the sample under the conditions of the test.

17.2 Principle

Iodometric determination of the quantity of dichromate left unreduced, after the sample has been warmed with an excess of potassium dichromate in the presence of sulphuric acid.

* Not included in this ISO Recommendation as these determinations are still under study.