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INTERNATIONAL ORGANIZATION FOR STANDARDIZATION

ISO RECOMMENDATION

R 753

ACETIC ACID FOR INDUSTRIAL USE

METHODS OF TEST

1st EDITION
June 1968

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BRIEF HISTORY

The ISO Recommendation R 753, *Acetic acid 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. 652) 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.

CONTENTS

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

ISO Recommendation R 753 June 1968

ACETIC ACID FOR INDUSTRIAL USE

METHODS OF TEST

1. SCOPE

This ISO Recommendation describes methods of test for acetic acid 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

In all cases, take the sample of acetic acid in the liquid condition. If it is solidified, melt it completely in a warm room with the temperature not above 30 °C, and thoroughly agitate it by rolling the container or by other suitable means before sampling.

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 risk of contaminating the contents in any way.

PART I – METHODS OF TEST FOR GENERAL USE

3. DETERMINATION OF THE CRYSTALLIZING POINT OF GLACIAL ACETIC ACID

3.1 Principle

Determination of the temperature to which the slightly supercooled sample in fluid form rises during crystallization.

3.2 Applicability

The method is applicable only to 98 to 100 % (m/m) acetic acid.

3.3 Apparatus

3.3.1 *Test tube,* 150 mm × 25 mm.

3.3.2 *Thermometer,* of the mercury-in-glass type, graduated for use at 100 mm immersion, certified for accuracy, and complying with the following requirements :

Thermometer range °C	Graduations °C	Length		Diameter of stem mm	Distance from bottom of bulb to main scale mm	Certificate to show necessary corrections to readings
		Main scale mm	Bulb mm			
-0.5 to about 40.5	0.1	not less than 280	10 to 15	5.5 to 7.0	not less than 30	to within ± 0.05 °C

3.4 Procedure

3.4.1 Fill the dried test tube (3.3.1) with the test sample to a depth of about 100 mm, and insert the thermometer (3.3.2). Place the test tube in water at 10 to 11 °C so that the portion occupied by the sample is completely immersed, and allow it to remain without stirring, until the thermometer indicates about 2 °C below the expected crystallizing point. Then lift the tube out of the water and stir rapidly with the thermometer to induce the formation of minute crystals. At the moment crystallization begins, the temperature will rise rapidly and then remain constant for a few minutes. As soon as the steady temperature is approached, cease stirring and suspend the thermometer so that its bulb is centrally disposed in the crystallizing mass. Read to the nearest 0.05 °C the temperature at which the thermometer reading remains constant, apply the thermometer correction and record the corrected reading as the crystallizing point.

3.4.2 Prevent contamination of the sample with moisture during the test.

3.4.3 If, after cooling and stirring as described above, the temperature rise exceeds 3 °C the observed crystallizing point is liable to be below the true figure, and the operation should be repeated with less supercooling.

3.4.4 If crystallization will not begin after removal of the test tube from the cold water and vigorous stirring, the thermometer should be withdrawn and touched against some solid acetic acid previously prepared, then quickly re-inserted in the sample under test and the stirring resumed.

4. DETERMINATION OF ACETIC ACID CONTENT

4.1 Principle

Titration of acidity with a standard volumetric solution of sodium hydroxide using phenolphthalein as indicator, making allowance for any formic acid present.

4.2 Reagents

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

4.2.1 *Sodium hydroxide,* N standard volumetric solution.

4.2.2 *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 dilute sodium hydroxide solution.

4.3 Apparatus

Ordinary laboratory apparatus and

4.3.1 *Weighing pipette,* capacity 10 ml.

4.4 Procedure

4.4.1 Transfer, by means of the weighing pipette (4.3.1), an accurately weighed quantity of the test sample, equivalent to 2 to 3 g of glacial acid, to a 250 ml conical flask containing about 50 ml of recently boiled and cooled water. Suitable quantities based on various nominal strengths of the acid are given in the following Table :

Nominal strength acetic acid %	Mass of test sample to be taken g
98 to 100	2.5
80	3.0
60	4.0
40	6.0

4.4.2 Add 0.5 ml of phenolphthalein solution (4.2.2) and titrate with sodium hydroxide solution (4.2.1).

4.5 Expression of results

$$\text{Acetic acid content } (CH_3COOH) \text{ per cent by mass} = \frac{6.0 \times V}{M} - 1.3\,A$$

where

V is the volume in millilitres, of N sodium hydroxide solution (4.2.1) used,

M is the mass, in grammes, of the test portion,

A is the formic acid content, per cent by mass, determined by the method described in section 10.

5. DETERMINATION OF RESIDUE ON EVAPORATION ON A WATER BATH

Use the method described in ISO Recommendation R 759, *Method for the determination of residue on evaporation on a water bath.*

6. DETERMINATION OF IRON CONTENT

6.1 Principle

Conversion of any iron present in the sample into the sulphate by evaporation to dryness of the specimen with sulphuric acid, and colorimetric determination of the iron using 2.2'-bipyridyl.

NOTE. – Although this method specifies the use of a spectrophotometer 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 6.5.5).

6.2 Reagents

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

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

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

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

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

6.2.5 *Ammonium acetate,* 500 g/l solution.

6.2.6 *2.2'-bipyridyl,* 5 g/l hydrochloric acid solution. Dissolve 0.5 g of 2.2'-bipyridyl in 100 ml of N hydrochloric acid solution.

6.2.7 *Standard iron solution* (10 µg Fe/ml). Dissolve 0.7022 g of pure iron (II) ammonium sulphate hexahydrate ($FeSO_4.(NH_4)_2SO_4.6H_20$) in 50 ml of sulphuric acid solution (6.2.1) and dilute to 1000 ml with water. Dilute 100 ml of the solution thus obtained to 1000 ml with water.

6.3 Apparatus

Ordinary laboratory apparatus, and

6.3.1 *Spectrophotometer* or *photometer.*

6.4 Calibration charts

6.4.1 Place in 100 ml one-mark volumetric flasks the following quantities of standard iron solution (6.2.7) :

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

To each add 20 ml of nitric acid solution (6.2.2), 2 ml of urea solution (6.2.3) and 2 ml of hydroxylammonium chloride solution (6.2.4). Mix and allow to stand for 2 minutes. Then add 30 ml of ammonium acetate solution (6.2.5) and 5 ml of 2.2'-bipyridyl solution (6.2.6). Dilute to the mark with water.

6.4.2 Measure the optical densities of the solutions in the spectrophotometer or photometer (6.3.1), determining the optical density at a wave length between 510 and 520 nm.

6.4.3 Draw a graph plotting optical densities as a function of the quantities of iron (in micrograms) in 100 ml of the solutions.

6.5 Procedure

6.5.1 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 (6.2.1). Evaporate, first on a water bath and finally on a sand bath, until white fumes are just evolved.

6.5.2 Allow to cool, add a few drops of nitric acid solution (6.2.2), and re-evaporate until white fumes just cease to be evolved. If tarry products remain, add a few further drops of nitric acid solution (6.2.2) and again evaporate on the sand bath.

6.5.3 Take up the residue with 20 ml of nitric acid solution (6.2.2) 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 urea solution (6.2.3), stir and add 2 ml of hydroxylammonium chloride solution (6.2.4), mix and allow to stand for 2 minutes. Then add 30 ml of ammonium acetate solution (6.2.5) and 5 ml of 2.2'-bipyridiyl solution (6.2.6), and dilute to the mark with water.

6.5.4 Measure the optical density of the solution in the spectrophotometer or photometer (6.3.1) 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 paragraph 6.4, read the iron content (in micrograms per 100 ml) corresponding to this optical density.

6.5.5 As an alternative to measurement of optical density using a spectrophotometer or photometer, the test solution prepared as in clause 6.5.3 may be compared visually with a series of standard matching solutions prepared under similar conditions, and its iron content (in micrograms per 100 ml) deduced.

6.6 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 6.5.4 or clause 6.5.5.

7. 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 (7.4.1) should be reduced or increased and an appropriate adjustment made to the expression $\frac{0.05}{x}$ ml in clause 7.4.4.

7.1 Principle

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

7.2 Reagents

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

7.2.1 *Nitric acid,* approximately 5 N solution.

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

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

7.3 Apparatus

Ordinary laboratory apparatus.

7.4 Procedure

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

7.4.2 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.

7.4.3 To prepare the chloride solution of known concentration, add to a 100 ml Nessler cylinder 1.0 ml of the standard chloride solution (7.2.2), dilute to the mark with water, add 2 ml of nitric acid solution (7.2.1) and mix.

7.4.4 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 (7.4.1), dilute to the mark with water, add 2 ml of nitric acid solution (7.2.1), and mix.

7.4.5 Add to each Nessler cylinder 1 ml of silver nitrate solution (7.2.3) 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.

7.5 Expression of results

A sample required to contain not more than x % of Cl does so if the turbidity produced from its solution (7.4.4) is equal to or less than that produced from the chloride solution of known concentration (7.4.3).

8. 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 (8.4.1) should be reduced or increased and an appropriate adjustment made to the expression $\frac{0.1}{x}$ ml in clause 8.4.4.

8.1 Principle

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

8.2 Reagents

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

8.2.1 *Sodium carbonate,* N solution.

8.2.2 *Hydrochloric acid,* N solution.

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

8.2.4 *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.

8.3 Apparatus

Ordinary laboratory apparatus.

8.4 Procedure

8.4.1 Weigh 100 ± 1 g of the test sample, add 0.2 ml of sodium carbonate solution (8.2.1) 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 (8.2.2), transfer to a 250 ml one-mark volumetric flask, dilute to the mark with water, and mix.

8.4.2 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.

8.4.3 To prepare the sulphate solution of known concentration, add to a 100 ml Nessler cylinder 4.0 ml of the standard sulphate solution (8.2.4), dilute to the mark with water, add 2 ml of hydrochloric acid solution (8.2.2) and mix.

8.4.4 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 (8.4.1). Dilute to the mark with water, add 2 ml of hydrochloric acid solution (8.2.2) and mix.

8.4.5 Add to each Nessler cylinder 2 ml of barium chloride solution (8.2.3) 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.

8.5 Expression of results

A sample required to contain not more than x % of SO_4 does so if the turbidity produced from its solution (8.4.4) is equal to or less than that produced from the sulphate solution of known concentration (8.4.3).

9. LIMIT TEST FOR HEAVY METALS (INCLUDING IRON)

9.1 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.

9.2 Reagents

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

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

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

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

9.3 Apparatus

Ordinary laboratory apparatus.

9.4 Procedure

9.4.1 Pipette 25 ml of the test sample into a 250 ml one-mark volumetric flask. Dilute to the mark with water and mix well.

9.4.2 Transfer a 10 ml aliquot to a Nessler cylinder. Add aqueous ammonia (9.2.1) 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 (9.2.2) and mix well.

9.4.3 Preparation of agreed standard matching solution. To 20 ml of water contained in a second Nessler cylinder add an agreed volume of standard lead solution (9.2.3) and 1 ml of aqueous ammonia (9.2.1). Dilute to 50 ml with water and mix well. Add 0.1 ml (two drops) of sodium sulphide solution (9.2.2) and again mix well.

9.4.4 Compare the darkening of the test solution (9.4.2) with that of the standard matching solution (9.4.3).

9.5 Expression of results

Report the darkening produced in 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.

10. DETERMINATION OF FORMIC ACID CONTENT

10.1 Principle

Oxidation of the formic acid in the sample to carbon dioxide by mercuric chloride according to the reaction.

$$2\,HgCl_2 + HCOOH \rightarrow Hg_2Cl_2 + CO_2 + 2HCl$$

Iodometric determination of the mercurous chloride produced.

10.2 Reagents

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

10.2.1 *Sodium hydroxide,* N solution.

10.2.2 *Hydrochloric acid,* 2 N solution.

10.2.3 *Mercuric chloride,* 50 g/l filtered solution.

10.2.4 *Potassium iodide,* crystals.

10.2.5 *Iodine,* 0.1 N standard volumetric solution.

10.2.6 *Sodium thiosulphate,* 0.1 N standard volumetric solution.

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

10.3 Apparatus

Ordinary laboratory apparatus, and

10.3.1 *Conical flask* with ground-glass neck, capacity 250 ml.

10.3.2 *Reflux condenser,* highly efficient type, with ground glass joint to fit the flask (10.3.1).

10.3.3 *Microburette,* 5 ml graduated in 0.05 ml.

10.3.4 *Weighing pipette,* capacity 10 ml.

10.4 Procedure

10.4.1 Weigh by means of the weighing pipette (10.3.4) 5.0 ml of the test sample and transfer to the flask (10.3.1), add 30 ml of sodium hydroxide solution (10.2.1) followed by 10 ml of hydrochloric acid solution (10.2.2). Add 40 ml of mercuric chloride solution (10.2.3), connect the reflux condenser (10.3.2) to the flask, and heat for 2 hours on a boiling water bath.

10.4.2 Cool, add 5 g of potassium iodide (10.2.4) dissolved in 10 ml of water (the mercuric iodide formed redissolves) and run in, by means of a pipette, 5.0 ml of the iodine solution (10.2.5). Shake until the mercurous chloride dissolves and, from the microburette (10.3.3), back-titrate with the sodium thiosulphate solution (10.2.6) adding 0.5 ml of starch solution (10.2.7) just before the end point is reached.

10.4.3 Carry out a blank test using the same volumes of reagents, omitting the test portion.

10.5 Expression of results

$$\text{Formic acid content, (HCOOH), \% (m/m)} = \frac{0.23\,(V_1 - V_2)}{M}$$

where

V_1 is the volume, in millilitres, of 0.1 N sodium thiosulphate solution used in clause 10.4.3.

V_2 is the volume, in millilitres, of 0.1 N sodium thiosulphate solution used in clause 10.4.2

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

11. DETERMINATION OF ACETALDEHYDE CONTENT

11.1 Principle

Conversion of the aldehyde present in the sample quantitatively into an addition product, by reaction with a measured quantity of solution of sodium hydrogen sulphite according to the reaction.

$$CH_3CHO + NaHSO_3 \rightarrow CH_3 - \underset{\displaystyle SO_3Na}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - OH$$

Iodometric determination of the excess of sodium hydrogen sulphite.

NOTE. – This method will only determine acetaldehyde monomer. For total acetaldehyde content including polymers, see Part II, section 15.

11.2 Reagents

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

11.2.1 *Sodium hydrogen sulphite* solution freshly prepared. Dissolve 16.6 g of sodium metabisulphite ($Na_2S_2O_5$) in water and dilute to 1000 ml.

11.2.2 *Sodium thiosulphate,* 0.02 M standard volumetric solution.

11.2.3 *Iodine,* 0.02 N standard volumetric solution.

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

11.3 Apparatus

Ordinary laboratory apparatus, and

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

11.3.2 *Microburette,* 5 ml graduated in 0.02 ml divisions.

11.3.3 *Weighing pipette,* capacity 20 ml.

11.4 Procedure

11.4.1 Weigh 10 ml of the test sample by means of the weighing pipette (11.3.3) and transfer to a 50 ml one-mark volumetric flask containing 10 ml of water. Add 5.0 ml of sodium hydrogen sulphite solution (11.2.1) from the microburette (11.3.2), dilute to 50 ml with water, mix well and allow to stand for 30 minutes.

11.4.2 In a second 50 ml one-mark volumetric flask, prepare a blank solution by diluting 5.0 ml of sodium hydrogen sulphite solution (11.2.1) to 50 ml with water. Mix well and allow to stand for 30 minutes.

11.4.3 At the same time pipette 50.0 ml of iodine solution (11.2.3) into each of two 250 ml conical flasks (11.3.1) and place these in an ice-water bath.

11.4.4 At the end of the 30 minute period, pipette 20.0 ml of the analysis solution (11.4.1) into one of these flasks, and 20.0 ml of the blank solution (11.4.2) into the other. Titrate the two solutions with sodium thiosulphate solution (11.2.2), adding 0.5 ml of starch solution (11.2.4) just before the end point is reached.

11.5 Expression of results

$$\text{Acetaldehyde content, } (CH_3CHO), \% \text{ (m/m)} = \frac{0.110\,(V_1 - V_2)}{M}$$

where

V_1 is the volume, in millilitres, of 0.02 M sodium thiosulphate solution used for the analysis solution,

V_2 is the volume, in millilitres, of 0.02 M sodium thiosulphate solution used for the blank solution,

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

PART II – METHODS OF TEST FOR SPECIAL PURPOSES

In cases where the acetic acid is required for special purposes, for example, pharmaceutical, the following additional determinations may be required.

12. DETERMINATION OF ARSENIC CONTENT

12.1 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.

12.2 Reagents

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

12.2.1 *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.

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

12.2.3 *Sulphuric acid, d = 1.84.*

12.2.4 *Sodium chloride* acid solution. Mix one volume of sulphuric acid (12.2.3) 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.

12.2.5 *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 (12.2.4), and make up to 1000 ml with water.

12.2.6 *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 (12.2.4) 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.

12.2.7 *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 (12.2.4) and then with water.

12.2.8 *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. 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.

12.2.9 *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 (12.2.3), 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.

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

12.3 Apparatus

Ordinary laboratory apparatus, and

12.3.1 *Assembly* (see Fig. 1) consisting of

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

12.3.1.2 *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 (12.2.1), followed by another light layer of glass wool, and lastly, strips of damp lead acetate paper (12.2.2).

12.3.1.3 *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 (12.2.8).

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

12.3.3 *Graduated pipette,* 10 ml capacity, graduated in 0.1 ml divisions.

12.4 Procedure

12.4.1 *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 and 0.010 mg of arsenic according to the method given in clauses 12.4.1.1 and 12.4.1.2 below.

12.4.1.1 Into the flask (12.3.1.1), pipette 1 ml of standard arsenic solution (12.2.9) using the graduated pipette (12.3.3) 30 ml of acid sodium chloride solution (12.2.4), 10 ml of iron (III) – ammonium sulphate solution (12.2.5) and 20 ml of stannous chloride solution (12.2.6).

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 (12.2.7) and connect quickly to the neck of the hydrogen sulphide removal tube (12.3.1.2) provided with the exit tube (12.3.1.3) 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.

12.4.1.2 Repeat the above procedure using, instead of 1 ml, respectively 2, 4, 6, 8, and 10 ml of the arsenious oxide solution (12.2.9).

12.4.2 *Determination of the arsenic content of the sample.*

12.4.2.1 Carefully pour into a 250 ml borosilicate glass beaker containing 50 ml of water, a mass (M_1) of about 50 g of the test sample, weighed by difference in the ground glass stoppered flask (12.3.2). Add 5 ml of hydrogen peroxide solution (12.2.10). Evaporate almost to dryness on a sand bath.

Add 5 ml of sulphuric acid solution (12.2.3) 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*).

12.4.2.2 Using 10 ml of solution *X*, instead of the standard arsenic solution, proceed as in clause 12.4.1.1 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.

12.4.2.3 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.

12.5 **Expression of results**

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

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.

NOTE. – Acetic acid of analytical reagent quality contains only very small amounts of arsenic, and the amount of sample required to give a stain within the range of standards 1 to 10 µg may very well be the whole of the 50 g taken. In such cases, after evaporating down almost to dryness on the sand bath, add 7 ml of sulphuric acid (12.2.3) and evaporate down to white fumes. Dilute carefully with 30 ml of a 10 % solution of pure sodium chloride, and transfer to the apparatus described in clause 12.3.1. Add 10 ml of ammonium ferric sulphate solution (12.2.5) and 20 ml of stannous chloride solution (12.2.6) and proceed as indicated in clause 12.4. In this case the expression of results is :

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

13. DETERMINATION OF WATER CONTENT

Use one of the methods described in ISO Recommendation R 760, *Determination of water by the Karl Fischer method.*

14. DETERMINATION OF PERMANGANATE INDEX

14.1 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.

14.2 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 permanganate left unreduced, and subtraction of this quantity from the amount taken.

14.3 Reagents

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

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

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

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

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

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

14.4 Apparatus

Ordinary laboratory apparatus, and

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

14.4.2 *Two microburettes,* capacity 10 ml, graduated in 0.02 ml divisions.

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

14.5 Procedure

14.5.1 Into 50 ml of dilute sulphuric acid solution (14.3.1) contained in one of the stoppered 250 ml flasks (14.4.1), pipette 5 ml of the test sample and mix thoroughly.

14.5.2 Add, at 20 ± 0.5 °C, potassium permanganate solution (14.3.2) from a microburette (14.4.2) until a permanent red colour is established and then add a further 10 ml of potassium permanganate solution. Note the total amount added. Leave in the dark to react for 40 minutes at 20 ± 0.5 °C.

14.5.3 Determine the excess of potassium permanganate iodometrically, by adding an excess of potassium iodide solution (14.3.4) and titrating from the second microburette with sodium thiosulphate solution (14.3.3), adding 0.5 ml of starch solution (14.3.5) just before the end point is reached.

14.5.4 Carry out simultaneously a blank determination, in the second conical flask (14.4.1), using the above procedure and adding the same total volume of potassium permanganate solution (14.3.2) as that used in clause 14.5.2.

14.6 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 14.5.4,

V_1 is the volume, in millilitres, of M/30 sodium thiosulphate solution used in clause 14.5.3.

15. DETERMINATION OF TOTAL ACETALDEHYDE CONTENT

15.1 Principle

Depolymerisation of any paraldehyde present and entrainment of this regenerated acetaldehyde plus the monomeric acetaldehyde originally present, by distillation of the sample in acid medium into an excess of sodium hydrogen sulphite solution according to the reaction

$$CH_3CHO + NaHSO_3 \rightarrow CH_3 - \underset{\displaystyle SO_3Na}{\overset{\displaystyle H}{\overset{|}{\underset{|}{C}}}} - OH$$

Iodometric determination of the remaining unreacted sodium hydrogen sulphite, and calculation, by difference, of that combined with the aldehyde.

NOTE. – A blank determination is carried out in order to determine the actual amount of sodium hydrogen sulphite employed.

15.2 Reagents

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

15.2.1 *Sodium hydrogen sulphite solution,* freshly prepared. Dissolve 1.14 g of sodium metabisulphite ($Na_2S_2O_5$) in water and dilute to 100 ml.

15.2.2 *Iodine,* 0.1 N standard volumetric solution.

15.2.3 *Phosphoric acid,* $d = 1.71$, pure.

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

15.3 Apparatus (see Fig. 2)

Ordinary laboratory apparatus, and

15.3.1 *Flask* (A), 250 ml in borosilicate glass, fitted with a small splash-head (B), and adapter (C), and a reflux condenser (D) carrying a receiver adapter (E). All these items have ground glass joints.

15.3.2 *Conical flask,* 200 ml graduated at 50 and 100 ml (F).

15.3.3 *Weighing pipette,* capacity 20 ml.

15.3.4 *Microburette,* 10 ml graduated in 0.01 ml.

15.4 Procedure

15.4.1 Weigh a suitable volume (usually 10 ml) of the test sample by means of the weighing pipette (15.3.3), transfer it into the 250 ml flask(A)(15.3.1), containing 100 ml of water, and add 2 g of phosphoric acid (15.2.3). Attach the splash-head and condenser with its adapters (C) and (E).Heat the flask in order to bring to gentle boiling in a few minutes, and then slowly distil 50 ml of liquid directly into the 200 ml conical flask (15.3.2) containing 40 ml of water and 10 ml of sodium hydrogen sulphite solution (15.2.1) from a pipette. Cool the conical flask from the outside with iced water.

15.4.2 Rinse the condenser with water and, after allowing to stand at room temperature for 30 minutes, titrate the excess sodium hydrogen sulphite by means of the iodine solution (15.2.2) from the microburette (15.3.4), using 0.5 ml of starch solution (15.2.4) as indicator.

15.4.3 Perform under the same conditions a blank determination on 100 ml of water and phosphoric acid in the amount used in clause 15.4.1.

15.5 Expression of results

$$\text{Total acetaldehyde content, \% (m/m)} = \frac{0.22\,(V_2 - V_1)}{M}$$

where

V_2 is the volume, in millilitres, of 0.1 N iodine solution used in clause 15.4.3,

V_1 is the volume, in millilitres, of 0.1 N iodine solution used in clause 15.4.2,

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

16. DETERMINATION OF TOTAL HALOGEN CONTENT*

17. DETERMINATION OF TOTAL SULPHUR CONTENT*

18. DETERMINATION OF DICHROMATE INDEX

18.1 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.

18.2 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.

18.3 Reagents

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

18.3.1 *Potassium dichromate,* 0.1 N standard volumetric solution in dilute sulphuric acid. Dissolve 4.9 g of potassium dichromate in 500 ml of water, add 400 ml of sulphuric acid, $d = 1.84$, and dilute to 1000 ml with water.

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

18.3.3 *Sodium thiosulphate,* 0.1 M standard volumetric solution.

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

18.4 Apparatus

All apparatus should be cleaned before use by warming with chromic sulphuric acid mixture and rinsing.

Ordinary laboratory apparatus, and

18.4.1 *Two conical flasks,* glass stoppered, capacity 500 ml.

18.4.2 *Water bath,* controlled at 50 ± 2 °C.

18.4.3 *Microburette,* 10 ml graduated in 0.02 ml divisions.

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