International Standard 1388/7

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

Ethanol for industrial use — Methods of test — Part 7 : Determination of methanol content [methanol contents between 0,01 and 0,20 % (V/V)] — Photometric method

Éthanol à usage industriel — Méthodes d'essai — Partie 7 : Dosage du méthanol [teneurs de 0,01 *à* 0,20 % *(V/V)] — Méthode photométrique*

First edition — 1981-11-01

UDC 661.722 : 543.42 : 547.261 **Ref. No. ISO 1388/7-1981 (E)**

Descriptors : industrial products, ethanols, tests, determination of content, carbinols, spectrophotometric analysis.

Price based on 4 pages

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards institutes (ISO member bodies). The work of developing International Standards is carried out through ISO technical committees. Every member body interested in a subject for which a technical committee has been set up has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 1388/7 was developed by Technical Committee ISO/TC 47, *Chemistry*, and was circulated to the member bodies in February 1980.

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

Australia
Austria
Belgium
Brazil
Bulgaria
China
Czechoslovakia
France
Germany, F.R.
Hungary
Italy
Korea, Rep. of
Philippines
Poland
Romania
South Africa, Rep. of
Switzerland
Thailand
United Kingdom
USSR

The member body of the following country expressed disapproval of the document on technical grounds :

Netherlands

International Standards ISO 1388/1 to ISO 1388/12 cancel and replace ISO Recommendation R 1388-1970, of which they constitute a technical revision.

Printed in Switzerland

INTERNATIONAL STANDARD **ISO 1388/7-1981 (E)**

Ethanol for industrial use — Methods of test — Part 7 : Determination of methanol content [methanol contents between 0,01 and 0,20 % (V/V)] — Photometric method

1 Scope and field of application

This part of ISO 1388 specifies a photometric method for the determination of the methanol content of ethanol for industrial use.

The method is applicable to products having methanol contents between 0,01 and 0,20 % (V/V).

This document should be read in conjunction with ISO 1388/1 (see the annex).

2 Principle

Conversion of the methanol present in a test portion to formaldehyde by oxidation with a solution of potassium permanganate in phosphoric acid. Reaction of the formaldehyde formed with chromotropic acid.

Photometric measurement of the violet coloration obtained at a wavelength of about 570 nm.

3 Reagents

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

3.1 Potassium permanganate, 30 g/l solution in phosphoric acid.

Dissolve 3 g of potassium permanganate in a little water, add 15,5 ml of orthophosphoric acid solution, ϱ 1,69 g/ml, dilute to 100 ml with water and mix.

3.2 *Di*sodium disulphite [sodium metabisulphite ($Na_2S_2O_5$)], 100 g/l solution.

Dissolve 10 g of sodium metabisulphite in water and dilute to 100 ml.

3.3 4,5-Dihydroxynaphthalene-2,7-disulphonic acid (chromotropic acid), solution in sulphuric acid.

3.3.1 Preparation of the solution

Dissolve 0,1 g of chromotropic acid, or its *di*sodium salt, in 10 ml of water. Add, while cooling, 90 ml of sulphuric acid, ϱ approximately 1,81 g/ml, about 90 % (m/m) solution, and mix.

Prepare this solution at the time of use.

If the solution causes significant coloration during colour development of the compensation solution (5.3.1) or the blank test solution (5.2), purify the chromotropic acid, or its *di*sodium salt, in accordance with the procedure specified in 3.3.2.

3.3.2 Purification of the chromotropic acid

Dissolve about 10 g of chromotropic acid, or its *di*sodium salt, in 25 ml of water. If the *di*sodium salt is used, add, while cooling, 2 ml of sulphuric acid, ϱ approximately 1,84 g/ml, to convert it to the free acid. Add 50 ml of methanol, heat just to boiling and filter through a sintered glass filter funnel, porosity grade P 10*.

Add 100 ml of propan-2-ol to the solution to precipitate the chromotropic acid. Collect the precipitate on a sintered glass filter funnel, porosity grade P 10, and wash it with small portions of propan-2-ol. Allow to dry, initially in air, and finally in a desiccator over sulphuric acid, ϱ approximately 1,84 g/ml, about 98 % (m/m) solution, as desiccant.

If, after purification, the blank test solution is still coloured, reject the chromotropic acid.

3.4 Methanol, standard solution corresponding to 0,05 % (V/V) of methanol.

Place 1,00 ml of absolute methanol in a 250 ml one-mark volumetric flask, add a quantity of methanol-free ethanol corresponding to 99 ml of anhydrous ethanol, dilute to the mark with water and mix.

---

* See ISO 4793, *Laboratory sintered (fritted) filters — Porosity grading, classification and designation.*

Place 25,0 ml of this solution in a 200 ml one-mark volumetric flask, dilute to the mark with water and mix.

1 ml of this standard solution contains 0,000 5 ml of methanol.

4 Apparatus

Ordinary laboratory apparatus, and

4.1 Water bath, capable of being controlled at 70 ± 2 °C.

4.2 Spectrophotometer, or

4.3 Photoelectric absorptiometer, fitted with filters ensuring maximum transmission in the region of 570 nm.

5 Procedure

5.1 Test portion and preparation of the test solution

Take as the test portion a volume (V_2) of the laboratory sample corresponding to 5,0 ml of anhydrous ethanol and place it in a 100 ml one-mark volumetric flask. Prepare the test solution by diluting to the mark with water and mixing.

5.2 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 used for the determination, but replacing the test portion by a volume of methanol-free ethanol corresponding to 5,0 ml of anhydrous ethanol.

5.3 Preparation of the calibration graph

5.3.1 Preparation of standard solutions, used for the preparation of standard colorimetric solutions

Into a series of six 100 ml one-mark volumetric flasks, place the volumes of the standard methanol solution (3.4) indicated in the following table, dilute to the mark with a 5 % (V/V) solution of methanol-free ethanol in water, and mix.

Standard methanol solution (3.4)	Corresponding volume of methanol
ml	ml
0*	0
1,00	0,000 5
2,50	0,001 25
5,00	0,002 5
10,00	0,005
20,00	0,010

* Compensation solution.

5.3.2 Preparation of standard colorimetric solutions, for photometric measurements carried out in cells of optical path length 1 cm

Into a series of six test tubes, place 2,0 ml of each of the dilute standard methanol solutions (5.3.1).

5.3.3 Colour development

Add, to each tube, 1,0 ml of the potassium permanganate solution (3.1), and, after 15 min, 0,6 ml of the *di*sodium disulphite solution (3.2). To these solutions, which shall be colourless, add, while cooling with ice, 10,0 ml of the chromotropic acid solution (3.3), and heat on the water bath (4.1), controlled at 70 ± 2 °C, for 20 min. Remove the tubes from the water bath and allow to cool.

NOTES

1 If the colour of the compensation solution is more intense than that of the most dilute standard colorimetric solution, purify the chromotropic acid, or its *di*sodium salt, as specified in 3.3.2.

2 Prepare a new calibration graph each time a new bottle of chromotropic acid is used.

5.3.4 Photometric measurements

Carry out photometric measurements on each standard colorimetric solution (5.3.2) using either the spectrophotometer (4.2), set at a wavelength of about 570 nm, or the photoelectric absorptiometer (4.3) fitted with appropriate filters, after having adjusted the instrument to zero absorbance against a 5 % (V/V) solution of ethanol in water.

5.3.5 Plotting the graph

Deduct the absorbance of the compensation solution from those of the standard colorimetric solutions (5.3.2). Plot a graph having, for example, the volumes, in millilitres, of methanol in the standard solutions (5.3.1) as abscissae and the corresponding corrected values of absorbance as ordinates.

5.4 Determination

5.4.1 Colour development

Take 2,0 ml of the test solution (5.1), place it in a test tube and proceed as specified in 5.3.3.

5.4.2 Photometric measurements

Carry out photometric measurements on the test solution and on the blank test solution, proceeding as specified in 5.3.4, after having adjusted the instrument to zero absorbance against a 5 % (V/V) solution of ethanol in water.

6 Expression of results

By means of the calibration graph (5.3.5), determine the volumes of methanol corresponding to the values of the photometric measurements.

The methanol content, expressed as methanol as a percentage by volume, is given by the formula

$$\frac{(V_1 - V_0) \times 100}{V_2}$$

where

V_0 is the volume, in millilitres, of methanol found in the blank test solution;

V_1 is the volume, in millilitres, of methanol found in the test solution;

V_2 is the volume, in millilitres, of the test portion.

Annex

ISO Publications relating to ethanol for industrial use

ISO 1388/1 — General.

ISO 1388/2 — Detection of alkalinity or determination of acidity to phenolphthalein.

ISO 1388/3 — Estimation of content of carbonyl compounds present in small amounts — Photometric method.

ISO 1388/4 — Estimation of content of carbonyl compounds present in moderate amounts — Titrimetric method.

ISO 1388/5 — Determination of aldehydes content — Visual colorimetric method.

ISO 1388/6 — Test for miscibility with water.

ISO 1388/7 — Determination of methanol content [methanol contents between 0,01 and 0,20 % (V/V)] — Photometric method.

ISO 1388/8 — Determination of methanol content [methanol contents between 0,10 and 1,50 % (V/V)] — Visual colorimetric method.

ISO 1388/9 — Determination of esters content — Titrimetric method after saponification.

ISO 1388/10 — Estimation of hydrocarbons content — Distillation method.

ISO 1388/11 — Test for detection of furfural.

ISO 1388/12 — Determination of permanganate time.