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**Petroleum products and other  
liquids — Ethanol — Determination  
of total acidity by potentiometric  
titration**

*Produits pétroliers et autres liquides — Éthanol — Dosage de l'acidité  
totale par titration potentiométrique*

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Case postale 56 • CH-1211 Geneva 20  
Tel. + 41 22 749 01 11  
Fax + 41 22 749 09 47  
E-mail [copyright@iso.org](mailto:copyright@iso.org)  
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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see [www.iso.org/directives](http://www.iso.org/directives)).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see [www.iso.org/patents](http://www.iso.org/patents)).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 28, *Petroleum products and lubricants*, Subcommittee SC 7, *Liquid biofuels*.

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## Introduction

Diluted hydrous solutions of organic acids, e.g. acetic acid, can corrode many materials. Thus, it is necessary to determine and keep at low values the acid content in the final product.

An ethanol sample can have organic acids from the productive process, from its handling, contained in additives, or due to sample degradation or contamination. The relative content of those components can be determined by titration with a strong alkaline solution.

The numeric result of total acidity is a measure of the amount of acid components in the sample. Total acidity is used as a quality control parameter of final product to prevent long-run corrosion problems.

For this reason, final product obtained from a blend of ethanol and other fuels has to have a limited acidity.

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# Petroleum products and other liquids — Ethanol — Determination of total acidity by potentiometric titration

**WARNING** — The use of this International Standard can involve hazardous materials. This International Standard does not purport to address all the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

## 1 Scope

This International Standard specifies a test method for the determination of total acidity of ethanol by potentiometric titration. The total acidity is reported as acetic acid mass, in milligrams, per ethanol volume, in litres, or as mass percent of acetic acid (% m/m), if the density of ethanol is known.

NOTE 1 For the purposes of this International Standard, the terms “% m/m” and “% v/v” are used to represent the mass fraction and the volume fraction of a material, respectively.

NOTE 2 This method was evaluated with ethanol samples with different water contents (0,7 % m/m and 7 % m/m) and acidity values (5 mg to 50 mg HAc per litre of sample).

## 2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

### 2.1

#### total acidity

amount of acids contained in the ethanol sample, calculated as acetic acid, determined by potentiometric titration with a strong alkaline solution, as given in this International Standard

## 3 Reagents and materials

**3.1 Deionized water**, with a maximum conductivity of 1  $\mu\text{S}/\text{cm}$ , Grade 2 or equivalent.

**3.2 Potassium hydrogen phthalate** ( $\text{KHC}_8\text{H}_4\text{O}_4$ ), standard grade.

**3.3 Solution of lithium chloride (LiCl) in ethanol**, 1 mol/l to 3 mol/l.

**3.4 Buffer solution**, with pH 4 and pH 7.

NOTE The above values of pH are only indicative. The values shown on the buffer certificates are those which are intended to be used in the analysis.

**3.5 Hydrochloric acid solution** (HCl), 1,0 mol/l, a solution prepared in accordance with the following or a commercially available standardized hydrochloric acid solution of equivalent concentration.

— In order to prepare HCl, 1,0 mol/l, transfer  $(84,0 \pm 0,5)$  ml of concentrated hydrochloric acid (37 % v/v) to a 1 000 ml volumetric flask containing about its half capacity of water (3.1). Complete the volume and homogenize the solution. Stock the solution in an amber flask at a temperature below 25 °C.

— This solution has a 6 mo shelf life.

**3.6 Sodium hydroxide solution** (NaOH), 1,0 mol/l, a solution prepared in accordance with the following or a commercially available standardized sodium hydroxide solution of equivalent concentration.

- In order to prepare NaOH, 1,0 mol/l, weigh in a beaker (40,0 ± 0,1) g of sodium hydroxide, dissolve with 200 ml of water (3.1) and stir until complete dissolution, and homogenize. Transfer to a volumetric flask of 1 000 ml and complete the volume with water (3.1). Stock the solution in a polyethylene flask and keep at a temperature below 25 °C.
- This solution has a 2 mo shelf life.

**3.7 Sodium hydroxide solution** (NaOH), 0,02 mol/l, a solution prepared in accordance with 3.7.1 or a commercially available standardized sodium hydroxide solution of equivalent concentration.

**3.7.1** In order to prepare NaOH, 0,02 mol/l, transfer to a 500 ml volumetric flask (10,0 ± 0,1) ml of sodium hydroxide solution, 1,0 mol/l, and complete the volume with water (3.1) and homogenize. Stock the solution in a polyethylene flask and keep at a temperature below 25 °C. The reagent shall be restandardized frequently enough to detect concentration changes. The solution shall be protected against carbon dioxide absorption. The solution has a 15 d shelf life.

**3.7.2** Determine the actual molar concentration of sodium hydroxide solution (3.7.1) as follows.

- a) Dry the potassium hydrogen phthalate (3.2) in a drying oven at (120 ± 5) °C for a minimum of 2 h and store in a desiccator.
- b) In a beaker, weigh approximately 100 mg of potassium hydrogen phthalate [(3.7.2 a)] and record the mass value.
- c) Add 100 ml of water (3.1) and stir until complete dissolution.
- d) Start the procedure as follows if the solution and the apparatus system are at a temperature around 20 °C to 25 °C.
- e) Carry out a potentiometric titration with the sodium hydroxide solution 0,02 mol/l (3.7.1) until the equivalency point using the apparatus described in Clause 4, and after checking the apparatus calibration according Clause 5.
- f) Using 100 ml of water (3.1), carry out a blank potentiometric titration with the sodium hydroxide solution 0,02 mol/l (3.7.1) until the equivalency point using the apparatus described in Clause 4.
- g) Calculate molar concentration of the solution using Formula (1):

$$C = \frac{m}{(V - V_0) \times 204,23} \quad (1)$$

where

- $C$  is the actual molar concentration of solution, in mol/l;
- $m$  is the mass of potassium hydrogen phthalate, in mg;
- $V$  is the volume of sodium hydroxide solution 0,02 mol/l used for titration of potassium hydrogen phthalate solution [3.7.2 e)], in ml;
- $V_0$  is the volume of sodium hydroxide solution 0,02 mol/l used for blank titration [3.7.2 f)], in ml;
- 204,23 is the molar mass of potassium hydrogen phthalate, in g/mol.



**3.7.3** The NaOH concentration is determined as an average of three analyses. The relative standard deviation (RSD) of three determinations shall be lower than 1 %.

**WARNING** — HCl and NaOH are corrosive. It can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water.

## 4 Apparatus

**4.1 Automatic volumetric potentiometric titrator.**

**4.2 Glass electrode and reference system**, of silver/silver chloride (Ag/AgCl) or combined glass electrode with reference system of silver/silver chloride (Ag/AgCl), single liquid junction and LiCl 1,0 mol/l to 3,0 mol/l in ethanol as internal electrolyte.

**4.3 Magnetic or mechanical stirrer.**

**4.4 Analytical balance**, with 0,1 mg precision.

**4.5 Burette**, of 10 ml maximum capacity.

**4.6 Burette**, of 20 ml minimum capacity.

**4.7 Volumetric pipette**, of (50 ± 0,05) ml capacity.

**4.8 Volumetric flasks**, of 100 ml, 500 ml, and 1000 ml capacity.

**4.9 Desiccator.** <https://standards.iteh.ai/catalog/standards/sist/ec2fa867-8058-4825-a764-cf67315adf0f/iso-17315-2014>

**4.10 Oven**, with an accuracy of (120 ± 5) °C.

**4.11 Polyethylene flask**, of 1 000 ml capacity.

**4.12 Amber flask**, of 1 000 ml capacity.

## 5 Apparatus calibration

**5.1** Calibrate the electrode according to manufacturer's instructions using pH 4 and pH 7 buffer solutions.

**5.2** If the calibration slope is lower than 0,91, carry out the electrode treatment as described in [5.3](#) and repeat the electrode verification.

**5.3** Perform the electrode treatment by dipping it alternately in NaOH 1 mol/l solution and HCl 1 mol/l solution at least three times, keeping the electrode for 10 s in each dipping.

## 6 Procedure

**6.1** Start the procedure described in [6.2](#) if the ethanol sample and the apparatus system are at a temperature around 20 °C to 25 °C.