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Ethanol — Determination of total acidity by potenciometric titration

Éthanol — Dosage de l'acidité totale par titration potentiométrique

ICS 75.160.20

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Foreword

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0 Introduction

0.1 Warning

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

0.2 Significance and use

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 may 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 may 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 others fuels must have a limited acidity.

Ethanol — Determination of total acidity by potenciometric titration

1 Scope

This 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 mg) per ethanol volume (in l), or as mass percent of acetic acid (% m/m), if the density of ethanol is known.

2 Term and definition

For the purposes of this Standard the following definition applies:

2.1 Total acidity

Amount of acids contained in the ethanol sample that can be titrated with a strong alkaline solution.

NOTE   In this Standard total acidity is reported as acetic acid mass (in mg) per ethanol volume (in l), or as mass percent of acetic acid (% m/m), if the density of ethanol is known.

3 Reagents and materials

3.1   Deionized water with a maximum conductivity of 1 µS/cm.

3.2   Potassium hydrogen phthalate ($KHC_8H_4O_4$), reagent grade.

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

3.4   Buffer solution with pH 4 and pH 7.

NOTE   The above values of pH are only indicative. It shall be considered for use the values presented in the buffer's certificates.

3.5   Hydrochloric acid solution (HCl), 1.0 mol/l.

3.5.1   Preparation of hydrochloric acid solution: transfer (84.0 ± 0.5) ml of concentrated hydrochloric acid (37% v/v) to a 1000 ml volumetric flask containing about its half capacity of deionized water. Complete the volume and homogenize the solution. Stock the solution in an amber flask at a temperature below 25 ºC. This solution has a 6 months shelf life.

3.6   Sodium hydroxide solution (NaOH)*, 1.0 mol/l.

3.6.1   Preparation of sodium hydroxide solution: weight in a beaker (40.0 ± 0.1) g of sodium hydroxide, dissolve with 200 ml of deionized water and stir until complete dissolution and homogenize. Transfer to a volumetric flask of 1000 ml and complete the volume with deionized water. Stock the solution in a polyethylene flask and keep at a temperature below 25 ºC. This solution has 2 months shelf life.

3.7   Sodium hydroxide solution (NaOH)*, 0.02 mol/l.

3.7.1 Preparation of sodium hydroxide solution: 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 deionized water and homogenize. Stock the solution in a polyethylene flask and keep at a temperature below 25 ºC. This solution has 15 days shelf life. Determine the actual molar concentration of this solution as follows:

a) Weigh in a beaker approximately 100 mg of potassium hydrogen phthalate, previously dried in a drying oven at (120 ± 5) ºC for a minimum of 2 h and stored in a desiccator, and record the mass value.

b) Add 100 ml of deionized water and stir until complete dissolution.

c) Carry out a potentiometric titration with the sodium hydroxide solution 0.02 mol/l until the equivalency point using the apparatus described in item 4.

d) Calculate molar concentration of the solution using the following equation:

$$C = \frac{m}{V \times 204.23}$$

Where:

   C is the actual molar concentration of solution, in mol per liter;

   m is the mass of potassium hydrogen phthalate, in milligrams;

   V is the volume of sodium hydroxide solution 0.02 mol/l used in titration, in milliliters;

   204.23 is the molecular weight of potassium hydrogen phthalate, in grams per mol.

e) Use three determinations to calculate the average concentration of the NaOH solution, since these results do not present a deviation higher than 1%.

NOTE

1 It is recommended the calibration of the titration apparatus (including the electrode) with the buffer solutions of pH 4 and pH 7 according to procedures of item 5 prior to standardization of sodium hydroxide solution 0.02 mol/l by potentiometric titration.

2 For the NaOH solutions preparation the temperature range must stay around 20 -25 °C.

* **WARNING — 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 1.0-3.0 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 ml capacity.

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

4.9   Desiccator.

4.10   Drying oven with the capacity to reach (120 ± 5)° C.

4.11   Polyethylene flask of 1000 ml capacity.

4.12   Amber flask of 1000 ml capacity.

5   Apparatus calibration

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

5.2   If the calibration slope is lower than 0.91, carry out the electrode treatment as described at item 5.3 and repeat the electrode verification.

5.3   Perform the electrode treatment 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   Add precisely to a suitable flask 50 ml of ethanol sample and insert the electrode and reference system or the combined electrode in such a way that the liquid junction is completely immersed.

6.2   Stir the sample gently to avoid development of bubbles.

6.3   Titrate the ethanol sample with the NaOH 0.02 mol/l solution using a burette of 10 ml maximum capacity according to the following titration parameters:

a)   dynamic addition of titrator;

b)   minimum increment of 0.01 ml and maximum of 0.05 ml;

c)   the next increment shall be add if the signal do not change more than 5 mV at each 10 s (30 mV/min.);

d)   the minimum waiting time between increments shall be 5 s and the maximum 20 s;

e)   minimum addition of 0.3 ml of the titrant after the equivalent point.

6.4   The end point of titration will be determined with the first derivative of inflection point of titration curve.

6.5   Repeat the procedure in order to have three results, since these results do not present a deviation higher than method repeatability. Calculate the final result as the average of the three values.

NOTE

1 External CO_2 sources can change ethanol acidity. In order to avoid possible interferences, the exposure of the ethanol sample to the air should be minimized.

2 It has been observed that after a certain number of analyses the electrode reduce its efficiency due to dehydration. It is recommended to treat the electrode according to item 5.3 at every 5 determinations.

3 For the test the temperature range must stay around 20 -25 °C.

7 Calculation

7.1 Calculate the total acidity of ethanol in mg/l, using the following equation:

$$AT = \frac{C \times 60.05 \times 1000}{V_1} \times V_2$$

Where:

AT   is the total acidity expressed as acetic acid mass, in mg, per ethanol volume, in liters;

60.05   is the molecular mass of acetic acid, in grams per mol;

C   is the actual molar concentration of sodium hydroxide solution (NaOH), 0.02 mol/l, in mol per liters;

V_1 is the volume of ethanol sample used, in milliliters;

V_2 is the volume of sodium hydroxide solution 0.02 mol/l used to reach the equivalence point of titration, in milliliters.

7.2 Calculate the total acidity of ethanol in mass percent of acetic acid (%m/m), using the following equation:

$$AT = \frac{C \times 60.05 \times 0.1}{d \times V_1} \times V_2$$

Where:

AT is the total acidity expressed as mass percent of acetic acid (%m/m);

C is the actual molar concentration of sodium hydroxide solution (NaOH), 0.02 mol/l, in mol per liters;

60.05 is the molecular mass of acetic acid, in grams per mol;

d is the density of ethanol, in grams per milliliters;

V_1 is the volume of ethanol sample used, in milliliters;

V_2 is the volume of sodium hydroxide solution 0.02 mol/l used to reach the equivalence point of titration, in milliliters.

8 Expression of results

Report the total acidity result of the sample, in mg/l, to the nearest 0.1 mg/l, or in %m/m, to the nearest 0.0001%.