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Petroleum products and other liquids — Ethanol — Determination of electrical conductivity

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National foreword

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**Petroleum products and other
liquids — Ethanol — Determination of
electrical conductivity**

*Produits pétroliers et autres liquides — Éthanol — Détermination de
la conductivité électrique*



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Foreword

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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).

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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*.

Introduction

Conductivity is related to the electrical current which is achieved by the ions displacement into solution in an electrical field.

The importance of measuring conductivity is due to its role in corrosion processes which can harm metallic components and therefore cause bad engine functioning at long term.

Ethanol can be contaminated with ion solutions in many ways, such as water contamination, chemical treatment in industrial processes, addition of chemical additives, incorrect transportation and storage, generally related to the cleanliness of tanks.

The ascertainment of the conductivity is usually carried out through the measurement of the electrical conductance between two platinum electrodes, immersed in an electrolytic solution and connected to a source of alternating electromotive force of a typical frequency. The resulting current is directly proportional to the number of ions present in the solution, mobility and ionic valence, and temperature.

In the measuring of the conductance, it is essential to use an alternating current in order to eliminate the undesirable effects of faradaic currents. In the case of an alternating resultant current, an inversion of the polarization occurs every half cycle and, consequently, the inversion of the flow of the migration of the ions, leading to a non-faradaic process, which comprises the formation of a double electrical layer in the electrode-solution interface, called double electrical layer, with the potential decreasing linearly in the first part and exponentially in the second part.

In an alternating fashion, the surfaces of the electrodes act as capacitors; the capacitive current increases with the frequency and the size of the electrodes. The control of these variables is in order, so that the alternating current flows preferentially in the form of non-faradaic processes. With an alternating current, there is a reduction of the polarization effect and, as a consequence, an absence of faradaic currents.

In this sense, platinization, that is, covering the surface of the electrodes with a layer of platinum black, increases its surface area significantly and, consequently, its capacitance which causes a reduction in the faradaic current. Further, as a result of the increase in capacitance, there is a reduction in the capacitive reactance, favouring the flow of current in the cell.

For both a metallic or electrolytic conductors, the Ohm Law ($E = I \cdot R$) sets forth that the intensity of the current (I) which passes through an electrical conductor is inversely proportional to the resistance (R), where E represents the difference in potential and the inverse of the resistance is the conductance ($G = 1/R$). Further information is provided in [Annex A](#).

Petroleum products and other liquids — Ethanol — Determination of electrical conductivity

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 the electrical conductivity in ethanol fuel and mixtures (including E85) in the range of $0,5 \mu\text{S}\cdot\text{cm}^{-1}$ to $4 \mu\text{S}\cdot\text{cm}^{-1}$ at a temperature of $25 \text{ }^\circ\text{C}$. The electrical conductivity is determined from the measured electrical conductance.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3170, *Petroleum liquids — Manual sampling*

ISO 3171, *Petroleum liquids — Automatic pipeline sampling*

3 Terms and definitions

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

3.1

conductivity

electrical current which is achieved by the ions displacement into the solution in an electrical field

Note 1 to entry: The determination of the electrical conductivity is carried out by means of a direct conductivity meter (5.1) measurement, using a measuring cell (5.2) suitable for low conductivity measurements. The measurement is carried out at a sample temperature of $(25,0 \pm 0,1) \text{ }^\circ\text{C}$.

4 Reagents

4.1 Analytical grade anhydrous ethanol, for cleaning and rinsing the conductivity cell and the sample vessel before undertaking the measurements.

4.2 KCl calibration solution, with 70 % de-ionized water and 30 % 1-propanol (99 %), approximately $5 \mu\text{S}\cdot\text{cm}^{-1}$, or certified reference material approximately $5 \mu\text{S}\cdot\text{cm}^{-1}$.

KCl solution with 70 % deionized water and 30 % 1-propanol 99 %, until $25 \mu\text{S}\cdot\text{cm}^{-1}$ or less, Certified Reference Material until $25 \mu\text{S}\cdot\text{cm}^{-1}$ or less, may also be used when it is not possible to carry out calibration using the above-mentioned solution.

4.3 De-ionized or distilled water, with a maximum conductivity of $0,5 \mu\text{S}\cdot\text{cm}^{-1}$ or less for cleaning and rinsing the sample vessel and the measuring cell.

5 Apparatus

5.1 Conductivity meter, which can be operated adequately with a $0,1 \text{ cm}^{-1}$ cell constant operating at a frequency of the alternating voltage between 50 Hz and 500 Hz directly to the measuring cell, with manual or automatic temperature correction and a resolution of $0,01 \mu\text{S}\cdot\text{cm}^{-1}$.

5.2 Electrical conductivity cell, built with material which is inert to pure ethanol or fuel ethanol (including E85).

The cell shall be platinised or non-platinised with a constant of $(0,1 \pm 0,02) \text{ cm}^{-1}$.

5.3 Integrated thermo compensator with a conductivity cell, with a minimum resolution of $0,1 \text{ }^\circ\text{C}$.

5.4 Thermostatic bath, or another system capable of maintaining the temperature at $25 \text{ }^\circ\text{C}$, with a minimum resolution of $0,1 \text{ }^\circ\text{C}$.

5.5 Temperature sensor, with a minimum resolution of $0,1 \text{ }^\circ\text{C}$, preferably, integrated to the conductivity cell in order to provide to the system the minimal interferences.

Temperatures near $(25,0 \pm 0,1) \text{ }^\circ\text{C}$ are supposed to be measured.

5.6 Magnetic stirrer, which will be useful for assuring temperature homogeneity in the sample. PTFE (polytetrafluoroethylene-coated) stirring magnet shall be used.

5.7 Thermostable sample vessel, having a capacity of 20 ml to 500 ml or any proper container (glass, plastic, or stainless steel made), into which the sample to be measured is filled.

The sample vessel shall be designed to ensure that the sample to be measured can be maintained at a temperature $(25,0 \pm 0,1) \text{ }^\circ\text{C}$.

6 Sampling

6.1 Unless specified otherwise, samples shall be taken in accordance with ISO 3170 or ISO 3171 and/or the requirements of national standards regarding the sampling of fuels.

6.2 Only glass bottles shall be used for samples. Sampling should be carried out using ensured clean glass flasks in order to avoid any contamination. Rinse the flask with the product before sampling. Avoid a stopper made up of any materials that can react with, or contaminate samples.

7 Apparatus calibration

7.1 Cleaning of the sample vessel

Before the measurement, the sample vessel (5.7) is rinsed several times with ethanol (4.1). The rest of the ethanol used for rinsing shall be dripped off. If there are any visible contaminations (e.g. stains) on the inner glass surface of the sample vessel, the vessel shall not be used.

7.2 Cleaning of the measuring cell

The measuring cell shall be cleaned thoroughly with water and rinsed with ethanol (4.1) or ethanol fuel before the measurement. If there are any visible contaminations (e.g. stains) on the inner surface of the measuring cell, the cell shall not be used.

NOTE Special care should be addressed if saline samples were in contact with the sample vessel or measurement cell. Rinse thoroughly with water, drying them afterwards. Finally, devices should be rinsed with ethanol. Sample may be poured down directly from the sample container into the sample vessel. In case an intermediate vessel is required for transferring, concerns must be addressed to evaluate cleanliness of the intermediate vessel.

7.3 Checking the cell constant

7.3.1 Principle

The conductivity meters (5.1) usually display in the checking procedure information about cell constant. This information is relevant due to electrodes surface area which is related to measurement accuracy.

7.3.2 Procedure

7.3.2.1 The procedure shall be as follows:

- a) insert in the conductivity meter (5.1) the value of electrolytic conductivity according to calibration solution value (4.2), following meter manufacturer's instructions;
- b) rinse the conductivity cell (5.2) using calibration solution (4.2);
- c) transfer the calibration solution (4.2) to a thermostatic vessel or any proper container (glass, plastic, or stainless steel made) in case of using a thermostatic bath (5.4). The transfer shall be carried out until covering measurement electrodes and temperature sensor (5.5);
- d) stir gently the sample, for at least 1 min, assuring temperature homogeneity;
- e) carry out measurement reading to $(25,0 \pm 0,1)$ °C. The cell constant shall be considered suitable when reading is between $0,08 \text{ cm}^{-1}$ to $0,12 \text{ cm}^{-1}$;

7.3.2.2 When the cell constant fails to meet the requirements, rinse the cell according to manufacturer's instructions and repeat 7.3.2.1.

8 Measurement procedure

8.1 Using thermostatic bath or thermostatic vessel

The procedure shall be as follows:

- a) rinse cell with sample prior to determination;
- b) transfer a portion of the sample to the container in the thermostatic bath (5.4) or thermostatic vessel until covering measurement electrodes and temperature sensor assuring temperature at $(25,0 \pm 0,1)$ °C;
- c) stir the sample gently for at least 1 min, assuring temperature homogeneity. Once a constant temperature of $(25 \pm 0,1)$ °C has been reached in the solution, stop stirring, and the measuring can be started.

8.2 Using thermo compensation

The procedure shall be as follows:

- a) set the conductivity meter (5.1) to reference temperature (25 °C) and adjust temperature correction coefficient to 2,2 %/°C as indicated in Formula (1);
- b) rinse cell with sample prior to determination;
- c) transfer a portion of sample to vessel up to cover measurement electrodes and temperature sensor, assuring temperature is between 10 °C and 40 °C;
- d) stir the sample for at least 1 min, assuring temperature homogeneity, stop stirring and record conductivity reading.

9 Expression of results

Report the electrical conductivity of the sample at 25 °C, expressed in $\mu\text{S}\cdot\text{cm}^{-1}$ rounded to the nearest 0,01 $\mu\text{S}\cdot\text{cm}^{-1}$ or in $\text{S}\cdot\text{m}^{-1}$ rounded to the nearest 0,01 $\text{S}\cdot\text{m}^{-1}$.

In case the conductivity meter does not perform the temperature correction automatically, use Formula (1):

$$C = \kappa_0 \times [1 - 0,022 \times (T - 25^\circ\text{C})] \quad (1)$$

where

C is the corrected conductivity at 25 °C, expressed in $\mu\text{S}\cdot\text{cm}^{-1}$;

κ_0 is the observed conductivity at test temperature (°C), expressed in $\mu\text{S}\cdot\text{cm}^{-1}$;

0,022 is the correction temperature coefficient (2,2 %/°C);

T is the sample test temperature expressed in °C.

10 Repeatability, r

The difference between successive measured conductivity values obtained by the same operator with the same apparatus under constant operating conditions on identical test material at the same fuel temperature would, in the long run, in the normal and correct operation of the test method, not exceed 0,08 $\mu\text{S}\cdot\text{cm}^{-1}$.

11 Reproducibility, R

The difference between two single and independent measurements of conductivity obtained by different operators working at the same location on identical test material at the same fuel temperature would, in the long run, in the normal and correct operation of the test method, not exceed 0,22 $\mu\text{S}\cdot\text{cm}^{-1}$.

Annex A (informative)

Guidance on conductance and conductivity

A.1 Conductance

Since R is expressed in ohms, the conductance is expressed in ohm^{-1} , mhos, or S (Siemens). The conductance is directly proportional to the area of the transversal section A and inversely proportional to the length l of a uniform conductor; so,

$$G = \kappa A/l \text{ or } \kappa = G l/A \quad (\text{A.1})$$

where κ is a proportionality constant called specific conductance. The constant κ is the conductance (G) when the parameters A and l are numerically equals. When A and l are based on the centimetre, κ is the conductance of a cube with a cm on each side. The unit for specific conductance is $\text{ohm}^{-1}\cdot\text{cm}^{-1}$.

A.2 Conductivity definition by Resistance

In another method, the resistance, R (ohms), opposing itself to the passage of the current through an electrolytic medium contained between two electrodes of an area A (cm^2), and that are at a length l (cm), is expressed by:

$$R = \rho l/A \text{ or } R = \rho \cdot K_{\text{cell}} \quad (\text{A.2})$$

The constant ρ is the resistance (R) when the parameters l and A are numerically equals. Therefore, $R = \rho =$ resistivity or specific resistance ($\text{ohms}\cdot\text{m}$) and K_{cell} , is the constant of the cell,

$$K_{\text{cell}} = l/A \quad (\text{A.3})$$

Thus, the conductivity (C) is given by:

$$C = 1/\rho = 1/R \cdot l/A \quad (\text{A.4})$$

A useful definition for the electrolytic conductivity C , is obtained by combining Formulae (A.3) and (A.4):

$$C = K_{\text{cell}} / R \quad (\text{A.5})$$

A.3 Interferences

It is worth noting that the conductivity is influenced by the following:

- ionic concentration: the conductivity increases with the increase in the concentration of ions in the solution;
- ionic mobility: specific for each ion;
- temperature: since increasing temperature affects the kinetic energy of the ions, it increases their mobility and consequently the conductance of the solution;
- cell constant: the conductivity depends on the dimensions of the cell.

The temperature affects the measurement of the conductivity and, therefore, must be corrected through automatic correction of the equipment or internal adjustments, such as a thermostatic bath. The exposure of the sample to the atmosphere can cause changes in the conductivity/resistivity due to the loss or gain of dissolved gases. This is extremely important in the cases of ethanol with low concentrations of dissolved ionized materials. Carbon dioxide, normally present in the air, can change the conductivity/resistivity of pure ethanol. The exposure of the sample to the air should be, in these terms, avoided or minimized.

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