



# SLOVENSKI STANDARD SIST EN 14077:2004

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Petroleum products - Determination of organic halogen content - Oxidative  
microcoulometric method

Mineralölerzeugnisse - Bestimmung des Gehaltes an organisch gebundenem Halogen -  
Verfahren der oxidativen Mikrocoulometrie

Produits pétroliers - Détermination de la teneur en halogènes organiques - Méthode par  
microcouloométrie oxydante

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## ICS:

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Naftni proizvodi na splošno

Petroleum products in  
general

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EUROPEAN STANDARD  
NORME EUROPÉENNE  
EUROPÄISCHE NORM

**EN 14077**

December 2003

ICS 75.080

English version

## Petroleum products - Determination of organic halogen content - Oxidative microcoulometric method

Produits pétroliers - Détermination de la teneur en  
halogènes organiques - Méthode par microcoulométrie  
oxydante

Mineralölerzeugnisse - Bestimmung des Gehaltes an  
organisch gebundenem Halogen - Verfahren der oxidativen  
Mikrocoulometrie

This European Standard was approved by CEN on 1 October 2003.

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EN 14077:2003 (E)

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## Foreword

This document EN 14077:2003 has been prepared by CEN /TC 19, "Petroleum products, lubricants and related products", the secretariat of which is held by NEN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by June 2004, and conflicting national standards shall be withdrawn at the latest by June 2004.

In this standard annex A is normative.

This document includes a Bibliography.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard : Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the United Kingdom.

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## EN 14077:2003 (E)

## 1 Scope

The method is directly applicable to the determination of low contents (2 mg/kg to 100 mg/kg) of organic halogen in petroleum products such as gasolines, middle distillates and residual fuels. The method can also be applied to crude oils; however, no precision data have been established for this additional product type. Except for fluorine (F), the organic halogens chlorine (Cl), bromine (Br) and iodine (I) that may be present in the sample are determined quantitatively. The halogen is reported as the equivalent number of chloride ions. A sample preparation is described for the removal of inorganic halides from residual fuels, before the determination of the organic halogen content. This procedure is essential to obtain a result of organic halogen only.

**NOTE** The total halogen content can be measured by ISO 15597 'Petroleum and related products – Determination of chlorine and bromine content – Wavelength-dispersive X-ray fluorescence spectrometry method'. This method does not use a combustion step, but it requires a sample preparation according to clause 7 of this standard to determine the organic halogen content.

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

## 2 Normative references

This European Standard incorporates by dated or undated reference, provisions from other publications. These normative references are cited at the appropriate places in the text, and the publications are listed hereafter. For dated references, subsequent amendments to or revisions of any of these publications apply to this European Standard only when incorporated in it by amendment or revision. For undated references the latest edition of the publication referred to applies (including amendments).

EN ISO 595-2, *Reusable all-glass or metal-and-glass syringes for medical use - Part 2: Design, performance requirements and tests (ISO 595-2:1987)*.

EN ISO 3170, *Petroleum liquids - Manual sampling (ISO 3170:1988, including Amendment 1:1998)*.

EN ISO 3171, *Petroleum liquids - Automatic pipeline sampling (ISO 3171:1988)*.

EN ISO 3696, *Water for analytical laboratory use - Specification and test methods (ISO 3696:1987)*.

ISO 595-1, *Reusable all-glass or metal-and-glass syringes for medical use - Part 1: Dimensions*.

## 3 Terms and definitions

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

### 3.1

#### organic halogen

all organically bound halogen, which are converted to the halide ion under the conditions of the test, titrated with electrolytically generated silver ions and expressed as the equivalent number of chloride ions

**NOTE** Under the conditions of this test, organic halogen compounds include organic compounds of chlorine (Cl), bromine (Br) and iodine (I). It does not include organic compounds of fluorine (F). Some inorganic halide compounds, if not quantitatively removed, are also determined as organic halogen.

### 3.2

#### residual fuel

residue of any distillation process, applied to hydrocarbon mixtures derived from crude petroleum and obtained either directly or through a specific process, which is intended to be used as a fuel oil or a fuel oil component

**NOTE** Residual fuel is implied to be any hydrocarbon mixture, which cannot be fully vaporized under conditions normally applied in physical distillation processes. For the purpose of this standard this also includes fuel oils, other than those obtained as overhead product of a physical distillation process, derived from waste materials

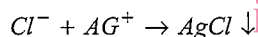
### 3.3 distillate fuel

distillate product of any distillation process, applied to hydrocarbon mixtures derived from crude petroleum and obtained either directly or through a specific process, which is intended to be used as a fuel oil or a fuel oil component

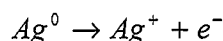
**NOTE** Distillate fuel is implied to be any hydrocarbon mixture, which can be fully vaporized under conditions normally applied in physical distillation processes. For the purpose of this standard this also includes distillate fuel oils, containing non-distillable additives such as ignition and flow improvers. It does not include distillate fuels, containing additives or other non-distillable substances originating from other products not primarily intended as fuel oils e.g. those originating from waste materials.

## 4 Principle

A microcoulometer is set up and its performance checked with the aid of organic liquid standards. Where appropriate, the sample is diluted with a suitable solvent. Inorganic halide compounds, if present, are removed by extraction with water. The (diluted) sample is injected into a heated zone of the pyrolysis tube where it evaporates. The gaseous products are entrained by a flow of argon to the combustion tube where oxygen is mixed with argon and combustion takes place. The combustion products, including the hydrogen halide, are sparged through a sulfuric acid dryer into a coulometric cell and titrated with electrolytically generated silver ions according to:



The silver ions consumed are coulometrically replaced at the generator anode:



The current required to restore the silver ion content is a measure of the halide titrated. The current flow in microcoulomb/sec is recorded as a peak on a strip chart, and the peak area integrated either mechanically or electronically. The halide is reported as the equivalent number of chloride ions. The content of halogen in the sample is then calculated in the appropriate units selected.

## 5 Reagents and materials

Use only reagents of recognised analytical grade and water conforming to grade 3 of EN ISO 3696.

### 5.1 Gases

Molecular sieve scrubbers may be used to ensure adequate purity of the gases.

**5.1.1 Oxygen**, 99,98 % minimum purity.

**5.1.2 Argon**, 99,99 % minimum purity. Helium of equal purity is an acceptable alternative.

**5.2 Diluent, xylene.** Determine the organic halogen content according to 9.2 of this method. The result shall be preferably below 1 mg/kg and in any case below 2 mg/kg.

**5.3 Nitric acid w**, 5 mol/l, aqueous. Cautiously dilute 325 ml of analytical grade concentrated nitric acid (density 1,42 g/ml) to 1 l with water, whilst stirring.

**5.4 Sulfuric acid**, concentrated.

**5.5 Acetic acid**, glacial.

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## 5.6 Hydrazine sulfate

## 5.7 Quality control compounds

5.7.1 Chlorotetradecane, 98,0 % minimum purity

5.7.2 Chlorobenzene, 98,0 % minimum purity

## 5.8 Control Solutions

## 5.8.1 Stock solution

Prepare a 10 000 mg/kg stock solution as follows: weigh approximately 2,5 g ( $m_1$ ) of chlorotetradecane or 1,2 g ( $m_1$ ) chlorobenzene to the nearest 0,1 mg into a clean 50 ml glass bottle. Add approximately 35 g ( $m_2$ ) of xylene weighed to the nearest 0,1 mg and mix well. The stock solution is stored in a well closed bottle. Do not use screw-caps with PVC inlays. Calculate the exact content by means of the following equation:

$$C_s = \frac{m_1 \times 35,453 \times 10^6}{M \times (m_1 + m_2)} \quad (1)$$

where:

$C_s$  is the chlorine (Cl) content of stock solution, in mg/kg;

$m_1$  is the mass of quality control compound, in g;

$m_2$  is the mass of xylene, in g;

$M$  is the molecular mass of quality control compound.

NOTE For chlorotetradecane  $M = 232,84$ ; for chlorobenzene  $M = 112,56$ .

A fresh solution should be prepared weekly.

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## 5.8.2 Working control solutions

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Prepare working control solutions containing approximately 100 mg/kg, 50 mg/kg and 10 mg/kg chlorine (Cl) daily by appropriate dilution of the stock solution with xylene in clean glass bottles. Calculate the exact content of each working standard to the nearest 0,1 mg/kg by means of the following equation:

$$C_w = \frac{m_s}{m_s + m_x} \times C_s \quad (2)$$

where:

$C_w$  is the chlorine (Cl) content of working control solution, in mg/kg;

$C_s$  is the chlorine (Cl) content of stock solution, in mg/kg;

$m_s$  is the mass of stock solution taken, in g;

$m_x$  is the mass of xylene added, in g.

## 5.9 Electrolyte

Electrolyte solution. 75 parts by volume of glacial acetic acid with 25 parts of water. Add approximately 0,1 % (m/m) hydrazine sulfate.

NOTE When using a coulometric system including a salt bridge (instead of a capillary), it is advantageous to add about 1 % of sodium perchlorate to the electrolyte.



## 6 Apparatus

### 6.1 General

Usual laboratory apparatus and glassware, together with the following.

### 6.2 Round bottom flask and condenser

A round bottom flask, 500 ml capacity, to which is attached a straight or mushroom-type reflux condenser. The condenser shall be fitted to the flask by means of a ground-glass joint. All glassware shall be chemically clean.

### 6.3 Electric heating mantle, to fit a 500 ml round bottom flask

The heating mantle shall be provided with a facility to allow stirring by means of a magnetically driven stirring bar.

### 6.4 Balance, readability 0,1 mg

### 6.5 Microcoulometer, with attached furnace, cell, controls, and electronics

#### 6.5.1 Pyrolysis furnace

An electric furnace consisting of one or two independently controlled temperature zones and a heated inlet section that can maintain a temperature sufficient to volatilize all the organic sample. The electric furnace should be capable of maintaining a temperature high enough to combust the sample and to convert the halogens into hydrogen halides.

#### 6.5.2 Pyrolysis tube

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Made from quartz and constructed in such a way that the sample is completely vaporised in an inert gas in the inlet section, and swept into the oxidation zone, where it mixes with oxygen and is burnt. The inlet end of the tube holds a septum for introducing the sample by syringe and provisions for entry of oxygen and inert gas.

NOTE Modern equipment utilises an interchangeable injection cassette, which holds the provisions for entry of the gases as well. If such a system is used an extra gas flow is added to the scrubber and titration cell to prevent sulphuric acid from entering the combustion tube (see 6.5.4)

#### 6.5.3 Titration cell, containing two pairs of electrodes and an inlet for the combustion gases

The sensor reference electrodes (of silver-plated platinum) detect changes in titrant ion ( $Ag^+$ ) content. The generator anode and cathode (of silver-plated platinum and a platinum coil respectively) maintain the titrant ion ( $Ag^+$ ) content in the cell. The cell should be supported on a suitable magnetic stirrer. An  $Ag-AgCl$  coulometric cell is light sensitive and should therefore be placed in a dark compartment or otherwise be shielded from light.

#### 6.5.4 Scrubber

A scrubber containing concentrated sulphuric acid is placed between the pyrolysis tube and the titration cell to remove water of combustion. To be fully effective an electrical heating tape should be wound around the scrubber to keep this at a temperature of at least 100 °C.

The scrubber shall have a nominal capacity of 12 ml to 15 ml and a filling height of nominally 4 cm to 5 cm. It shall be filled with concentrated sulphuric acid up to 25 % to 40 % of its nominal capacity. To prevent sulphuric acid from entering the combustion tube a one-way valve (or ball valve) is mounted in the scrubber inlet. An extra gas flow (either oxygen or argon) of  $(40 \pm 10)$  ml/min is added to the scrubber to ensure a steady flow of gas to the coulometric cell and also to prevent sulphuric acid from entering the combustion tube.

6.5.5 Microcoulometer, having variable attenuation and gain control and capable of measuring the potential of the sensor/reference electrode pair, and comparing this potential with a bias potential.