



SLOVENSKI STANDARD

SIST EN 13723:2002

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Petroleum products - Determination of low lead contents in gasolines - Wavelength-dispersive X-ray fluorescence spectrometry (XRF)

Mineralölerzeugnisse - Bestimmung niedriger Bleigehalte in Kraftstoffen - Wellenlängendispersive Röntgenfluoreszenz-Analyse (RFA)

Produits pétroliers - Détermination des faibles teneurs en plomb dans les essences pour moteurs - Spectrométrie de fluorescence de rayons x dispersive en longueur d'onde (FRX)

Ta slovenski standard je istoveten z: EN 13723:2002

ICS:

75.160.20 V^ \ [æ [l æ Liquid fuels

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EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 13723

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ICS 75.160.20

English version

**Petroleum products - Determination of low lead contents in
gasolines - Wavelength-dispersive X-ray fluorescence
spectrometry (XRF)**

Produits pétroliers - Détermination des faibles teneurs en
plomb dans les essences pour moteurs - Spectrométrie de
fluorescence de rayons x dispersive en longueur d'onde
(FRX)

Mineralölerzeugnisse - Bestimmung niedriger Bleigehalte in
Kraftstoffen - Wellenlängendispersive Röntgenfluoreszenz-
Analyse (RFA)

This European Standard was approved by CEN on 5 April 2002.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.



EUROPEAN COMMITTEE FOR STANDARDIZATION
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Foreword

This document EN 13723:2002 has been prepared by Technical Committee 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 January 2003, and conflicting national standards shall be withdrawn at the latest by January 2003.

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, Iceland, Ireland, Italy, Luxembourg, Malta, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

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EN 13723:2002 (E)

1 Scope

This European Standard specifies a method for the determination of the lead content of gasolines with a lead concentration from 4 mg/l to 25 mg/l.

NOTE For the purpose of this European Standard, the term “% (V/V)” is used to represent the volume fraction.

WARNING: The use of this European Standard can 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 3170, *Petroleum liquids - Manual sampling (ISO 3170:1988, including Amendment 1:1998)*.

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

3 Principle

The test portion and a bismuth solution as internal standard are mixed in a given volume ratio and exposed, in a sample cell, to the primary radiation of an X-ray tube.

A mixture of 2,2,4-trimethylpentane (isooctane) and toluene with bismuth as internal standard is measured as blank solution under the same conditions.

The ratio of the Pb $L_{\alpha 1}$ net count rates to the Bi $L_{\alpha 1}$ gross count rates is calculated by subtracting the corresponding ratio found for the blank.

The lead concentration is determined from a calibration graph previously prepared by means of lead standard solutions and a blank solution.

This procedure is independent of the type of lead compounds and of the composition of the sample.

4 Chemicals and solvents

Use only reagents of recognized analytical grade, unless otherwise specified.

4.1 2,2,4-trimethylpentane (isooctane).

4.2 Toluene.

4.3 Kerosene, regular grade.

Kerosene is used as solvent where conveniently available. Alternatively, a blank solution (4.7) can also be used.

4.4 Lead-2-ethylhexanoate, or a certified lead reference standard.

4.5 Triphenylbismuth or bismuth-2-ethylhexanoate, pure, or a certified, commercially available solution.

4.6 Ethylhexanoic acid, minimum purity 98 %.

4.7 Blank solution.

Mix 50 % (V/V) of 2,2,4-trimethylpentane and 50 % (V/V) of toluene.

4.8 Lead stock solution, $c(\text{Pb}) = \text{approx. } 100 \text{ mg/l}$.

Commercially available lead stock solutions can be used or be prepared as follows:

Dissolve the appropriate quantity of lead compound (4.4) in kerosene (4.3) or in the blank solution (4.7). Store the solution in a tightly stoppered brown glass bottle protected from light and at temperatures between 18 °C and 28 °C. The solution shall be checked before use for absence of cloudiness. In case of doubt, a new solution shall be prepared.

4.9 Bismuth internal standard solution, $c(\text{Bi}) = \text{approx. } 0,8 \text{ g/l}$.

Commercially available bismuth standards can be used or be prepared as follows:

Dissolve the appropriate quantity of bismuth compound (4.5) in kerosene (4.3) or in blank solution (4.7). In order to stabilize the solution, add 5 % (V/V) of 2-ethylhexanoic acid (4.6). If cloudiness occurs, filter the solutions through a fritted glass filter (5.5).

The bismuth solution has to be protected against humidity. Store the solution in a tightly stoppered brown glass bottle protected from light and at temperatures between 18 °C and 28 °C. The solution shall be checked before use for absence of cloudiness. In case of doubt, a new solution shall be prepared.

5 Apparatus

Usual laboratory apparatus and glassware, together with the following.

5.1 Wavelength-dispersive X-ray fluorescence spectrometer, capable of being operated conforming to the general requirements given in Table 1. It shall be set up according to the manufacturer's instructions.

Table 1 - General requirements for the spectrometer

Anode	rhodium, molybdenum, tungsten or gold target
Voltage	50 kV to 75 kV
current	40 mA to 60 mA
power	$\geq 2,0$ kW
collimator	fine
analyzing crystal	
optical path	lithium fluoride ($2d = 4,028$ nm)
cell window	helium
	Polyester or polypropylene film, thickness approx.
	$4\text{ }\mu\text{m}$ to $6\text{ }\mu\text{m}$, lead-free
detector	scintillation detector with pulse-height analyser

NOTE Other systems, like systems with lower power, can also be used, provided that they have been validated to fully meet the other requirements in 5.1, 8.2 and 12.

5.2 One-mark pipettes, conforming to ISO 648, capacity 2 ml and 20 ml, or suitable dispenser.

5.3 Volumetric flasks, with ground glass stopper.

5.4 Conical flasks, with conical ground glass stopper.

5.5 Fritted glass filter, $10\text{ }\mu\text{m}$ to $16\text{ }\mu\text{m}$ pore size.

5.6 Analytical balance, capable of weighing to the nearest 0,1 mg.

6 Samples and sampling

Unless otherwise specified in the commodity specification, samples shall be taken as described in EN ISO 3170 or EN ISO 3171, and/or in accordance with the requirements of national standards or regulations for the sampling of the product under test.

7 Calibration solutions

7.1 Preparation of lead calibration solutions

Dilute in volumetric flasks (5.3) the lead stock solution (4.8) using the blank solution (4.7) to obtain calibration solutions with approximate, but precisely known lead concentrations of 30 mg/l, 20 mg/l, 10 mg/l, 5 mg/l, 1 mg/l.

Store the calibration solutions in dark bottles.

7.2 Preparation of calibration solutions by addition of the internal standard

Using the pipettes or suitable dispenser (5.2), mix thoroughly ten parts by volume, e.g. 20 ml, of each of the lead calibration solutions and the blank solution with one part by volume, e.g. 2 ml, of the bismuth internal standard solution (4.9) in conical flasks (5.4) and seal with the ground glass stoppers to avoid evaporation losses.

8 Calibration

8.1 General

Set up and check the spectrometer (5.1), and then purge the optical path thoroughly with helium (see NOTE 1 in 8.2).

8.2 Calibration graph

Transfer a suitable amount of each of the prepared calibration solutions and blank solution (7.2) into sample cells and place them into the spectrometer. The use of a loose cover for the sample cells is recommended in order to avoid excessive pressure and deformation of the film. Flush the optical path with helium (see NOTE 1) and expose the cells successively to the radiation of the X-ray tube.

NOTE 1 While purging with helium is not absolutely necessary for this specific analysis, it can be necessary for other following test series measuring other constituents in the same apparatus. Since it is essential, however, to have constant equilibrium gaseous conditions in the optical path, purging with helium is recommended in this test method.

Measure for each solution the count rates, I , of the Pb $L\alpha_1$ line at 0,117 5 nm, of the Bi $L\alpha_1$ line at 0,114 4 nm and of the background radiation at 0,119 4 nm.

The settings of the X-ray spectrometer shall be such that over the entire measurement period, the Bi $L\alpha_1$ line will give at least 100 000 counts.

Calculate for each solution the ratio, R , of the Pb $L\alpha_1$ net count rate to the Bi $L\alpha_1$ gross count rate using the following equation:

$$R = \frac{I_{0,1175} - I_{0,1194}}{I_{0,1144}}$$

where

$I_{0,1175 \text{ nm}}$ is the gross count rate of the Pb $L\alpha_1$ line;

$I_{0,1194 \text{ nm}}$ is the count rate of the background radiation;

$I_{0,1144 \text{ nm}}$ is the gross count rate of the Bi $L\alpha_1$ line.

Calculate for each calibration solution the corrected count rate ratio, R_c , using the following equation:

$$R_c = R - R_b$$