SLOVENSKI STANDARD

SIST EN 12766-3:2005

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Naftni derivati in rabljena olja - Določevanje PCB in sorodnih proizvodov - 3. del: Prepoznavanje in kvantitativno določevanje polikloriranih terfenilov (PCT) in polikloriranih benzil toluenov (PCBT) z metodo plinske kromatografije (GC) in uporabo detektorja na zajetje elektronov (ECD)

Petroleum products and used oils - Determination of PCBs and related products - Part 3: Determination and quantification of polychlorinated terphenyls (PCT) and polychlorinated benzyl toluenes (PCBT) content by gas chromatography (GC) using an electron capture detector (ECD)

Mineralölerzeugnisse und Gebrauchtöle - Bestimmung von PCBs und verwandten Produkten - Teil 3: Bestimmung und Berechnung der Gehalte von polychlorierten Terphenylen (PCT) und polychlorierten Benzyltoluolen (PCBT) mittels Gaschromatographie unter Verwendung eines Elektroneneinfang-detektors (ECD)

Produits pétroliers et huiles usagées - Détermination des PCB et produits connexes - Partie 3: Détermination et quantification des polychloroterphényles (PCT) et des polychlorobenzyltoluenes (PCBT) par chromatographie en phase gazeuse (CPG) avec utilisation d'un détecteur a capture d'électrons (DCE)

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This European Standard was approved by CEN on 14 October 2004.

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 Central Secretariat 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 Central Secretariat has the same status as the official versions.

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

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Foreword

This document (EN 12766-3:2004) 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 May 2005, and conflicting national standards shall be withdrawn at the latest by May 2005.

EN 12766 consists of the following parts under the general title *Petroleum products and used oils – Determination of PCBs and related products*:

— *Part 1: Separation and determination of selected PCB congeners by gas chromatography (GC) using an electron capture detector (ECD)*

— *Part 2: Calculation of polychlorinated biphenyl (PCB) content*

— *Part 3: Determination and quantification of polychlorinated terphenyls (PCT) and polychlorinated benzyl toluenes (PCBT) content by gas chromatography (GC) using an electron capture detector (ECD)*

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

1 Scope

This document specifies a method of test for the determination of polychlorinated terphenyls (PCT) and polychlorinated benzyl toluenes (PCBT) in petroleum products and related materials by means of a specified gas chromatographic separation procedure. Following the gas chromatographic separation, quantification procedures are described for PCT Aroclor 5442, PCT Aroclor 5460 and PCBT (Ugilec 141).

This document is applicable to unused, used and treated (e.g. dechlorinated) petroleum products including synthetic lubricating oils, to petroleum products and synthetic lubricating oils suitably recovered from other materials (e.g. from waste materials) and to mixtures of vegetable oils.

NOTE 1 This document has been developed as an extension of EN 12766 Parts 1 and 2 to provide a method of determining the total PCB content in accordance with Articles 2, 3 and 4 of EC Directive 96/59/EC [1]. The total PCB content is calculated by summation of PCB content, determined according to EN 12766-2, and PCTs and PCBTs according to this document.

The three classes of materials measured in this standard can be quantified if they occur at concentrations greater than given in Table 1.

Table 1 — Concentrations for quantification

Class of material	Minimum concentration	Method applied
PCB, polychlorinated biphenyls	8 mg / kg	(EN 12766-2 – Method A)
	4 mg / kg	(EN 12766-2 – Method B)
PCT	10 mg / kg	(EN 12766-3)
PCBT	5 mg / kg	(EN 12766-3)
Total PCB and related products [a]	25 mg / kg	(EN 12766-2 and EN 12766-3)
[a] This value is only a best estimate. Real field conditions may, depending on the concentrations in the three different classes, result in other, more limited or more improved application ranges. It is the user's responsibility to demonstrate that the analysis has been performed in a valid calibrated concentration range.		

NOTE 2 In order to simplify and rationalize the analytical operations required for an effective, fast and economic inventory of equipment containing liquids classified as PCBs (as defined by Directive 96/59/EC [1]), it is recommended firstly to determine, using an appropriate screening method, the total chlorine content (in mg/kg). Examples for analytical procedures to determine total chlorine content in fresh, used, or treated insulating oils are:

i) pre-dosed colorometric kits to measure 25 mg/kg or 50 mg/kg total chlorine (ref: US EPA SW-846 Method 9079);

ii) electrochemical methods in the range 2 mg/kg to 2 000 mg/kg of total chlorine (ref: DEXSIL® L-2000 DXC - US EPA SW-846 Method 9079 and US EPA SW-846 Method 9078);

iii) wavelength dispersive X-ray fluorescence; or

iv) oxidative microcoulometry or other scientifically validated analytical methods.

From the total chlorine measured for a specific sample, a theoretical maximum equivalent PCB content can be calculated. When this maximum equivalent PCB content is significantly lower than the limit prescribed by Directive 96/59/EC [1] (50 mg/kg total PCBs) or by local standards (e.g. 25 mg/kg total PCBs), the sample may be considered as "PCB-free".

NOTE 3 When the total chlorine content in a sample is higher than the limits described above, it becomes necessary to proceed with gas chromatographic analysis in accordance with this document using the total chlorine content as:

i) a guide to establish the level of dilution necessary to operate within the linear range of the ECD detector (EN 12766-1:2000, 10.3.2);

ii) a method of calculating the ratio between total chlorine content and total PCB for quality control purposes;

iii) a method for the classification of the hazard posed by the oil (e.g. at the end of its life cycle, for regeneration, use as fuel and/or disposal in accordance with local regulations).

NOTE 4 For the purposes of this document, the terms "% (*m/m*)" and "% (*V/V*)" are used to represent respectively the mass fraction and the volume fraction.

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

2 Normative references

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

EN 12766-1:2000, *Petroleum products and used oils - Determination of PCBs and related products - Part 1: Separation and determination of selected PCB congeners by gas chromatography (GC) using an electron capture detector (ECD)*

EN 12766-2, *Petroleum products and used oils - Determination of PCBs and related products – Part 2: Calculation of polychlorinated biphenyl (PCB) content*

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

3 Terms and definitions

As defined in several regulations and legislation, the term "PCB" includes "PCT" and also "PCBT". For the purposes of this document, however, "PCB" is defined on a molecular, chemical basis and its measurement and quantification is described in EN 12766 Part 1 and Part 2. Also, the terms "PCT" and "PCBT" are defined in chemical terms, and this document describes their measurement and quantification.

For analytical results to comply with Directive 96/59/EC, the total sum of PCB obtained from EN 12766-2 and PCT plus PCBT obtained from this document is required.

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

3.1
polychlorinated biphenyl
PCB
biphenyl substituted by one to 10 chlorine atoms

NOTE For legal purposes, congeners with one, two or ten chlorine atoms may be excluded from this definition.

3.2
polychlorinated terphenyl
PCT
terphenyl substituted by one to 14 chlorine atoms

NOTE There are 8 557 possible congeners of polychlorinated terphenyls.

3.3
polychlorinated benzyl toluene
PCBT
family of compounds monomethyl-polychlorobiphenyl methane

3.4
congener
any chlorinated derivative of biphenyl or terphenyl irrespective of the number of chlorine atoms

3.5
decachlorobiphenyl
DCB
PCB congener 209

NOTE This congener is used as reference and as an internal standard.

4 Principle

A sample preparation (clean-up) procedure is used to remove most of the impurities likely to interfere with the determination. The clean-up procedure is chosen according to the type of sample. A range of clean-up procedures is described in EN 12766-1:2000, Clause 8 and B.1 to B.5.

Groups of PCT and PCBT congeners are determined by gas chromatography using a high efficiency narrow-bore capillary column, an electron capture detector and an internal standard.

PCBT and PCT are separated into groups of overlapping congeners and the types of gas chromatograms obtained for PCBT and the Aroclor mixtures of PCT are shown in Annex A. Experimental relative retention times (*ERRT*) are calculated. Calibration and quantification of specified identified peaks are achieved using standard mixtures and an internal standard. Some marker congeners (three for each commercial mixture, chosen from the ones with high relative abundance) are quantified and total PCT and PCBT is calculated.

5 Reagents and materials

Use only reagents of recognized analytical grade and water conforming to Grade 3 of EN ISO 3696. All reagents and materials including those used for clean-up shall be free from PCB, PCT and PCBT contamination and compounds interfering in the ECD. If preparations of solutions are expressed volumetrically, such preparations may alternatively be conducted gravimetrically.

5.1 Reagents and materials for the sample preparation (clean-up)

5.1.1 Solvent, high purity, free from PCB contamination and low in compounds that respond in the ECD. Although heptane is preferred, cyclohexane or 2,2,4-trimethylpentane may also be used.

5.1.2 Sodium sulphate, granular, anhydrous.

5.1.3 Sulphuric acid, of purity 96 % *(m/m)* to 98 % *(m/m)*.

5.1.4 Separation material, silica gel, active, particle size 100 µm to 200 µm.

5.1.5 Columns, for solid phase extraction, of the types given in a) and b):

b) 3 ml silica gel column, of adsorbent mass 500 mg, particle size 40 µm;

c) 3 ml benzenesulphonic acid column, of adsorbent mass 500 mg, particle size 40 µm.

5.1.6 Column adapter, for joining two columns.

5.1.7 **Vacuum manifold column processor** (optional).

The reagents and materials for alternative and additional clean-up procedures are as described in EN 12766-1:2000, Annex B.

5.2 Reagents and materials for the GC analysis

NOTE The purity of all the gases should be at least 99,99 % *(V/V)*. The gas line should be fitted with a moisture filter and an oxygen absorber cartridge.

5.2.1 **Hexachlorobenzene**, of purity greater than 99 % *(V/V)*.

5.2.2 **Carrier gas**, either helium or hydrogen.

5.2.3 **Make-up gas**, either nitrogen, or a mixture of argon and methane in the volume ratio of 95 : 5.

5.3 Standard and reference solutions

NOTE The standard solutions specified in this sub-clause may be purchased as solutions of known concentration (precision ± 5%) in hydrocarbon solvent (5.1.1) prepared from pure materials, with a purity greater than 99 % *(m/m)*, or prepared by the user from pure materials.

5.3.1 **PCB congener 30 solution**, of nominal concentration 10 mg/l (used as a reference peak).

5.3.2 **PCB congener 209 (DCB) solution**, of nominal concentration 10 mg/l (used as a reference peak and as an internal standard).

5.3.3 **Internal standard solution**, comprising 2 mg/l congener 30 and 2 mg/l congener 209, prepared by pipetting 5 ml of solution (5.3.1) and 5 ml of solution (5.3.2) in a 25 ml volumetric flask and filling to the mark with solvent (5.1.1).

5.3.4 **Ugilec 141 (Ugilec T)**, in solvent (5.1.1), of accurately known concentration of approximately 100 mg/l.

5.3.5 **PCT (Aroclor 5442)**, in solvent (5.1.1), of accurately known concentration of approximately 100 mg/l.

5.3.6 **PCT (Aroclor 5460)**, in solvent (5.1.1), of accurately known concentration of approximately 100 mg/l.

5.3.7 **Standard solutions (PCBT Ugilec 141),** in solvent (5.1.1), of concentration 10 mg/l or different, provided that the response is in the linearity range of the GC detector (see also 10.3 in EN 12766-1:2000), prepared by adding Ugilec 141 (5.3.4) to 7 ml of solvent in a 10 ml flask, adding 1 ml of internal standard solution (5.3.3) and 1 g of base oil (5.4) weighed to the nearest mg and making up to the mark with solvent, to produce a standard solution of the required concentration.

5.3.8 **Standard solutions (PCT Aroclor 5442)**, in solvent (5.1.1), of concentration 10 mg/l or different, provided that the response is in the linearity range of the GC detector (see also 10.3 in EN 12766-1:2000), prepared by adding PCT Aroclor 5442 (5.3.5) to 7 ml of solvent in a 10 ml flask, adding 1 ml of internal standard solution (5.3.3) and 1 g of base oil (5.4) weighed to the nearest mg and making up to the mark with solvent, to produce a standard solution of the required concentration.

5.3.9 **Standard solutions (PCT Aroclor 5460),** in solvent (5.1.1), of concentration 10 mg/l or different, provided that the response is in the linearity range of the GC detector (see also 10.3 in EN 12766-1:2000), prepared by adding PCT Aroclor 5460 (5.3.6) to 7 ml of solvent in a 10 ml flask, adding 1 ml of internal standard solution (5.3.3) and 1 g of base oil (5.4) weighed to the nearest mg, and making up to the mark with solvent, to produce a standard solution of the required concentration.

5.4 Base oil

Unused, free from PCB, PCT and PCBT as reported in EN 12766-1:2000, note in 5.5.

5.5 Check sample

A standard mixture of PCT and PCBT in base oil in the medium range of calibration and of a concentration to lie in the linear response range of the ECD.

6 Apparatus

6.1 General provisions

All parts of the apparatus coming into contact with the sample, especially the packed columns for the liquid chromatographic clean-up, shall be free from PCB, PCT, PCBT and interfering compounds. Glassware shall be cleaned with solvent (5.1.1).

The use of disposable plastic pipette tips and plastic columns is permitted for single use. Special care shall be executed to demonstrate the appropriate cleanliness of single use materials.

The apparatus shall be usual laboratory apparatus and glassware, together with the following:

6.2 Gas chromatograph

As described in EN 12766-1:2000, 6.2.

This gas chromatograph shall be capable of resolving the peaks of standard stock solutions (5.3.7, 5.3.8 and 5.3.9) at least as well as shown in Figures A.1 to A.3. At least 21 peaks shall be observed for Ugilec 141 and 57 peaks for PCT Aroclor 5460 and 81 peaks for PCT Aroclor 5442. The chromatograph shall also be capable of reproducing the experimental relative retention times (ERRT) to within ± 0,001 5.

6.3 Columns

As described in EN 12766-1:2000, 6.3.

7 Sampling and sample preparation

Sampling and sample preparation shall be as described in EN 12766-1:2000, Clause 7.

In particular, before the clean-up, weigh approximately 1,0 g to the nearest mg of homogenized sample into a 10 ml volumetric flask. Add approximately 8 ml of solvent (5.1.1) and mix well. Add 1 ml of the internal standard solution (5.3.3) and make up to the mark with solvent.

If necessary, the determination or PCBT and PCT shall be performed at different dilutions of the sample with base oil (5.4) to bring the measurement into the linear range of the GC detector.

8 Clean-up procedure

In general the relatively simple procedure given in Clause 8 of EN 12766-1:2000 is sufficient for clean-up of samples. If this clean-up is unsatisfactory, one of the alternative procedures given in B.1 to B.5 of EN 12766-1:2000 may be used.

NOTE For insulating liquids it is possible to use the clean-up procedure described in B.2 of EN 12766-1:2000.

9 Operating conditions for the GC apparatus

9.1 Setting up the GC apparatus

The operating conditions described below have been found adequate, but should be optimised with each GC system so that gas chromatograms similar to those shown in Annex A are obtained from the standard stock solutions (5.3.7, 5.3.8 and 5.3.9). In the given example, hydrogen is used. Other carrier gases give different retention times.

9.2 Injectors

Set up the injector in accordance with the manufacturer's instructions.

NOTE Typical settings for this analysis are as follows:

a) for gas chromatograph with split/splitless injector:

splitless mode:	T = 240 °C to 280 °C
split valve closed between:	0,5 min to 1,5 min
split mode:	T = 250 °C to 280 °C
split ratio:	5 : 1

b) on-column injector T= 50 °C to 110 °C according to the solvent used.

9.3 Oven temperature programme

The oven temperature programme shall be selected to obtain a suitable chromatogram. The initial temperature and initial isothermal period shall be varied depending on the solvent and injection technique.

Typical settings are given in Table 2. These settings may be varied to obtain the required chromatogram.

Table 2 — Typical settings of oven temperature programme

Programme settings	At constant pressure	At constant flow (electronic regulation)
initial isothermal period	1 min	1 min
initial temperature	50 °C	50 °C
temperature programme	50 °C to 168 °C at 50 °C/min	50 °C to 168 °C at 50 °C/min
	168 °C to 290 °C at 4 °C/min	168 °C to 290 °C at 2,5 °C/min
isothermal period	290 °C for 30 min	290 °C for 46 min
cool down to	50 °C	90 °C

9.4 Carrier gas flow rate

a) constant pressure
Adjust the inlet pressure to e.g. 270 kPa for helium, to give a flow rate through the column of 1 ml/min at 130 °C.

b) constant flow (electronic regulation)
Adjust the flow to 1 ml/min through the column.