BRITISH STANDARD

BS EN 12766-3:2004
BS 2000-462.3:2004
Incorporating corrigendum no. 1

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)

The European Standard EN 12766-3:2004 has the status of a British Standard

ICS 75.080; 75.100

British Standards

National foreword

This British Standard is the official UK version of EN 12766-3:2004, incorporating corrigendum February 2007.

The start and finish of text introduced or altered by corrigendum is indicated in the text by tags AC〉 〈AC. Text altered by CEN corrigendum February 2007 is indicated in the text by AC1〉 〈AC1.

The UK participation in its preparation was entrusted to Technical Committee PTI/13, Petroleum testing and terminology.

A list of organizations represented on this committee can be obtained on request to its secretary.

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This British Standard was published under the authority of the Standards Policy and Strategy Committee on 7 December 2004

ISBN 978 0 580 59190 7

Amendments issued since publication

Amd. No.	Date	Comments
17068 Corrigendum No. 1	29 June 2007	See updated national foreword

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 12766-3

November 2004

ICS 75.080; 75.100

Incorporating corrigendum February 2007

English version

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)

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

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)

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.

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

Ref. No. EN 12766-3:2004: E

Contents

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):

[AC1⟩ a) 3 ml silica gel column, of adsorbent mass 500 mg, particle size 40 µm;

b) 3 ml benzenesulphonic acid column, of adsorbent mass 500 mg, particle size 40 µm. ⟨AC1]

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.

NOTE Hydrogen carrier gas is effective in reducing the pressure at the inlet of the column and analysis time.

9.5 Electron capture detector settings

The temperature shall be 300 °C to 350 °C.

Use the manufacturers recommended settings to give the best conditions for linearity of the detector.

The flow rate of the make up gas shall be between 20 ml/min and 40 ml/min, and shall be selected to give the best sensitivity for the compound being analyzed.

10 Check on instrumental performance and resolution

NOTE The instrument performance should be checked as described in EN 12766-1:2000, Clause 10.

Using the standard chromatographic parameters, run a suitable concentration of all the standard stock solutions (5.3.7, 5.3.8 and 5.3.9) within the linear range. Compare the sample chromatogram with the standard chromatogram, and verify the matching of the pattern to identify the mixture. Identify all the peaks by comparison with the chromatograms and tables in Annex A conforming to the requirements of 6.2.

11 Calibration

11.1 General

NOTE The gas chromatograph is calibrated in the linear range of the ECD. The calibration solution should contain an amount of base oil (5.4) similar to the final analysis solution so that the ECD interferences are comparable for both injections.

Submit 250 µl of each of the standard stock solutions (5.3.7, 5.3.8 and 5.3.9) to the clean-up procedure (see Clause 8). Inject each of the solutions into the GC, and run the GC in accordance with Clause 9.

11.2 Determination of experimental relative retention times (*ERRT*ᵢ)

[AC1⟩ Three marker peaks of each commercial mixture (5.3.7, 5.3.8 and 5.3.9) shall be identified and selected according to their relative abundance (see Table 3). ⟨AC1] An experimental relative retention time (*ERRT*) shall be determined with respect to congeners 30 and 209 (5.3.1 and 5.3.2) for each marker peak chosen (commercial mixture markers) by using the following equation:

$$ERRT_i = \frac{t_i - t_{30}}{t_{209} - t_{30}} \tag{1}$$

where

$ERRT_i$ is the experimental relative retention time of peak group "i";

t_{30} is the retention time for PCB congener 30 (reference standard);

t_{209} is the retention time for PCB congener 209 (internal standard);

t_i is the retention time of marker peak "i" from the time of injection.

The relative retention times of peaks of interest are listed in Table 3.

NOTE 1 PCB congener 30 (5.3.1) and PCB congener 209 (5.3.2) are chosen as reference peaks for the determination of *ERRT*s because they are isolated from congeners occurring in commercial mixtures and enable accurate repeatable values of *ERRT*s to be obtained.

NOTE 2 Three chromatograms of commercial mixtures are reported in Annex A. The marker peaks listed in Table 3 are labelled according to their congener group in these chromatograms to facilitate their identification.

Table 3 — Example for a list of marker peaks of commercial mixtures

Congener group	*ERRT* (example)	Relative Abundance (%)
(PCB 28)	0,117 2	[a]
(PCB 52)	0,185 4	[a]
(PCB 101)	0,356 7	[a]
UG 1	0,437 5	7,55
UG 2	0,460 2	11,55
UG 3	0,499 9	14,83
(PCB 153)	0,521 4	[a]
(PCB 138)	0,574 2	[a]
(PCB 180)	0,703 1	[a]
PCT5442-1 (PCT 01, Table A.2)	0,800 5	3,91
PCT5442-2 (PCT 05, Table A.2)	0,846 7	4,08
PCT5442-3 (PCT 06, Table A.2)	0,864 2	3,91
PCT5460-1 (PCT 05, Table A.3)	1,286 7	2,66
PCT5460-2 (PCT 11, Table A.3)	1,362 9	4,82
PCT5460-3 (PCT 13, Table A.3)	1,413 5	5,04

[a] for these cases relative abundance depends on the type of the technical PCB mixture.

11.3 Determination of experimental relative response factors ($ERRF_{i,j}$) for PCT

Determine the experimental relative response factors (with respect to PCB congener 209, 5.3.2) for the marker peaks chosen in the standard solutions of commercial mixtures (5.3.8 and 5.3.9) in accordance with the following equation:

$$ERRF_{i,j} = \frac{A_{i,j} \times W_s}{A_s \times W_{i,j}} \tag{2}$$

where

i is the index number for the selected PCT marker peak;

j is the index number for the selected commercial mixture (5.3.8, 5.3.9);

A_S is the signal area or height of the internal standard (PCB congener 209 (5.3.3));

$A_{i,j}$ is the signal area or height of the marker peak i in PCT commercial mixture j;

W_S is the concentration in mg/l of the internal standard (PCB congener 209);

$W_{i,j}$ is the concentration in mg/l of marker peak i in commercial mixture j. The concentration $W_{i,j}$ is calculated from the concentration of PCT type j in the calibration solution, multiplied by its relative abundance (in %) according to Table 3 for PCT type j, divided by 100.

Compile a calibration table, listing $ERRF_{i,j}$ for each marker peak selected as reported in Table 3. The standard solutions (5.3.8 and 5.3.9) of PCT Aroclor 5442 and PCT Aroclor 5460 have been subjected to chromatographic analysis during the calibration process.

For each marker peak i chosen from each commercial mixture j, the $ERRF$ shall be calculated by testing the standard solutions as given in 5.3.8 and 5.3.9.

11.4 Determination of experimental relative response factors ($ERRF_i$) for PCBT

Determine the experimental relative response factors (with respect to PCB congener 209) for the peaks chosen (markers of commercial mixtures) in accordance with the following equation:

$$ERRF_i = \frac{A_i \times W_s}{A_s \times W_i} \tag{3}$$

where

i is the index number for the three selected PCBT Congener groups;

A_i is the signal area or height of the chosen PCBT marker peak i;

A_s is the signal area or height of the internal standard (PCB congener 209);

W_i is the concentration in mg/l of group of congener group i.

W_s is the concentration in mg/l of the internal standard (PCB congener 209);

The concentration W_i is calculated from the concentration of PCBT in the calibration solution, multiplied by its relative abundance (in %) according to Table 3, divided by 100.

Compile a calibration table, listing $ERRF_i$ for each marker peak selected as reported in Table 3. The standard solution (5.3.7) of PCBT Ugilec 141 has been subjected to chromatographic analysis during the calibration process.

For each marker peak chosen in the commercial mixture, the $ERRF$ shall be calculated by testing the standard solutions (5.3.7).

12 Measurement

[AC1⟩ Inject a sample of the prepared test solution (see Clause 7), using the same volume as used for calibration (see Clause 11), onto the gas chromatograph. Record the chromatogram with the same operating conditions (see Clause 9) of the gas chromatograph as used in the calibration procedure. ⟨AC1]

The injected quantities of PCBs, PCT and PCBT compounds to be determined, and the internal standard shall be within the calibrated, linear response range of the detector. If necessary, the measurement procedure shall be repeated with different dilutions or sample sizes.

A check sample (5.5) shall be run with every batch of samples, or at least once every day. If the calculated content varies by more than ± 9 % on successive measurements, the system shall be recalibrated.

13 Calculation of results

Identify the chromatographic peaks by their experimental relative retention times (*ERRT*) as calculated for each peak using Equation (1), and the PCB, PCT and PCBT chromatographic patterns of the examples in Annex A.

There shall be no interferences with the selected PCT's or PCBT's. The internal standard method shall be used for the quantitative calculation of the chromatogram.

13.1 Calculation of PCTs

The mass for each PCT marker peak in the test portion shall be calculated by the internal standard method, using the experimental relative response factors:

$$m_{i,j} = \frac{m_s \times A_{i,j}}{A_s \times ERRF_{i,j}} \tag{4}$$

where

$m_{\mathrm{i,j}}$ is the mass (µg) calculated for the chosen PCT marker peak i in commercial mixture j;

m_{s} is the mass of the internal standard (PCB congener 209) in µg;

$A_{\mathrm{i,j}}$ is the signal area or height of the marker peak i in PCT commercial mixture j;

A_{s} is the signal area or height of the peak group of the internal standard (PCB congener 209);

$ERRF_{\mathrm{i,j}}$ is the relative response factor for the marker peak i in PCT commercial mixture j.

The PCT content of the sample (in mg/kg) shall be calculated according to the following equation:

$$PCT\ content = \frac{1}{3} \times \sum_i \sum_j \left(\frac{100}{Z_{i,j}} \times \frac{m_{i,j}}{m_0} \right) \tag{5}$$

where

m_0 is the mass of the sample in g;

$m_{\mathrm{i,j}}$ is the mass in µg calculated for PCT peak i and commercial mixture j;

$Z_{\mathrm{i,j}}$ is the relative abundance of peak i in the PCT mixture j (taken from Table 3).

13.2 Calculation of PCBTs

The mass of each PCBT marker peak in the test portion shall be calculated by the internal standard method, using the experimental relative response factors:

$$m_i = \frac{m_s \times A_i}{A_s \times ERRF_i} \tag{6}$$

where

m_{i} is the mass calculated for the chosen PCBT marker peak in µg;

m_s is the mass of the internal standard (PCB congener 209) in µg;

A_i is the signal area or height of the chosen PCBT marker peak i;

A_s is the signal area or height of the internal standard (PCB congener 209);

$ERRF_i$ is the relative response factor of the chosen PCBT marker peak in the PCBT commercial mixture i.

The PCBT content of the sample (in mg/kg) shall be calculated according to the following equation:

$$PCBT_{cont} = \frac{1}{3} \times \sum_i \left(\frac{100}{Z_i} \times \frac{m_i}{m_0} \right) \qquad (7)$$

where

m_0 is the mass of the sample in g;

m_i is the mass in µg, calculated for PCBT marker peak i in the commercial mixture;

Z_i is the relative abundance of peak "i" in the PCBT mixture (taken from Table 3).

14 Calculation of the total content of PCB and PCB related products

NOTE It is important to notice, that, when either one of the three groups PCB_{cont}, PCT_{cont}, or $PCBT_{cont}$ cannot be determined inside the application range given in the test method, the sum defined in this Clause cannot reliably be calculated, but only partial, single results may be reported in such cases.

The total content of PCB and related products, X, rounded to the nearest mg/kg, is given by the sum of the PCB, PCT and PCBT contents in accordance with the following equation:

$$X = A + B + C \qquad (8)$$

where

X is the sum of PCBs, PCTs and PCBTs, in mg/kg;

A is the content of PCBs, in mg/kg, calculated according to EN 12766-2, rounded to the nearest 0,1 mg/kg;

B is the content of PCTs, in mg/kg, calculated according to 13.1, rounded to the nearest 0,1 mg/kg;

C is the content of PCBTs, in mg/kg, calculated according to 13.2, rounded to the nearest 0,1 mg/kg.

In cases where either one or more components *A*, *B* or *C* cannot be determined within the application range given in this method (see Clause 1), the total content X cannot be calculated and no value for X shall be reported. For such instances it is suggested to report the partial results *A*, *B* and *C* separately, using the units and roundings as given above.

Any result for *A, B* or *C* outside and below the application range (see Clause 1), X shall be reported as:

"below Y", where Y is the limit for the corresponding class given in Clause 1.

If the results for two classes out of *A*, *B* or *C* are outside and below the application range, and in addition, the third result is inside but close to the application limit, then X shall be reported as:

"below Z", where Z is the limit of 25 mg/kg given in Clause 1.

15 Precision

15.1 General Information

It is an established fact that the analysis of the product classes described in this document is complex and non-trivial in terms of required time, cost and expertise. It also proved non-trivial to find reliable samples with different contents of PCBs, PCTs, and PCBTs, which are also well-suited for use in the inter-laboratory tests needed to establish reliable precision information.

Although EN ISO 4259 [2] has been used to calculate the precision values for repeatability and reproducibility given below, it should be explicitly stated that the values given in the following sub-clauses originate from a round robin exercise with participation of only 6 laboratories on 2 samples, which means that the data do not have the necessary number of degrees of freedom requested by EN ISO 4259.

The values given below shall therefore be handled and used with corresponding caution. Independent judgment from acknowledged experts, based on ample day to day field experience, however, suggest that the given values are realistic.

15.2 Repeatability

The difference, r, between two test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would in the long run, in the normal and correct operation of the test method, exceed the estimated values given in Table 4 only one case in twenty.

15.3 Reproducibility

The difference, R, between two single and independent results independently obtained by different operators operating in different laboratories on identical test material would in the long run, in the normal and correct operation of the test method, exceed the estimated values given in Table 4 in only one case in twenty.

Table 4 — Precision data estimates from CEN/TC 19 inter-laboratory exercises

Sample	**Nominal content,** (mg/kg)	**Measured content,** (mg/kg)	**Repeatability** ***r*** (mg/kg)	**Reproducibility** ***R*** (mg/kg)
RRT 2-1:				
A – PCB	22,6	24,4	2,8	7,6
B – PCT	31,3	28,6	4,2	8,5[1]
C – PCBT	30,4	20,3	3,6	6,7
X - Total	84,3	73,3	5,0	26,0
RRT 2-2:				
A – PCB	8,3	7,4	1,7	4,6
B – PCT	10,5	10,8	1,8	5,0
C – PCBT	5,0	3,7	2,8	2,7
X - Total	23,8	21,9	3,5	12,0[1]

[1] best estimate from current daily field experience

16 Test report

The test report shall include at least the following information:

a) type and identification of the sample under test;

b) reference to this document;

c) sampling procedure used (see Clause 7);

d) clean-up procedure used (see Clause 8);

e) results of the test (see Clause 14),
including the content of PCB, of PCT, of PCBT and the total of PCB and PCB related products;
also mentioning which calculation method ("A" or "B") of EN 12766-2 has been applied.

f) any deviation from the procedure described and any unusual features noted during the determinations;

g) date of the test.

Annex A
(normative)

Typical chromatograms

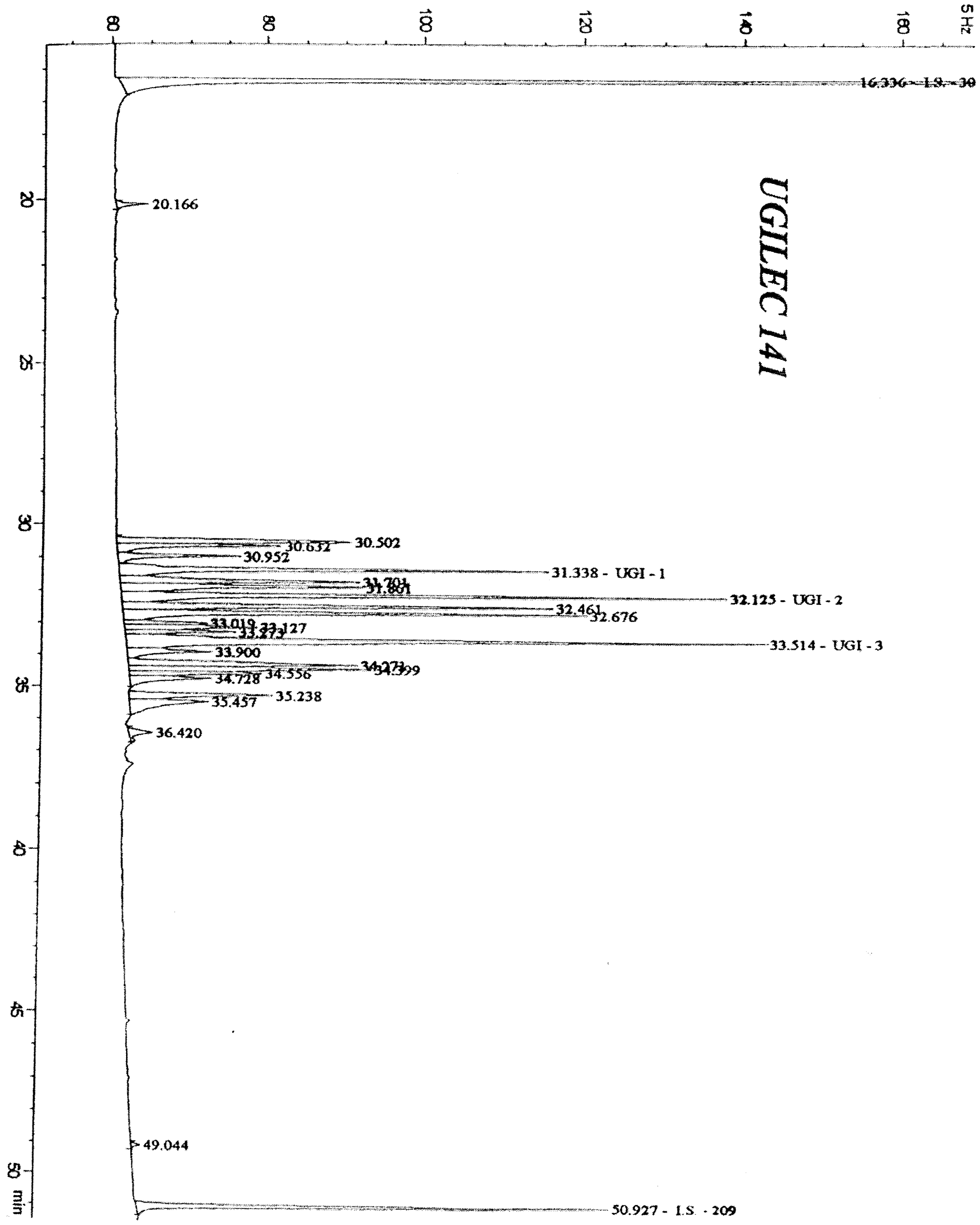

Figure A.1 — Typical chromatogram for Ugilec 141

NOTE PCB retention times and peak name/IUPAC No. data are taken from EN 61619:1997 [3]. Abundance figures for PCB are the abundance of those congeners in Aroclor 1260 (data taken from [4]). PCT data are supplied by Mr. Tumiatti from Sea Marconi, Torino, and apply to PCT mixture 5442 and PCT mixture 5460.

Table A.1 —Ugilec 141 peaks and PCB congeners (with relative abundance) in order of retention time for *ERRTs* in the range 0,408 to 0,641

Peak	***ERRT*** (example)	**Congener numbers, all Probables** (IUPAC No)	**Relative abundance** (%)
54	*0,408*	*87 / 115*	*1,61 / 0,12*
55	*0,416*	*85*	*0,75*
56	*0,422*	*136*	*1,14*
57	*0,427*	*77 / 110*	*0,15 / 3,09*
UG 1	**0,437 5**		**7,55**
59	*0,451*	*151 / 82*	*1,61 / 0,46*
60	*0,460*	*135*	*1,42*
UG 2	**0,460 2**		**11,55**
61	*0,468*	*107*	*0,26*
62	*0,474*	*123 / 149*	*0,27 / 3,56*
63	*0,477*	*118*	*2,86*
64	*0,495*	*134*	*0,37*
65	*0,499*	*114*	*0*
UG 3	**0,499 9**		**14,83**
66	*0,503*	*122 /131*	*0,27 / 0,11*
67	*0,510*	*146*	*0,77*
68	*0,521*	*132 / 153*	*1,99 / 5,25*
69	*0,528*	*105*	*1,59*
70	*0,546*	*141*	*1,20*
71	*0,550*	*179*	*0,67*
72	*0,559*	*130*	*0,24*
73	*0,564*	*137 / 176*	*0,10 / 0,42*
74	*0,574*	*138 / 160 / 163*	*3,29 / 0,02 / 0*
75	*0,579*	*158*	*0,77*
76	*0,590*	*126 / 129 / 178*	*0 / 0,45 / 0,99*
77	*0,601*	*175*	*0,09*
78	*0,607*	*187*	*1,43*
79	*0,616*	*183*	*0,64*
80	*0,627*	*128*	*1,04*
81	*0,636*	*167*	*0,16*
82	*0,641*	*185*	*0,45*

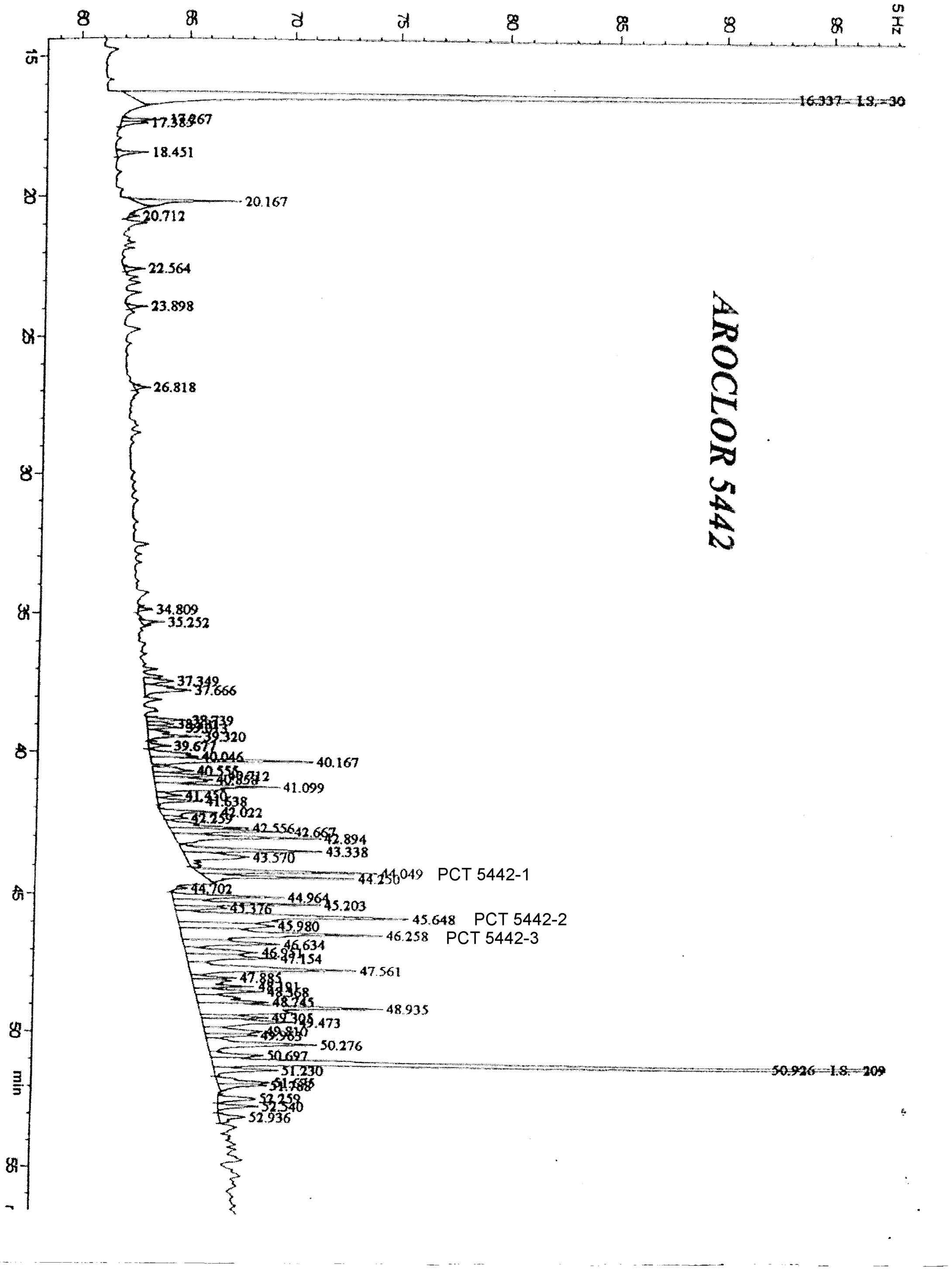

Figure A.2 — Typical chromatogram for PCT Aroclor 5442

Table A.2 —PCT Aroclor 5442 peaks and PCB congeners (with relative abundance) in order of retention times for *ERRTs* in the range 0,785 to 1,099

Peak	***ERRT*** (example)	**Congener number / all probables** (IUPAC No)	**Relative abundance** (%)
98	*0,785*	*196 / 203*	*0,69 / 0,99*
PCT01	**0,800 5**		**3,91**
PCT02	**0,806 6**		**2,24**
99	*0,812*	*189*	*0,11*
PCT03	**0,826 6**		**2,35**
PCT04	**0,833 5**		**2,61**
100	*0,838*	*195 / 208*	*0,68 / 0,17*
PCT05	**0,846 7**		**4,08**
101	*0,852*	*207*	*0,05*
PCT06	**0,864 2**		**3,91**
102	*0,877*	*194*	*1,3*
103	*0,885*	*205*	*0,15*
PCT07	**0,901 0**		**4,86**
PCT08	**0,923 5**		**2,45**
PCT09	**0,934 6**		**2,63**
PCT10	**0,941 6**		**3,82**
104	*0,945*	*206*	*0,45*
PCT11	**0,979 4**		**3,15**
PCT12	**0,991 8**		**2,37**
Decachlorobiphenyl	1,000	209	(internal standard)
PCT13	**1,007 2**		**2,28**
PCT14	**1,036 5**		**2,14**
PCT15	**1,045 0**		**1,93**
PCT16	**1,055 9**		**1,54**
PCT17	**1,098 5**		**1,36**

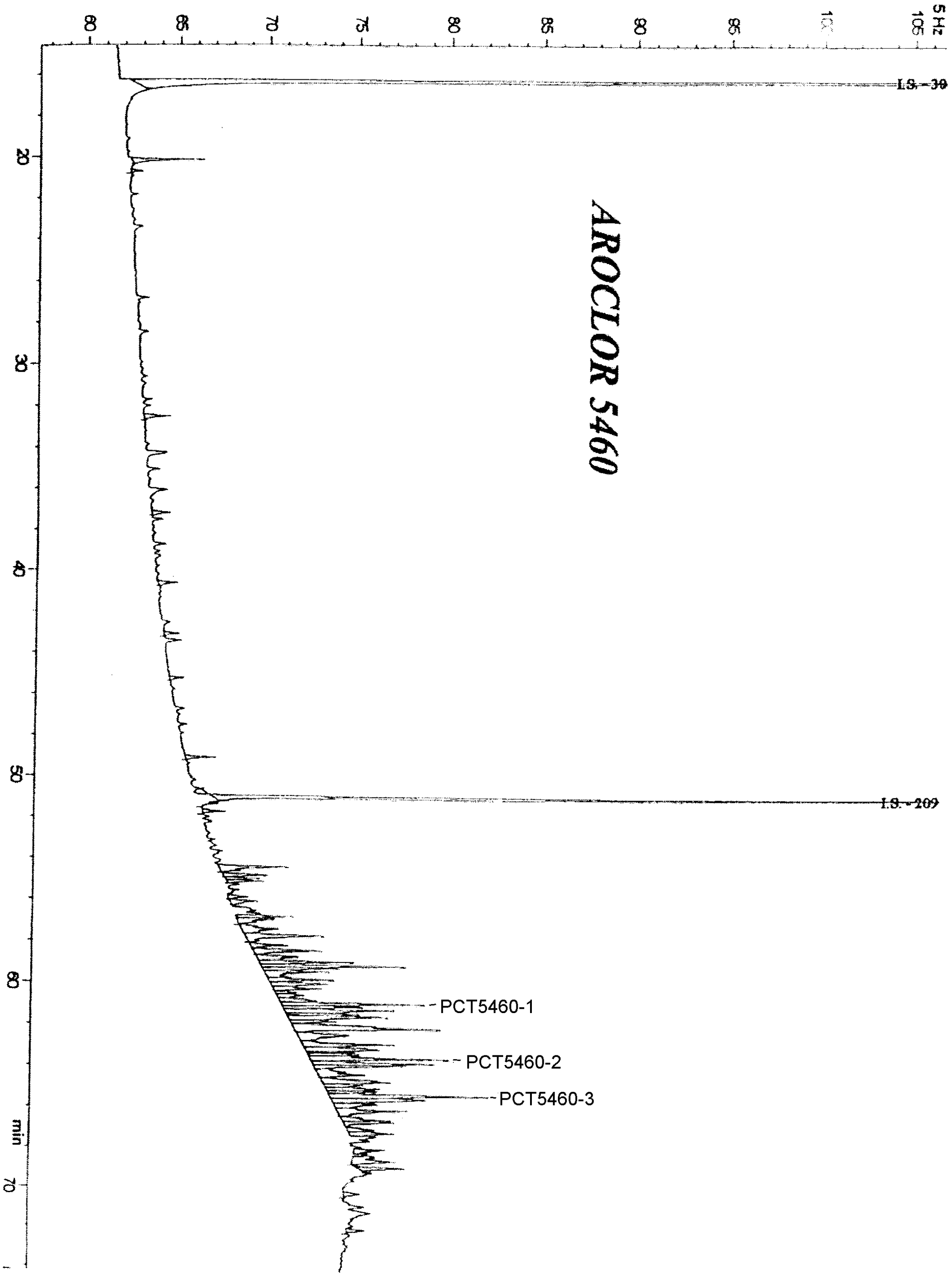

Figure A.3 — Typical chromatogram of PCT Aroclor 5460

Table A..3 — PCT Aroclor 5460 peaks (with relative abundance) in order of retention times for *ERRTs* in the range 1,193 7 to 1,609 1

Peak name	*ERRT*	Relative abundance (%)
Decachlorobiphenyl	1,000	
PCT01	1,193 7	1,23
PCT02	1,214 0	1,10
PCT03	1,229 5	1,66
PCT04	1,235 0	2,83
PCT05	1,286 7	2,66
PCT06	1,291 2	1,83
PCT07	1,295 4	2,39
PCT08	1,301 1	2,16
PCT09	1,304 6	1,92
PCT10	1,321 4	4,18
PCT11	1,362 9	4,82
PCT12	1,369 0	3,78
PCT13	1,413 5	5,04
PCT14	1,418 7	3,17
PCT15	1,425 3	2,10
PCT16	1,434 1	2,89
PCT17	1,450 6	2,20
PCT18	1,466 6	2,01
PCT19	1,508 3	2,03
PCT20	1,517 4	2,90
PCT21	1,555 0	0,65
PCT22	1,573 3	0,58
PCT23	1,582 9	0,90
PCT24	1,609 1	0,80

Bibliography

[1] *Council Directive 96/59/EC on disposal of polychlorinated biphenyls and polychlorinated terphenyls (PCB/PCT)*, 16 September 1996

[2] EN ISO 4259:1995, *Petroleum products — Determination and application of precision data in relation to methods of test (ISO 4259:1992/Cor. 1:1993)*

[3] EN 61619:1997, *Insulating liquids — Contamination by polychlorinated biphenyls (PCBs) — Method of determination by capillary column gas chromatography* (*IEC 61619:1997)*

[4] Schultz, Petrick and Duinker, *Complete Characterisation of PCB congeners in Commercial Aroclor and Clophen Mixtures by Multidimensional GC – ECD*: Environ Sci Technol., Vol 23 (7) 1989

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