SLOVENSKI STANDARD
SIST EN 12766-1:2000

01-julij-2000

Naftni derivati in rabljena olja - Določevanje PCB in sorodnih proizvodov - 1. del: Ločitev in določevanje izbranih PCB spojin s plinsko kromatografijo (GC) z uporabo detektorja na zajetje elektronov (ECD)

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)

Mineralölerzeugnisse und Gebrauchtöle - Bestimmung von PCBs und verwandten Produkten - Teil 1: Trennung und Bestimmung von ausgewählten PCB Congeneren mittels Gaschromatographie (GC) unter Verwendung eines Elektroneneinfang-Detektors (ECD)

Produits pétroliers et huiles usagées - Détermination des PCBs et produits connexes - Partie 1: Séparation et dosage d'une sélection de congéneres de PCB par chromatographie en phase gazeuse (CG) avec utilisation d'un détecteur a capture d'électrons (ECD)

Ta slovenski standard je istoveten z: **EN 12766-1:2000**

ICS:

75.080	Naftni proizvodi na splošno	Petroleum products in general
75.100	Maziva	Lubricants, industrial oils and related products

SIST EN 12766-1:2000 **en**

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 12766-1

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ICS 75.080; 75.100

English version

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)

Produits pétroliers et huiles usagées - Détermination des PCBs et produits connexes - Partie 1: Séparation et dosage d'une sélection de congénères de PCB par chromatographie en phase gazeuse (CG) avec utilisation d'un détecteur à capture d'électrons (ECD)

Mineralölerzeugnisse und Gebrauchtöle - Bestimmung von PCBs und verwandten Produkten - Teil 1: Trennung und Bestimmung von ausgewählten PCB Congeneren mittels Gaschromatographie (GC) unter Verwendung eines Elektroneneinfang-Detektors (ECD)

This European Standard was approved by CEN on 20 January 2000.

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

Central Secretariat: rue de Stassart, 36 B-1050 Brussels

Foreword

This European Standard has been prepared by Technical Committee CEN/TC 19 "Petroleum products, lubricants and related products", the secretariat of which is held by NNI.

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 September 2000, and conflicting national standards shall be withdrawn at the latest by September 2000.

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, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

In this standard, annexes A and B are normative, annexes C, D and E are informative.

This European Standard is one of a series of standards as listed below.

EN 12766, *Petroleum products and used oils - Determination of PCBs* [1] *and related products*

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

Part 2: Quantification of PCB content in analyzed samples [2]

Part 3: Determination and calculation of PCB related products [3]

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[1]) PCBs as defined in:
Council directive 95/59/EC of 1996-09-16 on the disposal of polychlorinated biphenyls and polychlorinated terphenyls. The definition includes PCBs proper, PCTs and also PCBTs (polychlorinated benzyltoluenes), tradename “Ugilec”.

[2]) Part 2 of EN 12766 is under development.

[3]) Part 3 of EN 12766 is under development

1 Scope

This European Standard specifies a method to determine the concentration of up to 12 individual or defined unresolved small groups of polychlorinated biphenyl (PCB) congeners in petroleum products and related materials by means of a specified gaschromatographic separation procedure. The gas chromatographic separation is valid for the different quantification procedures described in Part 2 of this European Standard.

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

NOTE 1 The nominal application range does depend on precision, the lower limit per single congener is about 0,2 mg/kg.

NOTE 2 For the purposes of this European Standard, the terms "% (*V/V*)" and "% (*m/m*)" are used to represent respectively the mass fraction and the volume fraction.

This European Standard does not apply to insulating liquids, for which a different method (EN 61619) is available. Depending on current legislation, it may be necessary to measure either total or individual PCB congeners. EN 61619 may be followed as an alternative method for the determination of total PCBs, using the clean-up stage described in clause 8 of this standard.

WARNING : The use of this 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 form 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 of revision. For undated references the latest edition of the publication referred to applies.

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

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)

3 Terms and definitions

For the purposes of part 1 of this standard, the following 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 can be excluded from this definition.

3.2

congener
all the chlorine derivatives of biphenyl, irrespective of the number of chlorine atoms

NOTE There are 209 possible PCB congeners. The congener numbers (see annex C) are for easy identification; they do not represent the order of chromatographic elution.

3.3

resolution
ratio of the distance between the maxima of two peaks to the average of their peak widths at the base, calculated as: $\frac{2\,\Delta t}{Y_a + Y_b}$ where Δt, Y_a and Y_b are as indicated in figure 1.

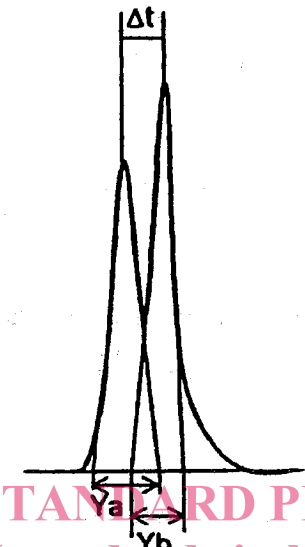

Figure 1 — Quantities for determination of the resolution

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

The PCB congeners are separated into single or small groups of overlapping congeners. Single congeners and unresolved groups are identified using a standard test mixture prepared from Aroclors[4)] and the gas chromatogram shown in annex A.1. Experimental relative retention times (*ERRT*s [clause 11]) are calculated. Calibration and quantification of the identified peaks are achieved using individual congeners and an internal standard.

NOTE 1 PCB congener 138 cannot be separated on the specified GC column (6.3) from congener 163. Overlaps of 25 - 35 % can be analysed in technical mixtures. The concentration of congener 138 determined by this method includes concentration of congener 163 evaluated by using the response factor of congener 138.

NOTE 2 It should be verified that congener 101 is completely resolved from congener 84 on the column (6.3) used in this method.

5 Reagents and materials

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

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4) The industrial use of PCB containing products is now generally forbidden. Aroclors are the only PCB containing products still available, and only for use as a reference material in testing. This information is given for convenience of the users of this European Standard and does not constitute an endorsement by CEN of these products.

5.1 General provisions

All reagents and materials including those for clean up (clause 8 and annex B) shall be free from PCB contamination and compounds interfering in the ECD.

Where preparations of solutions etc. are expressed volumetrically, such preparations may alternatively be conducted gravimetrically.

5.2 Reagents and materials for the sample preparation (clean up)

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

5.2.2 Sodium sulfate, granular, anhydrous.

5.2.3 Sulfuric acid, of purity 96 % (*m/m*) to 98 % (*m/m*).

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

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

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

5.2.6 Column adapter, for joining two columns

5.2.7 Vacuum manifold column processor (optional).

5.3 Reagents and materials for the GC analysis

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

5.3.2 Carrier gas, either helium or hydrogen.

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

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.

5.4 Standards

NOTE The standards specified in this clause can be purchased as solutions of known concentration (precision ± 5 %) in hydrocarbon solvent (5.2.1) prepared from pure materials (purity greater than 99 % (*m/m*)); or prepared by the user from pure materials.

5.4.1 Congener 30 solution, of nominal concentration 10 mg/l.

5.4.2 Congener 209 (DCB) solution, of nominal concentration 10 mg/l.

5.4.3 Internal standard solution, comprising 2 mg/l congener 30 and 2 mg/l congener 209, prepared by pipetting 5 ml of solution (5.4.1) and 5 ml of solution (5.4.2) in a 25 ml volumetric flask and filling up to the mark with solvent (5.2.1).

5.4.4 Certified calibration mixture solution, in solvent (5.2.1) including the 14 selected PCB congeners containing congener 18, 28, 31, 44, 52, 101, 118, 138, 149, 153, 170, 180, 194, and 209 at a concentration of 10 mg/l each, as recommended for this method (Annex D.3).

NOTE 1 Depending on the type of quantification, some of these congeners may not be required.

NOTE 2 Congener 170 is only used if the PCB content is evaluated according to part 2, method A.

5.4.5 Commercial Aroclors, in solvent (5.2.1):

a) Aroclor 1242 solution, 1 g/l concentration;
b) Aroclor 1254 solution, 1 g/l concentration;
c) Aroclor 1260 solution, 1 g/l concentration.

5.4.6 Test mixture solution, made up as follows:

A solution is prepared containing 0,5 mg/l of Aroclor 1242, 0,25 mg/l of Aroclor 1254 and Aroclor 1260 each, and 0,02 mg/l of congener 30 and congener 209 each in solvent (5.2.1).

5.5 Base oil, unused, free from PCB.

NOTE The following oil has been found suitable; RL 110 technical white oil, boiling range 370 °C to 570 °C (CEC L-33-T-82 RL 110).

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 and interfering compounds. The glassware shall be cleaned with solvent (5.2.1).
The apparatus shall be usual laboratory apparatus and glassware, together with the following:

6.2 Gas chromatograph

High resolution, with accurately reproducible oven temperature control, capable, when used with the appropriate column and conditions, of resolving the test mixture (5.4.6) at least as well as shown in figure A.1 (at least 90 peaks to be observed) and of reproducing the experimental relative retention time (*ERRT*) to within ± 0,0015.

The injector shall be either an on-column injector, or a split/splitless injector.

NOTE 1 When a split/splitless injector is used it is necessary to operate it in the splitless mode (9.2).

The gas chromatograph shall be equipped with ECD and gas supply systems as specified in the manufacturer's manuals.

NOTE 2 The ECD requires type approval in accordance with the national Regulations on Radiation Protection.

6.3 Columns

Each comprising a 5 % phenyl-methyl silicone stationary phase coated onto fused silica capillary column or an equivalent chemically bonded phase column. Their dimensions shall be as follows:

length:	50 m to 60 m
internal diameter:	0,2 mm to 0,25 mm
film thickness:	0,1 µm to 0,25 µm

NOTE For suitable columns and manufacturers see annex D.2.

7 Sampling and sample preparation

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.

Only glass or metal vessels shall be used for sampling, for storing samples and for determination.

NOTE 1 Pipette tips and columns made of plastics material are permitted.

The sample preparation method described below shall be used for liquid samples without a recognizable free water phase.

NOTE 2 If emulsified water is perceived as opacity in the sample solution, it can be ad- sorbed by adding anhydrous sodium sulfate in portions and shaking until a clear solution is obtained.

If the samples have a free water phase, it shall be separated from the oil phase prior to further analysis, e.g. by centrifuging and with the aid of a separating funnel. Petroleum products mixed with solids shall be separated beforehand by suitable means, e.g. by centrifugation and by extraction of the solids with the solvent.

Homogenize the sample using a high-speed stirrer or an ultrasonic bath; or shake the sample by hand for 3 min.

NOTE 3 The sample can, if desired, be heated slightly beforehand.

Weigh approximately 1,0 g to the nearest 1 mg of the homogenized sample into a 10 ml volumetric flask. Add approximately 8 ml of solvent (5.2.1) and mix well. Add 1 ml of the internal standard solution (5.4.3) and make up to the mark with solvent (5.2.1).

8 Clean-up procedure

8.1 In general, the relatively simple procedure given in 8.2 to 8.4 and illustrated by figure 2 shall be used before GC analysis of the sample solution. If this clean-up is unsatisfactory the alternative clean-up procedure given in annex B.1 can be used. Additional clean-up steps are given in annex B.2 to B.5.

NOTE 1 A clean-up of the prepared sample solution is necessary to avoid contamination of the GC-system and to remove compounds which interfere with the determination of PCB congeners. For complex sample compositions like waste oils, there is no general clean-up procedure available for all possible interfering compounds.

NOTE 2 Halogenated aromatic compounds like tetrachlorobenzyltoluenes are not removed by the clean-up procedures given in this standard. Interferences as reported in annex E (figure E.1) can result.

To determine the recovery of specified PCB congeners, submit solutions of standards in solvent (5.2.1) to the clean-up procedure and compare the results obtained with those obtained with similar solutions not submitted to the clean-up procedure. The calculated recovery of specified PCB congeners shall be greater than 95 % at a level of 1 µg/g each.

The above procedure does not take account of any oil present in the sample influencing the recovery from the clean-up columns. If this is suspected, recoveries shall be determined using standard solutions containing in addition either unused base oil (5.5) or a PCB free sample of the same oil as present in the sample at a concentration of approximately 10 % oil to solvent.

The specified solvent quantities for elution of the PCB from the columns (see 8.4 or annex B) shall be checked and if necessary optimized by determining the recovery when a new batch of materials is used.

NOTE 3 The recovery is not taken into account when the results are stated. If solvents other than heptane are used, then the elution volumes can differ.

8.2 Preparation of the silica gel/sulfuric acid separation material.

Activate the silica gel separation material (5.2.4) at 180 °C for 3 h before use.

Weigh (28 ± 1) g silica gel separation material (5.2.4) and (22 ± 1) g sulfuric acid (5.2.3), into a 200 ml conical flask, and shake until any lumps have disappeared.

WARNING: Wear face protection and gloves, because the mixture will become hot.

Store the mixture in a closed desiccator. The mixture shall be used within one week.

8.3 Preparation of the combined benzenesulfonic acid/sulfuric acid column

Directly prior to the sample preparation procedure, put (0,5 ± 0,05) g of the silica gel/sulfuric acid separation material prepared in accordance with 8.2 onto the top frit of the 3 ml benzenesulfonic acid/sulfuric acid column.

8.4 Preparation of the test solution

Set up the combined benzenesulfonic acid/sulfuric acid column on a 3 ml silica gel separating column with the aid of an adapter. Elute the two columns three times with 2 ml solvent (5.2.1) in order to purify the stationary phases, then use vacuum assisted drying.

Transfer 250 µl of the sample solutions prepared as described in clause 6, onto the silica gel/sulfuric acid stationary phase of the upper column, and flush with 0,5 ml solvent (5.2.1).

Apply the sample to the packing of the upper column e.g. by reducing pressure slightly. The sample shall be distributed evenly over the packing of the upper column. Elute the upper column twice with 1 ml solvent (5.2.1) after a period of at least 30 s. Remove the upper column.

Elute the silica gel separation column twice with approximately 0,5 ml solvent (5.2.1), and transfer the eluate to a 5 ml volumetric flask. Make up to the mark with solvent (5.2.1).

If necessary, determination of PCB shall be repeated at different dilutions of the sample with oil (5.5) to bring the measurement within the linear range of the ECD.

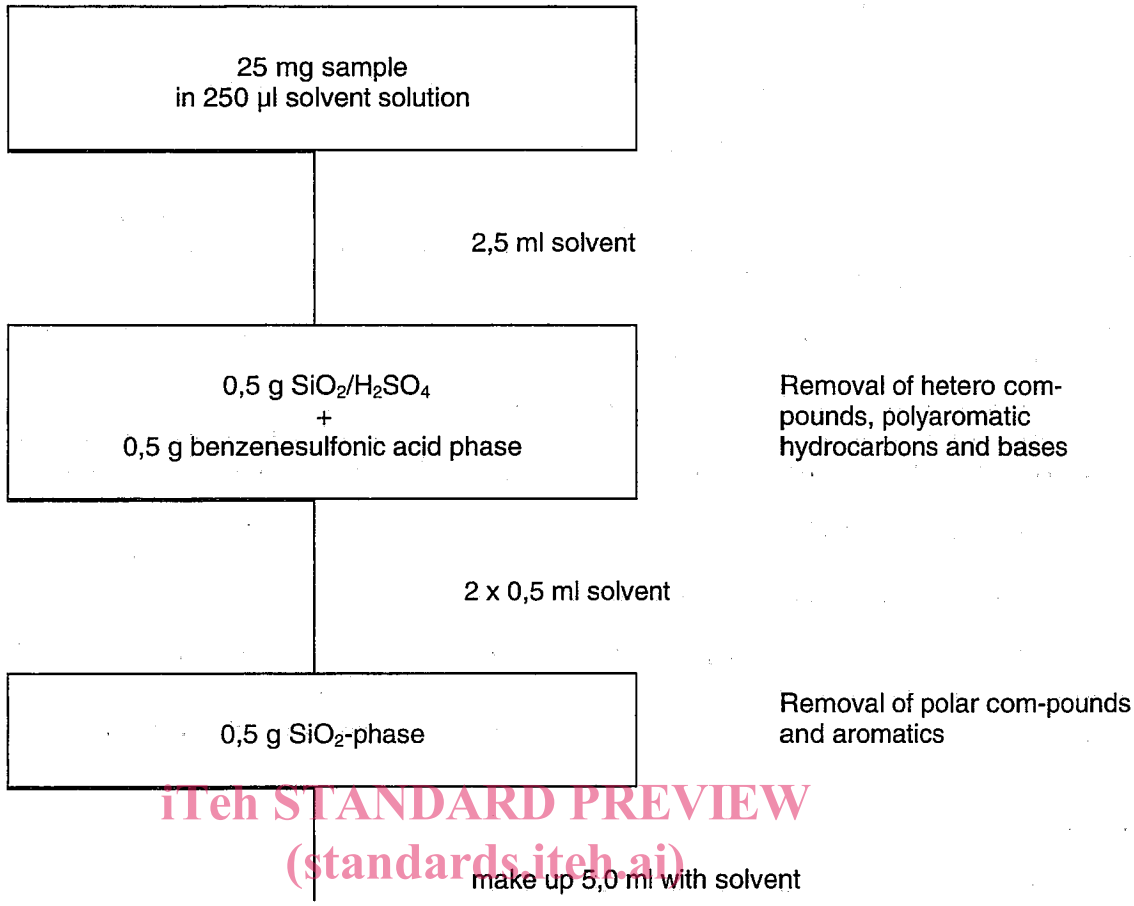

Figure 2 — Clean-up procedure

9 Gaschromatographic operating conditions

9.1 Setting up the GC apparatus

The operating conditions indicated in 9.2 to 9.5 have been found adequate but should be optimised with each GC system so that gas chromatograms similar to that shown in annex A.1 are obtained from dilutions of the test mixture 5.4.6. In the example given, 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 setting for this analysis are as follows:
a) for the 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) for the on-column injector: T: 50 °C to 110 °C depending on the solvent used.

9.3 Oven temperature programme

The oven temperature programme shall be selected to obtain a suitable chromatogram.

NOTE Typical settings are as follows:

initial isothermal period	1 min	or	0,5 min
initial temperature	50 °C	or	70 °C
temperature programme	50 °C to 168 °C at 50 °C/min 168 °C to 310 °C at 4,0 °C/min	or	70 °C to 130 °C at 40 °C/min 130 °C to 290 °C at 2,5 °C/min
isothermal period	10 min	or	5 min
cool down to	50 °C	or	70 °C

These settings may be varied to obtain the required chromatogram.

The initial temperature and initial isothermal period shall be varied depending on the solvent and injection technique.

9.4 Carrier gas flow rate

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

NOTE Hydrogen carrier gas is effective in reducing column pressure head analysis time.

9.5 Electron capture detector settings

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

Use the manufacturer's 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 to PCBs.

10 Check on instrumental performance

10.1 General provisions

When initially implementing this method and after major repairs and replacement of critical instrumentation components (specifically EC detector and GC column), each laboratory that uses this method shall operate a performance control programme. This should include verification of sensitivity, resolution and linearity range. It is recommended to monitor the performance routinely at appropriate time intervals.

10.2 Sensitivity check

The ECD shall have sufficient sensitivity to give a signal to noise ratio (S/N) greater than 20 for one picogram of hexachlorobenzene (5.3.1) injected on to the column, using the specified operating conditions (see clause 9).

10.3 Linearity check

The response of the electron capture detector (ECD) is proportional to the quantity of PCBs injected only within a limited range; if the quantities of PCBs passing through the detector become excessive, the response will cease to be linear.

Determine the linear range as given in 10.3.1 to 10.3.3.

10.3.1 Dilute standard (5.4.4) in suitable steps with solvent (5.2.1) until a linear response is obtained as shown in figure 3, e.g. 20, 50, 200, 1000, 5000, 10 000 times dilution.

Add congener 30 (5.4.1) as internal standard to the dilutions to give a final concentration of 10 ng/ml. Inject a suitable quantity into the GC (the same each time) into the GC according to the injection system using the chromatographic conditions in clause 9.

10.3.2 Measure the peak area or height (Rj) for the specified 12 congeners and congener 209 and calculate the injected amount (mj) of each congener in picogram for each dilution. Use the area or height of the congener 30 to check that the correct volume has been injected. The area/height of the congener 30 peak for the series of injections should not vary by more than 5% of the average for that series of injections. Tests that fall outside of this range shall be repeated.

Calculate the sensitivity factor (S_j) for each congener and each dilution using the following equation:

$$S_j = \frac{R_j}{m_j}$$

Where S_j, R_j and m_j are as indicated above.

Plot S_j versus m_j (see figure 3).

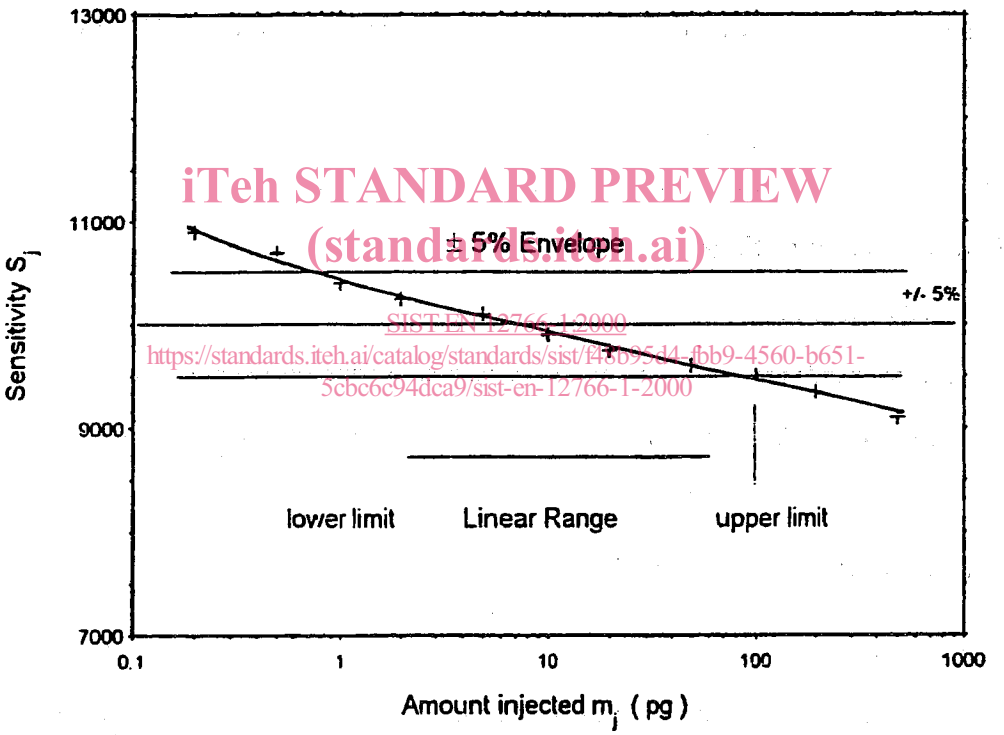

Figure 3 — Linearity check

10.3.3 The linearity plot is a line through the data points (figure 3). The upper limit of the linear range is the point where the plot crosses the - 5 % envelope and the lower limit level where the plot crosses the + 5 % envelope.

The linear range of the detector is defined in fig. 3.

NOTE A nonlinear calibration can be used applying the same criteria of a ± 5 % envelope as shown in fig. 3.

10.4 Resolution check

Using the standard chromatographic parameters run a suitable dilution of test mixture (5.4.6) in the linear range. Identify the peaks by comparison with the chromatogram in annex A.1.

The resolution of the pair of congener 28 and congener 31 shall be 0,5 (i.e. 50 %) or greater, for the pair of congeners 141/179 0,8 (i.e. 80 %) or greater, and for the pair of congeners 118/149 0,5 (i.e. 50 %) or greater.