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Analysis of polychlorinated biphenyls in transformer oils by automated on-line coupling reversed phase liquid chromatography-gas chromatography using the through oven transfer adsorption desorption (TOTAD) Interface

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An automated method for the direct analysis of polychlorinated biphenyls (PCBs) in transformer oil is presented. The proposed method uses the TOTAD (through oven transfer adsorption desorption) interface for the on-line coupling of reversed phase liquid chromatography and gas chromatography (RPLC-GC). In this fully automated system, the oil is injected directly with no sample pre-treatment step other than dilution with n-propanol and filtration. In the LC step, PCBs are separated from other components of the oils using methanol/water (90:10 v/v) as mobile phase, at a flow rate of 1 mL min^{-1}. The LC fraction containing the PCBs is automatically transferred to the GC by the TOTAD interface and GC analysis enables the separation of the PCB congeners. The proposed method is compared with two other methods: the European Norm (UNE-EN-61619) and that of the American Society for Testing and Materials (ASTM) (D4059-00). The proposed method practically eliminates the time-consuming sample preparation step and avoids errors caused by sample manipulation. The total PCB concentrations obtained with the three methods are similar.

Keywords: liquid chromatography-gas chromatography; on-line coupling; automated TOTAD interface; polychlorinated biphenyls; transformer oil

1. Introduction

PCBs have been intensively used in the manufacture of paints, pigments, and fire retardants as well as dielectric fluids in transformers. Congeners are characterised by their low water solubility but high lipid solubility, high chemical and thermal stability and, as a consequence by their persistence [1]. Classified as persistent organic pollutants (POPs), they are included in the priority pollutants list published by the US Environmental Protection Agency (EPA) [2] and by the European Union (EU) [3]. Owing to concerns

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related to toxicity, PCBs production was banned by the United States Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001. The Real Decreto 1378/1999 [4], in Spain, set 2010 as a deadline for carrying out the decontamination or disposal of equipment containing PCBs, except for slightly contaminated electrical transformers (between 50 and 500 mg kg^{-1}).

The analysis of PCBs in transformer oils is a difficult task owing to the complexity of the PCBs mixture, the nature of the matrix and the wide range of concentrations in which PCBs may be present. The procedure requires an extraction step followed by analysis with GC, using an electron capture detector (ECD), an electrolytic conductivity detector (ELCD) [5] or a mass spectrometer (MS) [6,7]. Other methods used to analyse PCBs are total chlorine determination by colorimetry [8] and immunoassay [9,10]. In the United States as several other countries, e.g. Argentina, ASTM D 4059-00 is applied [11]. In this method, after being diluted with a solvent, the sample is treated with sulfuric acid to eliminate the interferences from oil, while the aqueous phase is rejected. The resulting solution is analysed by GC with ECD. In the European Norm (UNE-EN 61619) [12], the sample is diluted in hexane and the PCBs are extracted by solid phase extraction (SPE) employing two columns, one of bencenosulfonic acid and other of silica gel. The extract is then analysed by GC with ECD.

Complete separation of all congeners cannot be achieved by single-column GC, although the problem can be solved by means of a multidimensional approach. In multidimensional GC (MDGC) techniques, two columns of different polarity and selectivity are coupled and PCBs insufficiently separated in the first column are introduced into the second column [13,14]. In addition, comprehensive GC ($GC \times GC$) has been evaluated for PCBs analysis [15]. In this method a serial nonpolar/more polar column configuration is combined on-line via a cryomodulator to generate a two-dimensional chromatogram. In LC-GC preseparation on a LC column is performed before GC analysis. On-line coupling LC-GC is a technique that combines the high separation efficiency of LC for sample preparation, avoiding and replacing the subsequent clean up steps, with the good performance of capillary gas chromatography separation [16–19]. It permits the elimination of practically all manual work, allowing one person to run a large number of samples in a short time.

Standard samples of PCBs have been analysed employing on-line coupled LC-GC, using normal phase in liquid chromatography and a loop-type interface to transfer PCB fractions [20]. However, the analysis of real samples, such as oil is a complex task because the normal phase in the LC step requires back-flushing of the column after each analysis in order to remove the heavy compounds, which may cause several problems that affect the performance of the column. The use of reversed phase in the LC step, rather than normal phase, avoids such problems. However, it must be taken into account that the transfer of polar solvents can be difficult because of the very large volumes of vapor that are produced per unit of liquid [21,22].

The TOTAD interface was developed in 1999 by Pérez and coworkers [23] and has been satisfactory used for the on-line coupling RPLC-GC analysis of different type of pesticides in olive oil, using a variety of detectors [24–26], as well as minor components in olive oil [27] and pesticides in nuts [28]. The purpose of this work was to develop a rapid method for the direct analysis of PCBs in transformer oils by on line coupling RPLC-GC using the TOTAD interface.

2. Experimental

2.1 *European and ASTM norm*

The materials and procedures carried out with the official methods are described in the respective standards: ASTM D 4059-00 [11] and UNE- EN 61619 [12]. The analyses of the samples by the ASTM method were carried out in the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) laboratory in Santa Fé (Argentina) and by the UNE method in the Repsol laboratory in Mostoles (Spain).

2.2 *TOTAD method*

The TOTAD method was developed and used to analyse the sample in the laboratory at the University of Castilla-La Mancha.

2.2.1 *Materials*

Biphenyl and decachlorobiphenyl used for the determination of the LC fraction were provided by the laboratory of the CONICET in Santa Fé (Argentina). The different Aroclor standards (1242, 1254 and 1260) and the PCB-free transformer oil were obtained from Dr. Ehrenstorfer (Augsburg, Germany). The transformer oil samples analysed were provided by a Spanish petrochemical company and CONICET in Santa Fé (Argentina).

The methanol and water of LC grade used as mobile phase and n-propanol used as dissolvent and cleaning eluent were purchased from LabScan (Dublin, Ireland). Tenax TA 80–100 mesh (Chrompack, Middelburg, the Netherlands) was used as packing material in the liner of the TOTAD interface, placed between two plugs of glass wool to keep it in place. The packed liner was conditioned under a helium stream, heated from 50°C to 350°C at 50°C/10 min and maintained for 60 min at this final temperature.

2.2.2 *Sample preparation*

Prior to RPLC-GC analysis, all samples were diluted in n-propanol (1:10) and then filtered through a 0.22 μm filter (Chromatography Research Supplies, Inc) and injected by means of the LC manual injection valve.

To spike oil, Aroclors (1242, 1254 and 1260) dissolved in transformer oil at 500 mg/kg were diluted in PCB-free transformer oil to obtain the desired concentration.

2.2.3 *Instrumentation*

The analyses were performed by on-line coupled LC-GC equipment equipped with an automated TOTAD interface (Figure 1); US patent 6,402,947 B1 (exclusive rights assigned to KONIK-Tech, Sant Cugat del Vallés, Barcelona, Spain). The TOTAD interface operation mode has been described elsewhere [23,29,30].

The LC system was composed of a manual injection valve (model 7125 Rheodyne, CA) with a 20 μL loop, a quaternary pump (HP model 1100), a column oven (HP model 1100) and a Diode-array ultraviolet (UV) detector (Perkin-Elmer model LC 235). The gas chromatograph (Konik model HRGC 4000B) was equipped with a TOTAD interface and an ECD. KoniKrom 32 (Konik, Sant Cugat Del Vallés, Barcelona) software was used to obtain data from LC and GC runs and to automate the process.

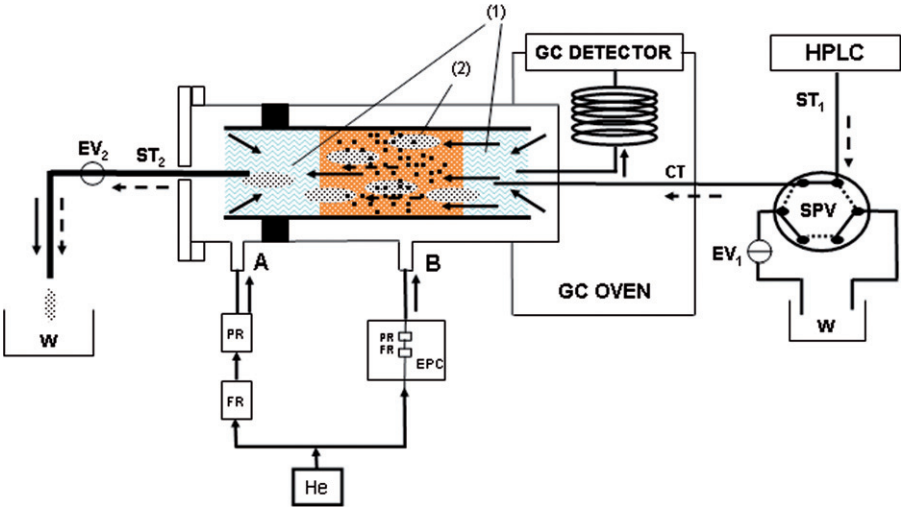

Figure 1. Automated TOTAD interface during the transfer step. Symbols: (1) glass wool; (2) sorbent (Tenax TA); (SPV) six-port valve; (EV_1 and EV_2) electrovalves 1 and 2; (EPC) electronic pressure control; (PR) pressure regulator; (FR) flow regulator; (solid arrows) gas flow; (dotted arrows) liquid flow; (ST_1) stainless steel tubing, 0.25 mm i.d., to transfer eluent from LC to GC; (ST_2) stainless steel tubing, 1 mm i.d., to allow the exit of liquids and gases; (CT) silica capillary tubing, 0.32 mm i.d.; (W) waste; (⬭) solvent; (•⁘) analytes.

2.2.4 *LC conditions*

LC preseparation was carried out on a 50×4.6 mm i.d. column packed with modified silica (C4, kromasil 100-10, Hichrom, Berks, UK) and maintained at 45°C. Methanol/water 90:10 (v/v) was used as eluent.

To ascertain the elution time of the fraction to be transferred to the GC, 20 µL of biphenyl and decachlorobiphenyl in PCB-free transformer oil at 50 mg L^{-1} were injected. The composition of the eluent at a flow rate of 1 mL min^{-1}, was maintained for 5 min. The gradient was then changed to reach 100% n-propanol within 1 min and maintained for 20 min to ensure the complete elimination of heavy components. The UV detection was performed at 205 nm.

In the PCBs analysis, the LC detector was not used and the LC column was directly connected to the six port valve by a stainless steel tube (0.25 mm i.d.). Recently filtered diluted oil (20 µL) was injected. The composition of the eluent was maintained constant. The flow rate was set at 1 mL min^{-1} until the elution of the fraction of interest began, and was then changed in 0.1 min to 0.2 mL min^{-1}. The flow rate was maintained constant until the transfer step had finished. After the transfer, the flow was raised to 2 mL min^{-1} and the gradient was raised to 100% n-propanol within 1 min and maintained for 20 min to ensure complete removal of the heavy compounds.

2.2.5 *LC-GC transfer*

Transfer was performed by means of a six-port valve connected to the LC column by a stainless steel tube of dead volume (ST_1) and to the GC by a silica capillary tubing

(62.15 cm length × 0.32 mm i.d., 50 μL internal volume; CT in Figure 1). The liner was packed with a 1 cm length of Tenax TA.

Initially, the TOTAD interface was stabilised at 40°C with EV1 closed and EV2 open. Helium flow was set to 500 mL min^{-1} through A and B. The GC oven temperature was maintained at 40°C. 20 μL of the sample was injected into the LC system. At the beginning, the eluent from the LC system was sent to waste. When the front of the PCB fraction reached the six-port valve, it was automatically switched, transferring the fraction to the GC. The helium pushed the solution through the glass liner. During the transfer time, PCBs were retained by the adsorbent inside the glass liner and the solvent was vented to waste through the ST_2 tubing.

When the transfer step was completed, the six-port valve was switched and EV1 opened. The LC eluent was sent to waste, as it was the solution in the capillary transfer CT, which was pushed out by the helium. Temperature and helium flow were maintained constant for 1 min to ensure the removal of all the remaining solvent in the glass liner and the CT tubing. Immediately afterwards EV1 and EV2 were closed, and the flow through B was interrupted while the flow through A was changed to 1.8 mL min^{-1}. Then the TOTAD interface was quickly heated to 275°C, maintaining this temperature for 5 min, and leading to the thermal desorption of the analytes, which were transferred to the GC column, pushed by the helium. GC analysis was then carried out. When the GC analysis was completed, EV2 was opened and the interface was cleaned by maintaining the helium stream at 300°C for 5 min, after which it was cooled to 40°C so that another analysis could be carried out.

2.2.6 *GC conditions*

Gas chromatographic separations were carried out on a Quadrex (Weybridge, U.K.) fused-silica column (30 m × 0.32 mm i.d.) coated with 5% Phenyl Methyl Silicone (film thickness 0.25 μm). During the transfer and the solvent elimination steps the oven temperature was kept at 40°C. During GC-ECD analysis, the column temperature was maintained at 40°C for 1 min. It was then raised to 230°C at 20°C min^{-1}, 5 min, and finally to 300°C at 10°C min^{-1}, 5 min. The ECD temperature was kept at 300°C. Helium was used as carrier gas at a flow rate of 1.8 mL min^{-1}.

2.3 *Statistical analysis*

Statistical analysis was performed with SPSS (Chicago, IL) 17.0 software.

3. Results and discussion

3.1 *Method optimisation*

Biphenyl and decachlorobiphenyl in transformer oil at 50 mg L^{-1}, the lightest and heaviest PCB, were used to determine the LC fraction to be transferred to the GC. Methanol : water was used as eluent in LC preseparation. Different proportions (70:30; 80:20; 90:10 and 95:5) were tested and methanol : water (90:10) was selected as the best option. It is important to establish the experimental RPLC conditions to ensure that PCBs do not overlap other main components of the oil. The lower the eluent strength, the larger the volume of the LC fraction to be transferred, although this is not a problem because solvent

elimination is almost complete when using the TOTAD interface [30]. However, the larger the volume to be transferred, the longer the time needed in the transfer step. Using 90:10 (v/v) as eluent composition allows a satisfactory degree of separation as well as a low volume of the LC fraction so that a short time is needed for the transfer step. This composition of the mobile phase allows rapid analysis and avoids interferences in the GC. With this eluent at a flow rate of 1 mL min^{-1}, PCBs elute from 0.85 to 2.35 min resulting in a transfer volume, from LC to GC, of 1.5 mL. The flow rate during the transfer step was decreased to 0.2 mL min^{-1} with the aim of increasing sensitivity, as previously described [24,31]. Using a flow rate of 0.2 mL min^{-1}, the transfer time was 7.5 min and the full analysis, LC preseparation, transfer time and GC analysis was less than half an hour, much lower than the time needed in the ASTM or UNE, which is nearly one hour.

3.2 *Identification and quantification peaks*

The identification of peaks was carried out based on profile chromatograms obtained in the ASTM standard [11]. This norm is based on the use of Aroclors 1242, 1254 and 1260 as standard because, together, these Aroclors contain all the peaks usually found in Aroclor mixtures, and they have been found to be the most common PCB contaminants in electrical insulating oils. Each peak is identified by a number corresponding to relative retention time with respect to p, p′-DDE (1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene). This procedure was used because it is the protocol in the ASTM method.

Figure 2 shows a chromatogram of a PCB-free transformer oil sample spiked with Aroclors 1242, 1254 and 1260, and analysed by the developed method. The chromatogram presented is similar to that obtained when a mixture of the three Aroclors were analysed by the ASTM norm. The isolation of PCBs from other oil constituents in the LC step was satisfactory and the PCB peak could be easily identified in the GC chromatogram although other compounds may be present.

To quantify the PCBs represented by each peak, calibration curves were used. The calibration curves for each peak were obtained taking in account the weight contribution of each peak to the total Aroclor weight, according to the literature, and are indicated in Table 1 [32]. For example, the weight contribution of peak 21 to Aroclor 1242 is 11.3%, which means that in an Aroclor 1242 sample at 5 mg L^{-1}, the concentration of peak 21 would be 0.565 mg L^{-1}. This calculation is necessary for all the peaks at different concentrations when the calibration curve is made. The total PCB content is the summation of the concentrations measured by all the peaks in the chromatogram.

3.3 *Analytical performances*

3.3.1 *Linearity and sensitivity*

In order to test the linearity of the method, 23 calibration curves were obtained, one for each peak. Calibration curves for PCBs 11 to 78 were obtained by analysing PCBs-free transformer oil samples spiked with Aroclor 1242; for PCBs 84 to 174 with Aroclor 1254 and for the rest of the PCBs with Aroclor 1260 at 5, 20, 50 and 200 mg L^{-1}. As can be observed in Table 1, the coefficient of determination were in all the cases higher than 0.988. It was not possible to determine the correlation coefficients of peaks 11 and 16 from Aroclor 1242 because it was not possible to quantify the peak areas at low concentrations. Detection limits for each peak are giving in Table 1. The detection limits were calculated as

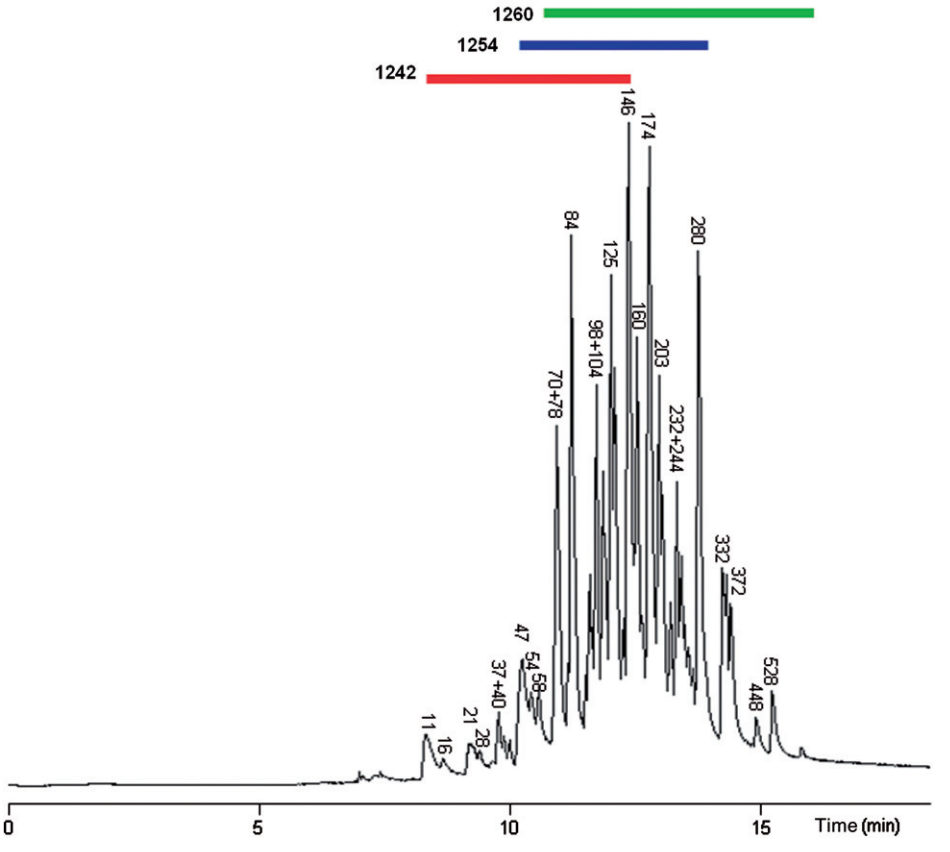

Figure 2. GC chromatogram obtained from on-line RPLC-GC-ECD (using the TOTAD interface) analysis of a transformer oil spiked with the Aroclors 1242, 1254 and 1260 to 25 mg L^{-1} and diluted to 10% with n-propanol.

the amount of product giving a signal equal to 5 times the background noise in the analysis of a free-PCBs transformer oil spiked at 25 mg L^{-1} with Aroclors 1242, 1254 and 1260. The detection limit for total PCBs was 1.5 mg kg^{-1}, similar to ASTM (2 mg kg^{-1}) and UNE (1 mg kg^{-1}) methods. In Spain, Real Decreto 1378/1999 establishes as an apparatus containing PCBs those containing PCBs at a concentration higher than 50 mg kg^{-1} [4]. Bearing in mind the established limits for PCBs in transformer oils, it can be considered that the method was sufficiently sensitive.

3.3.2 *Repeatability*

The repeatability was studied by injecting 20 μL of a transformer oil sample spiked with Aroclors 1242, 1254 and 1260 at 25 mg L^{-1} and prepared as indicated in the sample preparation section. Relative standard deviation (RSD) for the absolute areas of all the peaks corresponding to Aroclor 1254 and 1260 were less than 8% (average 6%), with the exception of peak 448, which was 10.2% (Table 1). The RSDs of the peaks of Aroclor 1242 were higher (average 12.6%), which, may be attributable to the greater volatility of

Table 1. Relative standard deviation (RSD) from the absolute peak areas, n = 5, of a PCB-free transformer oil spiked with Aroclors 1242, 1254 and 1260 at 25 mg L^{-1} and diluted in n-propanol (1:10). Coefficient of determination (R^2) for the linear range studied.

Aroclor	Peak	Mean Weight %	RSD	R^2 (5–200 mg L^{-1})	LD (mg kg^{-1})
1242	11	1.1	23.5	–	0.03
	16	2.9	8.5	–	0.10
	21	11.3	10.1	0.989	0.18
	28	11.0	9.4	0.994	0.27
	32	6.1	–	0.994	0.26
	37 + 40	22.6	6.3	0.996	0.26
	47	8.8	26.3	0.991	0.04
	54	6.8	11.4	0.988	0.05
	58	5.6	13.0	0.989	0.04
	70 + 78	13.9	4.8	0.998	0.03
1254	84	17.3	5.1	0.996	0.03
	98 + 104	21.1	5.3	0.993	0.04
	125	15.0	5.1	0.996	0.02
	146	10.4	5.0	0.993	0.01
	160	1.3	5.7	0.992	0.002
	174	8.4	5.7	0.999	0.01
1260	203	9.3	5.0	0.999	0.02
	232 + 244	9.8	5.1	0.999	0.03
	280	11.0	5.8	0.996	0.02
	332	4.2	5.7	0.999	0.02
	372	4.0	6.8	0.999	0.02
	448	0.6	10.2	0.996	0.01
	528	1.5	7.8	0.996	0.01

Table 2. Total PCB concentrations obtained in the analysis of different transformer oil samples using three different analytical methods.

	Concentration (mg kg^{-1})		
Sample	ASTM	UNE	TOTAD
A	7	5	8
B	11	6	7
C	5	4	n.d.
D	14	7	19
E	213	*	233
F	68	*	49
G	8	7	7
H	8	8	7
I	12	16	21
J	23	19	32
K	22	19	31
L	12	14	20

ASTM: American Society for Testing and Materials (D4059-00).
UNE: European Norm (EN-61619).
TOTAD: On-line RPLC-GC using the TOTAD interface method developed in the present work.
n.d.: undetected.
*: Sample lost and so impossible to analyse.

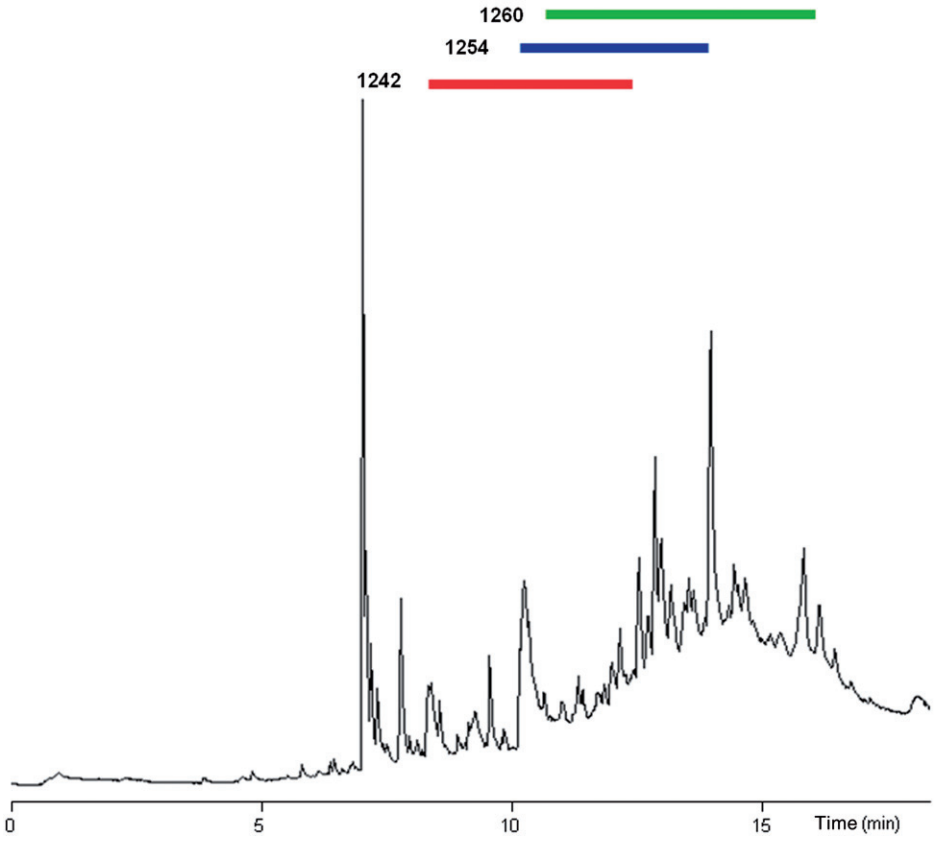

Figure 3. GC chromatogram obtained from on-line RPLC-GC-ECD (using the TOTAD interface) analysis of a real sample transformer oil sample. Total PCBs concentration 7 mg kg^{-1}.

congeners in this Aroclor. The RSD corresponding to peak 32 could not be calculated. Taking into account the good value of the coefficient of determination obtained for this peak (0.994), it is probable that an isolated case of contamination occurred during the experiments leading to the calculation of RSD. Therefore, it can be said that, in general, the method has good repeatability.

3.4 *Analysis of transformer oil samples*

The developed method was applied in the analysis of the transformer oil samples indicated in Section 2.2.1 which were also analysed by the UNE-EN-61619 and ASTM (D4059-00) by different operators, in different places and with different equipment [11,12]. Table 2 shows the results obtained.

A statistical test (one way ANOVA) was carried out. The P-value obtained was 0.462 higher than 0.05, so there were no significant differences between methods. Figure 3 shows the chromatogram obtained in the analysis of a real-life sample with a total PCB concentration of 7 mg kg^{-1}.

4. Conclusions

On-line coupling of RPLC-GC using the TOTAD interface can be used for the fully automated analysis of PCBs in transformer oils and has considerable advantage over the UE and ASTM methods, in that it uses smaller amounts of sample and requires less time. The proposed method practically eliminates the time-consuming sample preparation step and avoids errors caused by sample manipulation. The results obtained with the three different methods are similar.

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