

Determination of PCBs in Transformers Oil Using Gas Chromatography with Mass Spectroscopy and Aroclors (A1254:A1260)

Héctor Alfredo Robles Martínez,*¹ Germán Cuevas Rodríguez,¹ Daniel Hernández Castillo²

¹ Centro de Investigación en Materiales Avanzados S. C., Miguel de Cervantes # 120 Complejo Industrial Chihuahua 31109, Chihuahua, Chih., México. E-mail: hector.robles@cimav.edu.mx

² Universidad Simón Bolívar, Río Mixcoac # 48, Col. Insurgentes, México 03920, D.F.

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Abstract. The current study shows a calibration method in gas chromatography (GC) with detection by mass spectrometry (MS) to quantify polychlorinated biphenyls (PCBs) present in transformer oils. The calibration was carried out with a secondary standard composed of a mixture of Aroclors (A1254:A1260), in one to one proportion and a reference standard (1,3,5-trichlorobenzene). This last one was used to evaluate the answer of the MS. The limit of detection of the method was below 10 µg/mL, with ± 0.002 as deviation in the relative retention time (RRT) and 3.39 % as relative response factor (RRF). Finally, PCBs concentration in oil samples was determined from the calibration data.

Keywords: Polychlorinated Biphenyls, Transformer oils, Aroclor, Mass Spectrometry

Resumen. Se presenta un método de calibración en cromatografía de gases (GC) con detección por espectrometría de masas (MS) para cuantificar bifenilos policlorados (BPCs) presentes en aceites dieléctricos. La calibración se realizó con un estándar secundario compuesto por una mezcla de Arocloros (A1254:A1260), en proporciones (1:1) y un estándar de referencia (1,3,5-triclorobenceno). Este último fue utilizado para evaluar la respuesta del MS. El límite de detección del método fue menor a los 10 µg/mL, con un ± 0.002 de desviación en el tiempo de retención relativo (RRT) y un porcentaje del factor de respuesta relativa (RRF) de 3.39 %. Finalmente, se determinó la concentración de BPCs en muestras de aceite a partir de los datos de calibración.

Palabras clave: Bifenilos policlorados, Aceites dieléctricos, Aroclor, Espectroscopia de masas.

Introduction

The interest of the polychlorinated biphenyls (PCBs) as an environmental pollutant began in 1966 when they were catalogued as hazardous waste [1]. These compounds are chemically stable, a property that represents an economical advantage but that constitutes a disadvantage and risk from the environmental perspective, as it favours their bioaccumulation and biomagnification through the foodstuff chain [2]. These characteristics, together with their mobilization to long distances, have motivated the international prohibition of their production, importation and usage [3, 4].

PCBs are compounds artificially synthesized from the substitution of hydrogen atoms by chlorine atoms in the biphenyl molecule. This substitution is possible in any position and in combinations of 1 to 10 chlorine atoms in each molecule [5]. The 209 possible PCBs congeners have only been synthesized under laboratory conditions by Cadogan coupling. The synthesis of PCBs in commercial processes tends to favour specific substitution reactions with percentage of chlorination ranging from 20 to 80 % [6]. The number of individual congeners synthesized this way varies from 130-135 [7, 8]. However, 150 congeners have been reported in environmental samples [9].

This diversity of congeners, as well as their similar physical and chemical properties makes PCBs difficult compounds to analyse [10]. The analytical methods for PCBs are currently based on their separation by gas chromatography (GC) [11] using capillary columns with different polarities [9, 12] and specific detectors such as the flame ionization detector (FID)

[13], the electron capture detector (ECD) [14, 15] and mass spectrometry (MS) [16, 17]. The most important advantage of analysing PCBs by MS lays on its high selectivity since the chlorination levels among groups of congeners are efficiently distinguished. Besides, it discriminates substances that interfere on their identification and quantification [14].

The election of standards to quantify PCBs is based on a number of factors among which the type of sample, the availability of reference compounds, and eventually, the aim of the determination are included [14]. Three types of standards have been used to carry out this quantification. Commercial mixtures of Aroclors [18] that provide many of the congeners usually observed in environmental samples [19], groups of individual isomers, one per chlorination level [20] or selected according to their persistence and toxicity [9]. Among these last ones, the Commitment Bureau of Reference (BCR) suggests the use of the congeners listed in figure 1 [21].

The world tendency to remove the PCBs passives has promoted the need of quantifying and identifying them, to be able to determine the best option for their treatment and/or removal. Therefore, the objective of this study was to implement a calibration method in mass spectrometry (MS) to identify and quantify PCBs congeners in transformer oils and waste oil using mixtures of standards of Aroclor 1254 (A1254) and Aroclor 1260 (A1260).

The percentage of chlorination in commercial mixtures of different oil formulations for transformers ranges from 38.2 to 63.6 % [22] and from 5 to 9 chlorine atoms per molecule [23]. The main mixture, known as Askarel, contains 70 % Aroclor 1260 and 30 % tri- and tetrachlorobenzene approximately

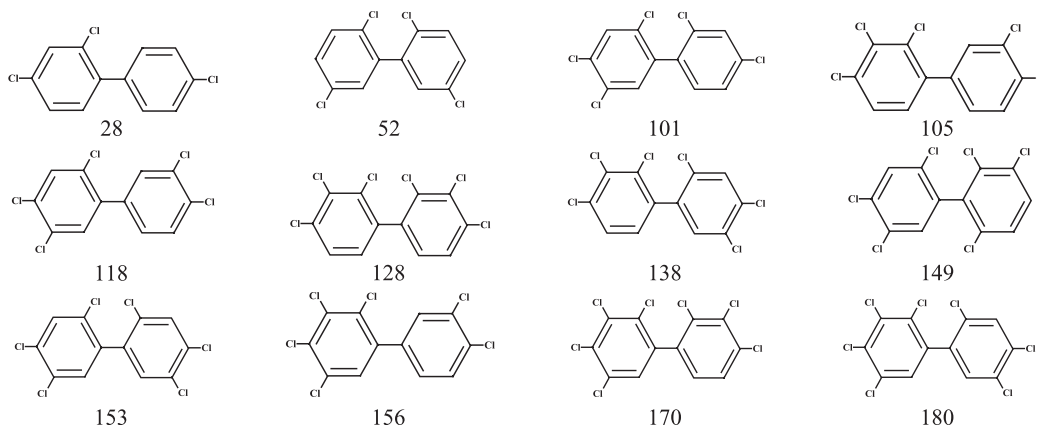


Fig. 1. PCBs selected for their inclusion on the BCR certification programs. The figure below the structure in designated by IUPAC.

[24]. This research tries to typify transformer oils as well as their waste. Therefore, the mixture of Aroclors 1254 and 1260 is the best option to evaluate this type of oils.

Materials and Methods

Instrumental Analysis of PCBs

The analysis of PCBs was carried out by an integrated system of gas chromatography, equipped with an automatic injection system and coupled to a mass spectrometric system with quadrupole polar detector (GC-MS) Agilent 5980-1472E. The separation of congeners was done in a 30 m × 0.25 mm X 0.25 μm Agilent HP-5MS column. Helium was used as the carrier gas at 18 psi pressure and 1.9 mL/min flow. The injector was kept at constant pressure and 250 °C temperature. The initial oven temperature was set at 70 °C, held for 2 min, then increased to 150 °C at a rate of 25 °C/min, then increased to 200 °C at a rate of 3 °C/min, then increased to 280 °C at a rate of 8 °C/min. The temperatures of the injector and detector were 270 °C. The injection volume was 1 μL in the splitless mode. Using mass range from 50 to 500 amu. The temperatures of the quadrupole, source and transference line were 150 °C, source 230 °C and 280 °C respectively. The equipment was operated in Scan mode (EI) at 1.52 scan/s [25].

Standard solutions

The mixtures of standards were obtained as Aroclors from Alltech and prepared in a 1:1 relationship (A1254:A1260). A standard of 1,3,5-trichlorobenzene (1,3,5-TCB) from Alltech was also purchased. It was used as standard of reference (SR). Solutions of 100, 50, 30, 25, 20, 10 and 5 μg/mL were prepared from the mixture A1254:A1260. The SR was added to all of them in a 1:100,000 proportions. All the solutions were prepared in hexane (HPLC).

PCBs Congeners

From the congeners present in the mixture of A1254:A1260, from two to three per chlorination level were selected for the evaluation of calibration parameters. The relative quantification of the secondary calibration standard (A1254:A1260) was developed with the “standard of reference (SR)” method, using 1,3,5-TCB, according to the American Chemical Society [26].

Quality control

The quality control of the method was evaluated with the following parameters: linearity, limit of detection (LoD), limit of quantification (LoQ), stability of retention time (RT), matrix sample effect, precision and reproducibility.

i.- The LoD and LoQ of the calibration method were calculated from the equations of Vogelgesang and Hädrich [27].

$$LoD = \frac{(y_{crit} - a)}{b} \quad (1)$$

where: (y_{crit}) critical signal height, (a) y intercept and (b) slope.

$$y_{crit} = a + S_y \cdot t_{f,\alpha} \cdot \sqrt{1 + \frac{1}{n} + \frac{\bar{x}^2}{\sum_{i=1}^n (x - \bar{x})^2}}$$

($t_{f,\alpha}$) t distribution with $f = n - 2$ dl and $\alpha = 0.05$, (\bar{x}) mean value of the concentration of all the analyses, (S_y) typical error

$$LoQ = \frac{(y_{DTM} - a)}{b} \quad (2)$$

where: (y_{DTM}) lower edge of the Gaussian distribution around 2·LoD,

$$y_{DTM} = \bar{y} + b \cdot [2 \cdot LoD - \bar{x}] + S_{y/x} \cdot t_{f,\alpha} \cdot \sqrt{1 + \frac{1}{n} + \frac{2 \cdot LoD - \bar{x}^2}{\sum_{i=1}^n (x_i - \bar{x})^2}}$$

(\bar{y}) mean value of the signal values of all calibration analyses
 ii.- The stability of the RT was determined by the evaluation of the mobility of the retention time (MRT) and the deviation of the relative retention time using the equations of Hoof and Hsieh [28].

The Relative Retention Time (RRT) is defined as the relation between the RT of each congener and the RT of the SR (Eq. 3)

$$RRT = \frac{RT_C}{RT_{SR}} \tag{3}$$

where; (RRT) relative retention time of each congener, (RT_C) retention time of each congener, (RT_{SR}) retention time of the standard of reference.

The RRT for each congener in each initial calibration concentration was compared to its average (Eq. 4).

$$\overline{RRT} = \sum_{i=1}^n \frac{RRT}{n} \tag{4}$$

The RRT deviation is the difference between Eq. 3 and 4.

iii.- Precision and reproducibility were obtained through the percentage of relative standard deviation and the percentage of difference of the continuous calibration, using the equations of van Hoof and Hsieh [28].

The percentage was determined with the relative response factor (RRF) for each congener, in each calibration concentration, using the following equations:

$$\%RSD = \frac{SD_{RRF}}{RRF} \cdot 100 \tag{5}$$

where (SD_{RRF}) standard deviation of the response factor per congener and (\overline{RRF}) mean relative response factor.

$$RRF = \frac{A_C \cdot C_{SR}}{A_{SR} \cdot C_C}; \overline{RRF} = \sum_{i=1}^n \frac{X_i}{n} \tag{6}$$

$$SD_{RRR} = \sqrt{\frac{\sum_{i=1}^n (RRF_i - \overline{RRF})^2}{n-1}} \tag{7}$$

where (A_C) total area of the standard mixture, (A_{SR}) area of the SR, (C_C) concentration of the standard mixture and (C_{SR}) concentration of the SR, (X_i) RRF in each concentration and (n) number of concentrations of calibration.

The continuous calibration was calculated with the percentage of difference (% D) of five analyses in GC-MS of the 30 µg/mL solution and the following equation:

$$\%D = \frac{RRF_C - \overline{RRF}}{\overline{RRF}} \tag{8}$$

where (RRFC) relative response factor of the continuous calibration.

iv.- In order to determine the matrix effect of the sample, an oil without PCBs, mainly composed of chlorobenzenes, was obtained. It was analysed in triplicate, previous addition of 20 µg/ml of the mixture of A1254:A1260. The result of this analysis was compared with the expected result when using Alltech's equations [29].

$$\%R = \frac{Conc_{cal}}{Conc_{exp}} \tag{9}$$

where (Conc_{exp}) expected concentration and (Conc_{cal}) calculated concentration.

$$Conc_{cal} = \frac{A_C \cdot C_{exp}}{RAF} \tag{10}$$

Quantification of samples of oils

Once the quantification factors were determined, samples of oil from transformers oil supplied by Semarnat, Delegación Chihuahua, were analysed. The samples were purified by cleaning process with H₂SO₄ and then passed through a Florisil® column, as established by the 600-481045 EPA method [30]. The washed oil was diluted in hexane in a 1:1000 proportion and analysed in triplicate in the GC-MS at the established conditions. The quantification of PCBs in transformer oils and waste oils is obtained from comparison with standards [31]. To carry out this calculation, the equation indicated in the EPA SW-846 method [5] and the calibration data from this study were used.

$$Conc = \frac{B \cdot V_1}{A \cdot W} \left[\frac{mg}{Kg} \right] \tag{11}$$

where V₁ is the volume of dilution in the sample, W is the weight of the sample in grams.

$$A = \frac{\text{Sum of standard Peak Heights (area)}}{\text{ng of standard injected}} [=] \frac{mm}{ng} \tag{12}$$

$$B = \frac{\text{Sum of the sample Peak Heights (area)}}{\mu L \text{ injected}} [=] \frac{mm}{\mu L} \tag{13}$$

Results and Discussion

Polychlorinated biphenyls identified in GC-MS

In order to determine the congeners present in the mixture of A1254:A1260 a chromatogram with the 100 µg/mL concentration was obtained (Figure 2). This figure shows the elution of 70 peaks, 40 of them have intensity bigger than 1 % of the total area, so they represent the integration area of the chromatogram spectra.

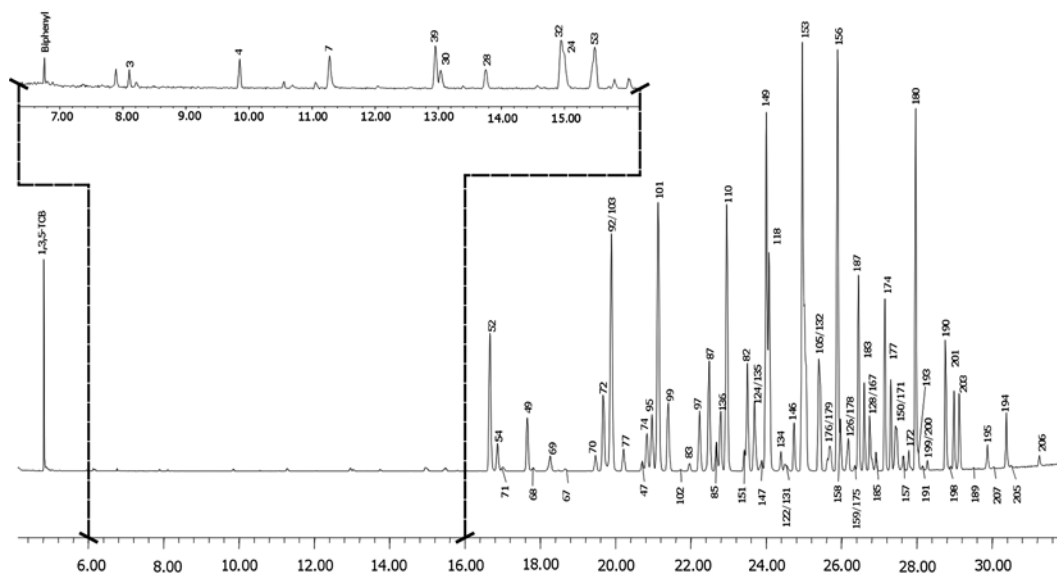


Fig. 2. Chromatogram of the mixture of standards of A1254:A1260 and 1,3,5-TCB. The dotted line in the figure is the enlargement of the range 6-16 min.

Using the NIST02 library from the Chemstation software, 82 compounds were identified in the mixture of standards; 80 of them are PCBs congeners, another one is the biphenyl and the remaining one is the 1,3,5-TCB. The congeners 92/103, 124/135, 122/131, 105/132, 176/179, 126/178, 159/175, 128/167, 156/171 and 199/200 are co-eluted among themselves so only one peak of their elution is observed in the chromatogram. Generally, PCBs elute in GC in an increasing order of the number of chlorine atoms in the biphenyl molecule [17]. This condition is fulfilled by the majority of the identified congeners. The congeners that elute in chlorination patterns different from their group of isomers might be presenting chemical ionization according to the substitution pattern. Plomley *et al.* [16] state that the elution among PCBs isomers depends on their molecular structure, specially on the number of chlorine atoms *ortho*-substituted.

Table 1 shows the structures, IUPAC identification number and the RT at which the PCBs congeners eluted. The distribution of these congeners is 1 mono-, 2 di-, 5 tri-, 12 tetra-, 18 penta-, 17 hexa-, 15 hepta-, 8 octa-, y 2 nonachlorobiphenyls. The biggest areas appear between penta- and octachlorobiphenyls, a characteristic feature of the Aroclors 1254 and 1260 [32]. Nine out of the twelve congeners recommended by the BCR as calibration standards were identified among them [21]. The missed congeners are: 24, 138 and 170.

PCBs selected for the calibration by GC-MS

From the 40 peaks with an intensity bigger than 1 %, 39 are PCBs, and the other one is the peak of 1,3,5-TCB. These peaks were used for the calibration with the mixture of Aroclors (A1254:A1260) and the SR.

Linearity, Limit of Detection (LoD) and Limit of Quantification (LoQ)

The areas of the chromatograms of the solutions of 100, 50, 25, 10, 5 $\mu\text{g/mL}$ are used to obtain the linearity, LoD and LoQ of the method. Each of them was analysed in triplicate. Wells *et al.* [33], state that in complex matrices such as those that contain PCBs, a multiple level calibration process has to be done. In such process, the number of concentrations of calibration must be representative of the matrix to analyse. Besides, Smyth [34] points out that a response curve for PCBs can be determined with a minimum of three concentrations. Therefore, to consider five concentrations ranging from 5 to 100 $\mu\text{g/mL}$ provides an appropriate tool for analyse of oils with PCBs.

Figure 3 shows the response curve of the calibration, which corresponds to a straight line with the equation $y = 1.093 \cdot 10^7 \cdot x - 3.275 \cdot 10^7$ and a correlation coefficient of 0.998, which indicates that the samples with PCBs can be quantified in a wide range of concentrations within the response curve.

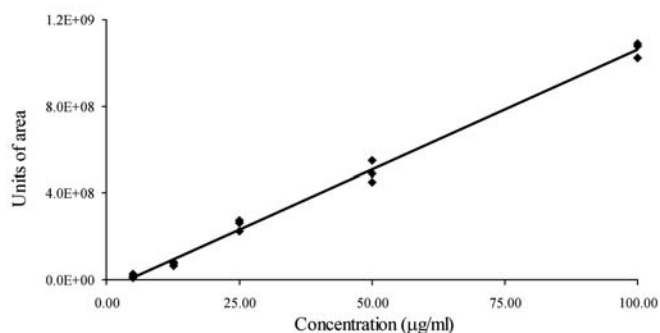


Fig. 3. Response curve of the PCBs calibration process

Table 1. Congeners identified in the mixture of A1254:A1260.

Structure	IUPAC	RT _(min)	Structure	IUPAC	RT _(min)	Structure	IUPAC	RT _(min)
Biphenyl		6.76	2,2',3',4,5	95	20.97	2,3',4,4',5,5'	167	26.75
4	3	8.10	2,2',3',4,5	97	22.23	2,2',3,3',4,4',6	171	27.44
2,2'	4	9.85	2,2',4,4',5	99	21.40	2,2',3,3',4,5,5'	172	27.79
2,4'	7	11.28	2,2',4,5,5'	101	21.13	2,2',3,3',4,5,6'	174	27.15
2,3,6	24	14.95	2,2',4,5,6'	102	21.73	2,2',3,3',4,5',6	175	26.35
2,4,4'	28	13.75	2,2',4,5',6	103	19.89	2,2',3,3',4,6,6'	176	25.69
2,4,6	30	13.04	2,3,3',4,4'	105	25.40	2,2',3,3',4',5,6	177	27.31
2,4',6	32	14.95	2,3,3',4',6	110	22.96	2,2',3,3',5,5',6	178	26.18
2,2',5	39	12.96	2,3',4,4',5	118	24.08	2,2',3,3',5,6,6'	179	25.63
2,2',4,4'	47	20.71	2',3,3',4,5	122	24.49	2,2',3,4,4',5,5'	180	27.97
2,2',4,5'	49	17.66	2',3,4,5,5'	124	23.69	2,2',3,4,4',5',6	183	26.61
2,2',5,5'	52	16.68	3,3',4,4',5	126	26.18	2,2',3,4,5,5',6	185	26.92
2,2',5,6'	53	15.48	2,2',3,3',4,4'	128	26.75	2,2',3,4',5,5',6	187	26.45
2,2',6,6'	54	16.87	2,2',3,3',4,6	131	24.54	2,3,3',4,4',5,5'	189	29.51
2,3',4,5	67	18.66	2,2',3,3',4,6'	132	25.40	2,3,3',4,4',5,6	190	28.76
2,3',4,5'	68	17.82	2,2',3,3',5,6'	135	23.69	2,3,3',4,4',5',6	191	28.15
2,3',4,6	69	18.27	2,2',3,3',6,6'	136	22.79	2,3,3',4',5,5',6	193	28.01
2,3',4',5	70	19.47	2,2',3,4',5,5'	146	24.74	2,2',3,3',4,4',5,5'	194	30.38
2,3',4',6	71	16.00	2,2',3,4',5,6	147	23.88	2,2',3,3',4,4',5,6	195	29.88
2,3',5,5'	72	19.68	2,2',3,4',5',6	149	24.01	2,2',3,3',4,5,5',6	198	28.88
2,4,4',5	74	20.84	2,2',4,4',6,6'	150	27.44	2,2',3,3',4,5,6,6'	199	28.28
3,3',4,4'	77	20.22	2,2',3,5,5',6	151	23.42	2,2',3,3',4,5',6,6'	200	28.28
2,2',3,3',4	82	23.50	2,2',4,4',5,5'	153	24.96	2,2',3,3',4,5,5',6'	201	28.99
2,2',3,3',5	83	21.96	2,3,3',4,4',5	156	25.90	2,2',3,4,4',5,5',6	203	29.13
2,2',3,4,4'	85	22.68	2,3,3',4,4',5'	157	27.64	2,3,3',4,4',5,5',6	205	30.50
2,2',3,4,5'	87	22.49	2,3,3',4,4',6	158	25.97	2,2',3,3',4,4',5,5',6	206	31.26
2,2',3,5,5'	92	19.89	2,3,3',4,5,5'	159	26.35	2,2',3,3',4,4',5,6,6'	207	30.04

The limits calculated with the equations 1 and 2 are LoD = 5 µg/mL and LoQ = 14.9 µg/mL. This LoD remains at the low concentrations of the calibration solutions which show that all congeners can be quantified in a wide range of concentrations within the response curve. The LoQ stays at the low calibration levels, so low concentrations can be quantified with a high confidence level. The LoQ establishes the linearity in the measurement in low and high concentrations [26], so it can be assumed that the response curve is also consistent when very concentrated samples, as in the case of dielectric oils, are analysed.

Stability of the retention time (RT)

To estimate the stability of the RT in the analysis of PCBs, it was necessary to use the TR of a representative group, in chlorination level and relative abundance of, the congeners present in the mixture of Aroclors and the RT of the SR (4.82 min). The congeners included were: 52, 92/103, 101, 118, 149, 153, 156, 187, 180 and 201. The MRT is evaluated with the coefficient of variation (CV) of the RT for the congeners selected. The SR was determined with a triplicate analysis of the solutions with concentrations of 100, 50, 25, 10 and 5 µg/mL. The coefficient of variation (CV) was used to determine the calibration window in the ChemStation Software and the stability in the column.

Table 2. Mobility of the retention time.

Structure	RTm (min.)	CV (%)
52	16.666	0.0019
92/103	19.891	0.0028
101	21.132	0.0029
118	22.955	0.0021
149	24.004	0.0020
153	24.961	0.0019
156	25.897	0.0019
187	26.452	0.0006
180	27.970	0.0017
201	28.990	0.0009
ER	4.826	0.0010

In table 2, the mean retention time (RTm) at which the selected congeners eluted as well as the chlorination level they represent and the CV are shown. During the analysis, the % CV for the majority of the congeners including the SR was beneath 0.01 %. Storr-Hansen [12] establishes a permitted tolerance value for PCBs of 0.02 % and 1 % for the SR, due to the influence that the peaks of less abundant congeners might have. Therefore, it can be said that the MRT is stable in the column and that the congeners identified in the window are consistent.

Table 3. Deviation of the RRT.

RTm	Solutions ($\mu\text{g/mL}$)				
	100	50	25	10	5
52	0.000	-0.001	0.001	0.000	0.000
92/103	0.000	-0.001	0.001	0.000	0.001
101	0.001	-0.002	0.001	0.000	0.000
118	0.000	-0.001	0.001	0.000	0.001
149	0.001	-0.002	0.001	0.000	0.000
153	0.001	-0.002	0.001	-0.001	0.000
156	0.001	-0.002	0.001	0.000	0.001
187	0.000	-0.002	0.001	0.000	0.000
180	0.000	-0.002	0.001	0.000	0.001
201	0.000	-0.002	0.000	0.000	--

On the other hand, the RRT requires the RT of the SR to be very stable [34]. The SR presents a CV of 0.001 % (table 2), so it can be used to determine the deviation in the RRT. The RRT is the difference between the equations 3 and 4. This difference must be zero or close to it. Differences higher than ± 0.02 implies that the congener has a lot of mobility and therefore, its quantification is not representative [28].

Table 3 shows the deviation of the RRT for the congeners to follow in this analysis. All of them exhibited values far below ± 0.02 . The congener 201 in the 5 $\mu\text{g/mL}$ solution is not showed because at this concentration the integration area was smaller than the minimum percentage required for its analysis with the software ChemStation. Even though, since the deviation of the RRT is consistent and shows low mobility, the quantitative determination of PCBs is reliable as there are no important variations in the RT of the congeners.

Precision and reproducibility

The RRF generated by each congener in each calibration level is very important when determining the validity of a calibration using a secondary standard (A1254:A1260) depending on the SR. The RRF as well as its average was obtained from equation 6a. The results obtained are shown in table 4. The

Table 4. Relative response factor.

Solution $\mu\text{g/ml}$	RRF	$\overline{\text{RRF-RRF}}$
100	1.027	-0.128
50	0.922	-0.233
25	0.918	-0.247
10	1.305	0.150
5	1.612	0.457

percentage of relative standard deviation (% RSD), obtained from the data in table 4 and equation 5 was 3.39 %. The limit value to consider that the data in the calibration show a good precision and reproducibility is < 20 %. Higher values than this imply serious errors on the PCBs determination.

The quality control establishes checks everyday to be carried out or continuous calibration as validation of the initial calibration, ensuring this way that the initial analytical conditions are kept [35]. For that purpose, the % D was determined in the continuous calibration with the equation 8, where a -10.17 % was obtained, which is considered acceptable since the permitted limit is ± 15 % [29] and even in complex matrices, such as PCBs, variations up to 25 % are accepted [28].

Matrix effect of the sample

The Percentage of Recovery (% R) obtained from equation 5 is 90.75 %. This recovery percentage implies that no significant matrix effect took place and that the results from the analysis of the transformer oils will not be affected by other organochlorinated compounds present in the transformer oils.

Identification of the PCBs in the transformer oils

The standards used in the quantification are important for obtaining analytical data. Due to this fact, the correspondence between Aroclor (1254:1260) formulations and the transformer oil was evaluated in this study. Figure 4 shows a chro-

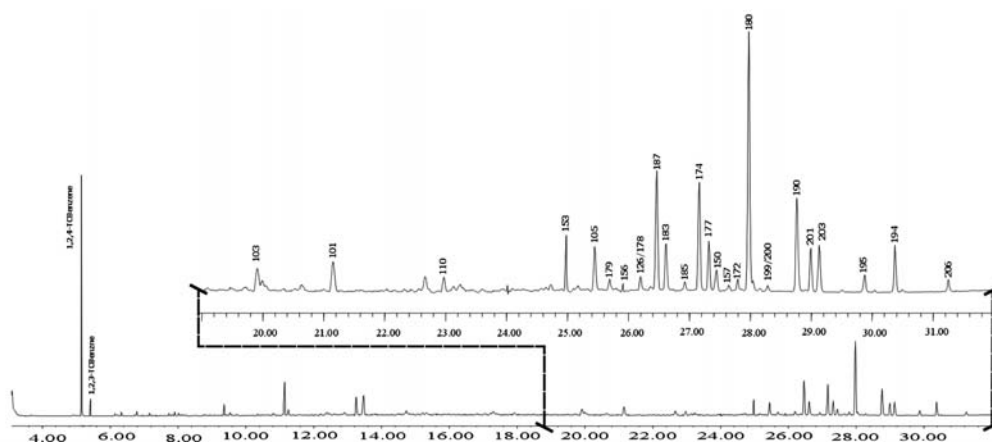


Fig. 4. Chromatogram of the transformer oil with PCBs and chlorobenzenes. The dotted line in the figure is the enlargement of the range 19-32 min.

matograph of this oil under the GC-MS conditions. Twenty six chlorinated compounds were identified in the chromatogram. Twenty four of these compounds were identified as PCBs congeners, whereas the other two chlorinated compounds were the 1,2,4-trichlorobenzene and 1,2,3-trichlorobenzene. The PCBs congeners identified in the oil sample were also identified in the mixture of standards, so it can be said that this mixture of standards represents the oil sample in a reliable way.

The concentration of transformer oil obtained from equation 11 was 2701.83 mg/kg so it must be considered a hazardous waste as the Norma Oficial Mexicana [36] establishes that all material on any physical state that contains PCBs in a concentration equal or higher than 50 mg/kg should be typified that way.

Conclusions

The advantage of using pure individual congeners as primary standards for the determination of the concentration of PCBs in different matrices is the most desirable option. However, it is limited to the availability of each congener and to its cost. On the other hand, technical mixtures of Aroclors are available at low cost and they have lots of the congeners commonly observed in environmental samples.

The mixture of Aroclors 1254 and 1260 has the majority of the congeners proposed for calibration by lots of the methodologies for the analysis of PCBs in environmental matrices. Besides, it contains all the PCBs present in the dielectric oils used in transformers. The 1,3,5-TCB proved to be a very efficient standard of reference as it showed a very stable behaviour during all the calibration process. The chromatographic conditions established for the system in the GC-MS provide an efficient separation of the congeners selected for the calibration, which is corroborated by the very low variability (± 0.002) in the deviation of the RRT. The analytical characteristics of the calibration obtained in this study present linearity higher than 98 % with LoD and LoQ what enables the identification and quantification of PCBs in dielectric oils in concentrations smaller than 5 $\mu\text{g/mL}$.

The method shows a good precision and reproducibility for the analysis of congeners, what is corroborated by the RRF value, smaller than 4%, which indicates consistence on the measurements and a % D of -10.17 that guarantees the stability of the calibration through time. The % R of the method was 90.79 %, which implies that a significant matrix effect did not take place.

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