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A simple and reliable method for separation of mineral oil/polychlorobiphenyl mixtures

Chems Eddine Gherdaoui[1,2], Zohra Bouberka[1,3], Jean-Philippe Delbarre[2], Olivier Hutin[2], Roger Sansano[2], Laurent Leclercq[4], Philippe Supiot[1] and Ulrich Maschke[1]

Abstract

Polychlorinated biphenyls (PCBs) were broadly applied worldwide as electrical insulators in transformers and power capacitors, due to their high dielectric constant and non-flammability. They were often added to mineral oils (MOs) and used as dielectric fluids, which are nowadays classified as hazardous waste. Indeed, the Stockholm Convention aims to eliminate the use of equipment with PCB content greater than 0.005 wt-% (=50 ppm) by 2025. Accurate identification and quantification of small traces of PCBs contained in MO thus represent a great analytical challenge. To achieve this goal, a simple, cost-effective and fast chromatographic process was developed to separate PCBs from MO, allowing to obtain reliable data to determine the concentration of PCBs, reduced to 2–3 ppm. Experimental and analytical methods, such as thin layer chromatography, column chromatography as well as gas chromatography coupled with mass spectroscopy, were applied to acquire a high level of qualitative and quantitative determination of PCBs in transformer MOs.

Keywords

Polychlorinated biphenyls, mineral oil, chromatographic separation, gas chromatography, mass spectroscopy

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Introduction

Polychlorinated biphenyls (PCBs) are synthetic aromatic compounds known by the trade names Pyralene, Aroclor and others (Erickson and Kaley, 2011). They refer to a family of 209 organochlorinated compounds consisting of two benzene rings substituted with 1–10 chlorine atoms in different positions (Ballschmiter and Zell, 1980). Their chemical and physical stability and non-flammability have made these compounds to be used mainly as electrical insulators not only in power transformers and capacitors, but also in some heaters and other electrical equipment (Erickson and Kaley, 2011; Rossberg et al., 2006).

PCB molecules have been revealed to be toxic, as they promote carcinogenic effects (Knerr and Schrenk, 2006). They have thus been classified as persistent organic pollutants (POPs) according to the Stockholm Convention (Stockholm Convention; Weber et al., 2011). Therefore, all transformer fluids containing PCBs are considered hazardous waste and therefore must be monitored (PCB-elimination-network, 2016; Xu et al., 2013). In fact, it is prohibited to hold devices containing PCBs above 50 ppm in the European Union (Council Directive 96/59/EC, 1996) pending their disposal by 2025 (Directive 2012/19/Eu, 2012; Regulation (Eu) 2019/1021, 2019).

Since the phaseout of PCBs, mineral oil (MO) has been used as an alternative in power transformers, especially due to its electromagnetic insulating power equivalent to that of PCBs (Rouse, 1998), its wide distribution and its low cost compared to other fluids, such as silicone and synthetic or vegetable ester oils, available in the market (Borsi and Gockenbach, 2005). However, transformer oils often contain variable amounts of PCBs (Pelitli et al., 2015).

Generally, PCB molecules are analysed using equipment with a capillary column usually filled with fused silica, and this technique is known as gas chromatography (GC) which is often coupled with an electron capture detector (ECD) (Barcauskaitė, 2019; Bunert et al., 2019). Other detectors can be coupled to GC to detect PCBs, which include the following: flame ionization detector is sensitive to the detection of volatile organic compounds (Huang et al., 2021); the flame photometry detector is mainly used for compounds containing sulphur or phosphorus compounds (Clark and Thurbide, 2015); the thermoionic detector, also called nitrogen-phosphorus

[1]Unité Matériaux et Transformations, Université de Lille, Villeneuve d'Ascq, France
[2]Maxei Group, Arras, France
[3]Laboratoire Physico-Chimie des Matériaux-Catalyse et Environnement, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf, Oran, Algeria
[4]IBMM, CNRS, ENSCM, University of Montpellier, France

Corresponding author:
Ulrich Maschke, Unité Matériaux et Transformations (UMET), Université de Lille, UMR CNRS N°8207, Bâtiment C6, Villeneuve d'Ascq, 59655, France.
Email: ulrich.maschke@univ-lille.fr

detector, is used for nitrogen or phosphorus compounds (Wang et al., 2016); the photoionization detector is adapted to the detection of ionizable compounds (Liaud et al., 2014); and the coupling with mass spectroscopy (MS) is sensitive for the detection of POPs (Ballschmiter et al., 1992; Li et al., 2021). However, despite their high sensitivity, GC detectors show a reduced efficiency of detection of PCBs in the presence of MOs of molar masses of around 1000 kg kmol^{-1}. At present, the ECD detector remains the most used reference for the analysis of halogenated compounds (De Kok et al., 1982). This detector captures some electrons from the sample, which reduces the measured current. The compensation for this reduction is recorded as a positive peak. As it is often the case for other GC techniques, a carrier gas should contain few oxygen and water impurities that can interact with the stationary phase and cause considerable problems such as high reference noise or column bleed in the output gas chromatogram, which reduces analyser sensitivity and column life. Impurities can also oxidize the radioactive nickel source of ECD detectors and therefore decrease their reactivity and lifetime, making it a major drawback of this conventional analytical technique (Bunert et al., 2017; Poole, 2013), justifying the broader use of MS for the detection of PCB. Nevertheless, another analytical difficulty, the detection and quantification of PCBs in the presence of MOs with molar masses exceeding 1000 kg kmol^{-1}, can be encountered. Indeed, the detection of PCBs in such media is considered to be the most difficult, especially for low-chlorinated PCBs which have physical and chemical characteristics very similar to those of MO from electrical transformers (Takada et al., 2001). Moreover, to analyse all PCBs and to avoid interference problems between PCBs and MO matrix derivatives, as well as to prevent pollution of detector ionization sources, it is necessary to combine a pre-treatment technique capable of extracting PCBs from MOs before their injection into the GC coupled with MS (GC-MS).

At present, the best known pre-treatment procedure is solid phase extraction (SPE) (Dmitrovic et al., 2002) combined with liquid–liquid extraction. This method requires the addition of dimethyl sulfoxide for SPE, water to immobilize the PCB mixture and hexane for liquid–liquid extraction which must be later dried by sodium sulphate (Crucello et al., 2020; Takada et al., 2001; Wittsiepe et al., 2014). This method is expensive and requires the use of many solvents.

This work aims to achieve a simple, reliable and inexpensive chromatographic analytical separation method to extract PCBs from transformer MO, to reduce the analysis time and to increase the sensitivity of detection and quantification of high- and low-chlorinated PCBs, without using many additional chemicals.

For this purpose, combined separation and chromatographic characterizations were first performed on model MO/PCB systems in the presence of 18 PCB molecules including the seven most common ones called indicator PCBs (Afful et al., 2013), and then applied to an industrial sample of MO contaminated with unknown PCBs provided by Maxei company. The chromatographic separation protocol was approved by thin layer chromatography (TLC), column chromatography filled with silica gel material under liquid petroleum ether flow and nitrogen flow to accelerate the separation of MO/PCB systems.

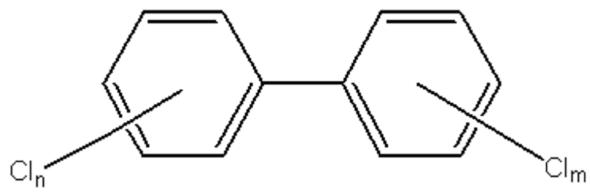


Figure 1. Generalized chemical structure of PCBs. The case $n = m = 0$ corresponds to the chlorine-free PCB N°0 (Biphenyl). PCBs: polychlorinated biphenyls.

The resulting fractions, free of MO molecules, can then be injected and analysed by GC-electronic ionization (EI)/MS-GC. This analytical and pre-treatment combination improves the detection sensitivity of MO/PCB systems without any pollution concern for the detector ionization source.

Materials and methods

Chemical products

Transformer MO. The transformer MO samples studied were supplied by a French company (Arras Maxei, Arras, France), and were mainly composed of three families of hydrocarbons: paraffins, naphthenes and non-chlorinated aromatics. A PCB-free virgin MO named *MO virgin* and a PCB-contaminated MO denominated *MO contaminated* were considered here. The latter has been used for long time in an industrial environment and contains *MO virgin* as MO as well as an unknown number and quantity of PCBs.

Polychlorinated biphenyls. The following PCB molecules were selected for this work (Figure 1): biphenyl (PCB N°0), 2-chlorobiphenyl (PCB N°1), 3-chlorobiphenyl (PCB N°2), 2,2′-dichlorobiphenyl (PCB N°4), 2,3-dichlorobiphenyl (PCB N°5), 2,4-dichlorobiphenyl (PCB N°7), 3,4-dichlorobiphenyl (PCB N°12), 3,5-dichlorobiphenyl (PCB N°14), 4,4′-dichlorobiphenyl (PCB N°15), 2,4,4′-trichlorobiphenyl (PCB N°28), 2,4′,5-trichlorobiphenyl (PCB N°31), 2,2′,5,5′-tetrachlorobiphenyl (PCB N°52), 3,3′,4,4′-tetrachlorobiphenyl (PCB N°77), 2,2′,4,5,5′-pentachlorobiphenyl (PCB N°101), 2,2′,3,4,4′,5′-hexachlorobiphenyl (PCB N°138), 2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB N°153), 2,3,3′,4,4′,5-hexachlorobiphenyl (PCB N°156), 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB N°180) and decachlorobiphenyl (PCB N°209) were provided by Sigma-Aldrich (St. Quentin Fallavier, France). The choice of PCBs was mainly focused on the so-called indicator PCBs accounting for nearly 80% of all PCBs: most often PCBs No. 118, 138, 153 and 180, but also PCBs No. 28, 52 and 101. In 2017, these seven indicator PCBs among the 209 congeners were selected by the Community Reference Office of the European Commission in Brussels as being the compounds to be searched for in priority in the analysis of organic matrices (sediment, blood, flesh, fat) due to their persistence and abundance in the environment as well as their toxicological properties (Turrio-Baldassarri et al., 1993). Other congeners of the same family with the same chlorine numbers have been added in this study to obtain more information on the chromatographic separation parameters.

Organic solvents. Petroleum ether (40–60) and acetone were purchased from Sigma-Aldrich (p.a. grade solvents). These reagents were used as received.

Determination of the molar mass of transformer MO. The molar mass of MO was determined by a matrix-assisted laser desorption ionization-time of flight/MS (MALDI-TOF/MS) using a nitrogen laser beam of wavelength 337 nm and pulse time 3 ns. MO was diluted to 1/100 in methanol and analysed using a 2,5-dihydroxybenzoic acid matrix. The result obtained was recorded over an interval from 99 to 1500 Da. The determination of the molar mass of MO was repeated three times.

Separation techniques

Thin layer chromatography. TLC analysis of MO and MO/PCB mixtures was carried out on aluminium supports (20 cm × 20 cm) covered with uniform layers of silica gel as stationary phase. The thickness of this layer was about 0.2 mm (200 µm). The TLC plates were placed in a rectangular tank containing the eluent which was a solvent mixture composed of 99 vol-% petroleum ether 40–60/1 vol-% acetone (Ciura et al., 2017; Nikolaev et al., 2019). The stains from the fractions deposited at 1 cm from the base of the layer migrate on the TLC plate more or less quickly based on the interactions between the mobile phase (eluent and MO/PCB) and the stationary phase. The visualization of the different spots on the TLC plates was performed under a UV lamp with a wavelength of 254 nm. The plate appears fluorescent green and the products that absorb UV radiation appear as dark spots. The obtained TLC result of a given compound was expressed by calculating the 'ratios to the front' value, R_f, corresponding to the ratio of the distance travelled by the compound to that of the solvent front. Each TLC analysis was repeated six times.

Silica column chromatography. Silica column chromatography (SCC) was carried out on a standard silica column (Silica 60 M, 0.04–0.063 mm, provided by Macherey-Nagel GmbH & Co. KG, Düren, Germany) (length: 33 cm, diameter: 3 cm), applying the solvent mixture used by TLC analysis (99 vol-% petroleum ether 60–40/1 vol-% acetone) as mobile phase. The obtained separation effects were controlled by TLC analysis. Indeed, the constituents of the MO/PCB mixtures migrated at different speeds on the support were thus separated. Migration of MO/PCB mixtures on the silica column was done under a controlled compressed nitrogen flow, to accelerate the separation. Each chromatographic column run was repeated six times.

Gas chromatography coupled with mass spectroscopy. The recovered separated fractions containing PCB compounds were analysed by GC-MS after drying in a vacuum oven at 70°C. The GC chromatograms and their associated MS spectra were obtained using a GC/MS apparatus (Clarus 680/Clarus 600 T from Perkin Elmer Waltham, MA, United States), equipped with a fused silica capillary column, which was maintained at 70°C (Elite-5 (5% Diphenyl) Dimethylpolysiloxane, 30 m × 0.53 mm (internal diameter), film thickness d_f=0.5 µm). The MS appliance was equipped with an EI source and a quadrupole filter (ion separator) at DC (U) and AC (V) voltages set by the equipment (Chamkasem et al., 2016).

Operating conditions of the GC-MS apparatus. The thermal conditions of the GC oven were as follows: the column has been maintained at a temperature of 70°C initially for 4 minutes then a ramp of 20°C minute^{-1} up to 120°C was applied. The temperature has then been raised to 250°C at a rate of 30°C minute^{-1}. The oven remained at this temperature for 20 minutes, and then the temperature was increased at a rate of 20°C minute^{-1} up to 300°C. The latter temperature was maintained for another 20 minutes. The temperatures of the injector and the transfer line were 300°C. The carrier gas used in our analysis was helium. The characteristic quantities of the chromatographic analysis (t_R (minute): retention time, t'_R (minute): reduced retention time, k': capacity factor, α: selectivity factor, N: number of theoretical plates, Rs: column resolution) were measured following the method described in Jennings (2000). The reduced retention time t'_R is given by equation (1):

$$t'_R = t_R - t_M \tag{1}$$

where t_M is the time required for a species that is not retained by the stationary phase to pass through the column. The capacity factor k' is given by equation (2),

$$k' = \frac{t'_R}{t_M} \tag{2}$$

describing the rate of progression of PCBs in the column. This is the ratio of the quantities of a PCB analyte present at equilibrium in the two adjacent stationary and mobile phase volumes. The selectivity factor α is given by equation (3),

$$\alpha = \frac{t'_R(B)}{t'_R(A)} = \frac{k'_A}{k'_B} \tag{3}$$

and represents the ability of the chromatographic system to 'distinguish' chemically between sample components. It is usually measured as a ratio of the retention (capacity) factors (k') of the two peaks and can be visualized as the distance between their apices. The number of theoretical trays N is given by equation (4):

$$N = 16\left(\frac{t_R}{\omega}\right)^2 \tag{4}$$

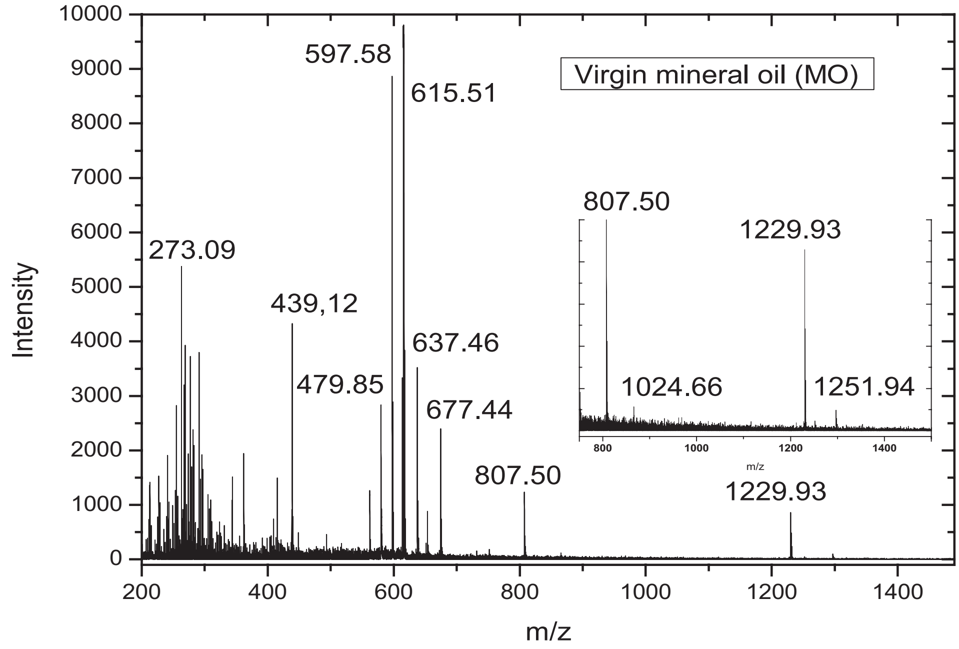


Figure 2. MALDI-TOF spectrum of virgin MO.
MALDI-TOF: matrix-assisted laser desorption ionisation; MO: mineral oil.

The efficiency of the column increases when N increases. Note that $\omega = 4\sigma$ (the width at the base of the peak). The resolution of a column (R_S) is given by equation (5):

$$R_S = 2\frac{t_R(B) - t_R(A)}{\omega_R - \omega_A} \quad (5)$$

and gives a quantitative measure of its ability to separate two PCBs: analytes A and B.

The detection and identification of PCB molecules was performed with the help of a reference standard which was FC-43 (Heptacosa). The masses obtained by MS were limited in the range between 30 and 620 $m z^{-1}$ due to the type of electron ionization source which is not able to fragment molecules with masses higher than 620 $m z^{-1}$. The ionization source temperature has been set at 280°C, and the voltage applied to the filament was 430 V.

Quantification of PCBs by GC-MS. Calibration curves were established allowing independent quantitative determination of individual PCB concentrations. For this purpose, each indicator PCB was analysed as a reference standard by GC-MS using a variety of concentrations ranging from 10 to 200 ppm, and signal area calculations were performed. The accuracy of this analytical method was verified by graphical representation applying the following linear function: Area-PCB = $P \times C$, where Area-PCB represents the peak area of a given PCB molecule as function of its concentration C, and P stands for the slope of this linear relationship. The R^2 coefficients of determination were obtained by linear regression analysis using Origin version 8 software (Supplemental Figure S1). Limit of detection (LOD) and of limit of quantitation (LOQ) were calculated from each calibration curve, according to the international regulatory agencies. LOD was obtained by 3.3 times the ratio of the standard deviation of their response (s) and the slope of the calibration curve (S), LOD = 3.3 × (SD of intercept × slope^{-1}). LOQ was obtained from LOQ = 10 × (SD of intercept × slope^{-1}). The precision was obtained considering the relative standard deviation for both samples and standard solutions. The accuracy was assessed using certified samples.

Results and discussions

Molar mass of transformer MO

The MALDI-TOF spectrum of virgin MO, shown in Figure 2, clearly proves that the molar mass of this oil exceeds 1000 kg kmol^{-1}, which does not allow its direct injection and analysis into GC instruments coupled with a MS or other detectors. Indeed, the spectrum shows fragments with masses of 600, 800 and 1200 $m z^{-1}$, thus confirming the need to separate PCBs from MO before carrying out the GC analysis.

Approval of the chromatographic protocol

The protocol for chromatographic separation of MO/PCB mixtures is shown in Figure 3. The different steps of the separation process can be described as follows: first of all, an initial qualitative evaluation via TLC of model systems composed of *MO virgin* in the absence and presence of one or more PCB molecules made it possible to separate qualitatively PCB and MO components. To implement quantitative and more sophisticated methods, a separation of *MO virgin*/PCB mixtures by SCC was necessary. After obtaining MO and PCB fractions separately, a primary vacuum distillation at 70°C was carried out. In this step,

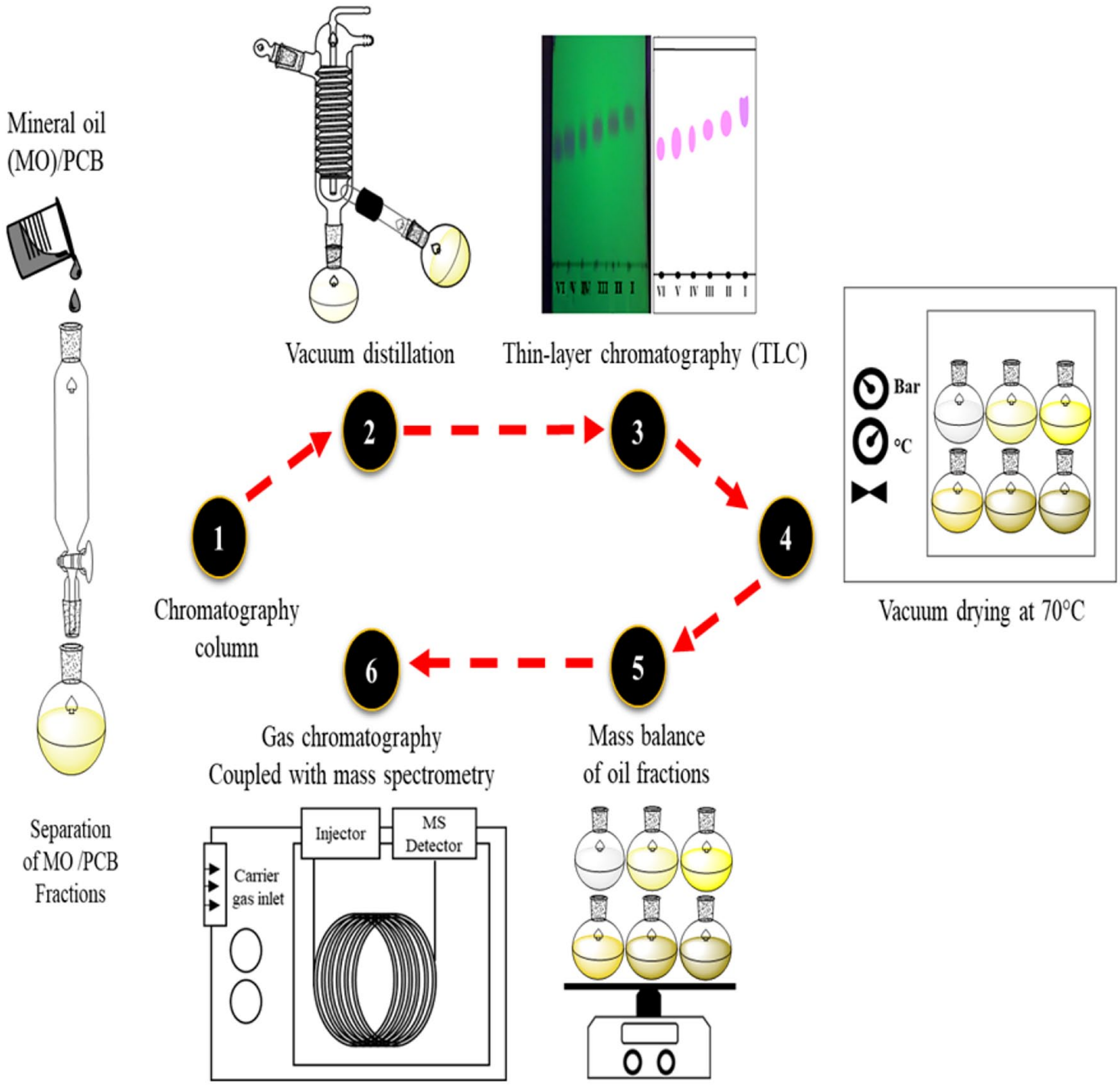


Figure 3. Chromatographic separation process of MO/PCB mixtures.
MO: mineral oil; PCB: polychlorinated biphenyl.

the organic solvents (petroleum ether and acetone) were vaporized and then recycled by condensation.

During the different steps of chromatographic separation, TLC analysis was systematically applied. It should be mentioned that the concentration effect of the deposited stains could hide the appearance of other fractions. Once distilled, the fractions were dried in a vacuum oven at 70°C to remove the traces of solvent. The penultimate step consists in elaborating the mass balance. The mass of *MO virgin*/PCB introduced into the column and then separated must correspond to the sum of the masses of the MO/PCB fractions (Σ *m* MO/PCB ≈ Σ mass of the MO/PCB fractions). This mass balance allowed to approve this protocol. The last step represents the most important one and it consists of studying the fractions containing PCBs by GC-MS analysis.

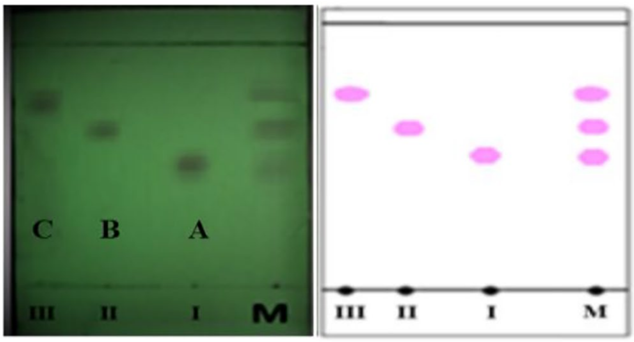
TLC and SCC of MO/PCB mixtures

To check for the feasibility of the separation protocol for MO/PCB mixtures, TLC analysis was performed on three pure PCBs, PCB N°0 (non-chlorinated biphenyl), PCB N°15, which has two chlorines in para position, and PCB N°209, the most chlorinated congener (10 chlorines) of the PCB family. It can be seen that the stain of PCB N°0, that is, in the absence of chlorines, migrates less quickly than the stains of PCB N°15 and PCB N°209. It can be deduced that the migration of PCBs on the thin silica layer is not related to the molecular weight of the PCB species, but rather to the polarity of the solvent and the interactions of the chlorines with the stationary phase. The chosen mobile phase (petroleum ether–acetone solvent mixture) is apolar: increasing the polarity of the PCB compound due to further chlorination leads to an increase in the migration rate. The results of the calculation of R_f values of PCBs N°0, N°15 and N°209 were found to be 0.55, 0.65 and 0.75, respectively (Table 1).

Similarly, *MO virgin*, MO/PCB N°0 and MO/PCB N°209 mixtures were fractionated by SCC and then qualitatively analysed by TLC. As a result, *MO virgin* presents three fractions, whereas the other two samples exhibit each four fractions. Calculation of R_f of all samples was subsequently performed.

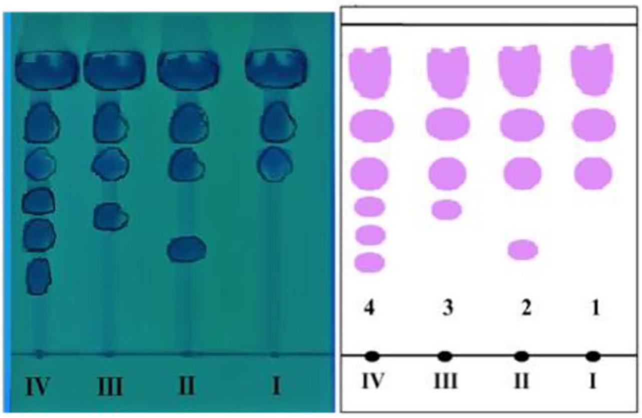
Table 1. Results of TLC analysis of MO/PCB systems.

Analysis of PCB



M – Mixture of PCBs N°0, 15 and 209
A – PCB N°0
B – PCB N°15
C – PCB N°209

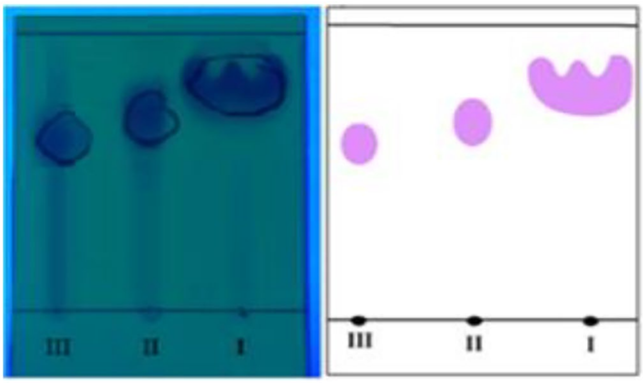
Before the separation of MO/PCB systems



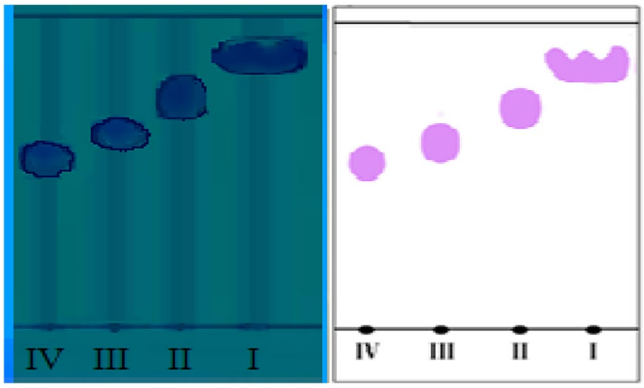
1 – *MO virgin* (MO)
2 – MO/PCB N°0
3 – MO/PCB N°209
4 – *MO contaminated* (unknown sample)

Control of the separated fractions of MO/PCB systems

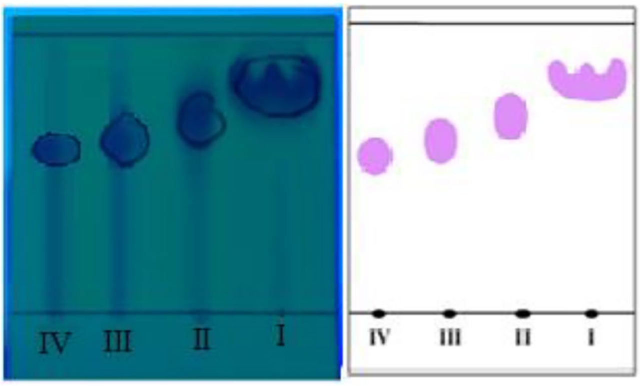
1 – *MO virgin* (MO)



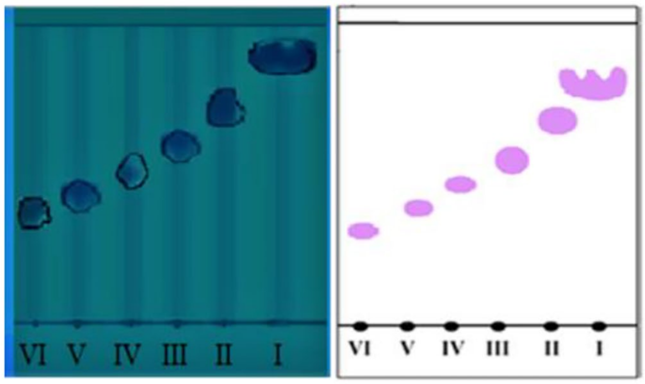
2 –MO/PCB N°0



3 – MO/PCB N°209



4 – *MO contaminated*



MO: mineral oil; PCB: polychlorinated biphenyl; TLC: thin layer chromatography.

The corresponding results of fractions 1, 2, 3 of *MO virgin* were found to be 0.98, 0.92 and 0.89, respectively. As expected, the same data were obtained for the MO part of the MO/PCB N°0 and MO/PCB N°209 mixtures. Moreover, the retention factors of the forth fractions yield almost the same values as those calculated for PCB N°0 and PCB N°209.

The MO compounds (paraffins, naphthenes, etc.) present a more polar character than PCBs, thus explaining that they were less retained by the stationary phase compared to PCBs, which migrate more slowly.

The unknown sample (*MO contaminated*) was also studied by the same chromatographic separation process, showing six fractions (Table 1). Further analysis by GC-MS was needed on the three fractions that do not belong to *MO virgin*, to detect, distinguish and quantify PCBs present in this mixture.

Detection and identification of PCBs in MO by GC-MS. To obtain accurate information on the qualitative and quantitative identification of individual PCBs by GC-MS, detailed analysis of model systems based on a series of 18 PCB compounds was undertaken. This preliminary study comprised an establishment of discrete calibration data for each PCB molecule as a function of concentration, and also investigation of detection limits, which were found around 2–3 ppm per PCB molecule.

The concentration of each PCB molecule in the model mixture is mentioned on the associated chromatogram. For example, in the case of the concentration of 100 ppm, the total PCB concentration is as follows: 100 ppm × 18 = 1800 ppm = 0.18 wt-%.

It will thus be demonstrated that the proposed chromatic separation method allows to determine the nature and concentration of PCB molecules far below the actual 50 ppm limitation of PCB content in transformer fluids. It will also be shown later (Table 2) that the retention times of PCB molecules obtained by GC remained constant comparing those from model PCB blends with those from PCB-containing fractions separated from MO/PCB mixtures by SCC.

Subsequently, model mixtures comprised of 18 PCB molecules (indicator PCBs, listed in Table 2) were prepared at different concentrations (10, 25, 50, 100, 150 and 200 ppm). For example, in the case of the concentration of 25 ppm, the total PCB concentration of the sample is as follows: 25 ppm × 18 = 450 ppm = 0.045 wt-%. The chromatograms of some of these PCB mixtures (25, 50 and 100 ppm) are shown in Figure 4, and the mass spectra associated with each molecule exhibiting specific retention times are shown in Figure 5. This method allowed detection, separation and identification of PCB molecules from model mixtures with different concentrations of PCBs, and also of PCB fractions separated from MO/PCB systems (Figure 6), by comparing the obtained retention times with those of injected PCB molecules (standards) and also with data retrieved from an electronic library (NIST/EPA/NIH Mass Spectral Library (NIST 14)).

Since PCB compounds possess similar chemical structures and differ only in the degree of chlorination, their vapour pressure was found directly proportional to the retention time on stationary phases of non-polar GC columns such as the one used in this report (Ballschmiter et al., 1993; Chamkasem et al., 2016). The molecular interactions of the PCB molecules with the stationary phase are thus governed by van der Waals forces (dispersive interactions). In addition, there are other effects affecting the separation of PCB on GC columns, like steric effects influencing the shape of the molecules, and dipole–dipole interactions.

The increase in the order of the separated PCBs in terms of the retention time followed essentially structure–retention relationships described in the literature (Li et al., 2016). For example, the shortest retention time of 7.6 minutes was observed for the unsubstituted biphenyl (PCB N°0), whereas the longest retention time of 34.6 minutes was found for the fully chlorinated PCB N°209. It can be seen that the chromatographic method applied also allowed the separation by GC of PCBs possessing the same number of chlorines, such as PCB N°4, N°5, N°7, N°12, N°14 and N°15 (Table 2).

The capacity (k') and selectivity (α) factors of PCBs calculated from their normal (t_R) and reduced (t_R') retention times allow to describe the rate of progression of PCB in the chosen stationary phase and to estimate the extent to which the latter can separate them. Indeed, three situations have to be distinguished (Chamkasem et al., 2016): $k' < 1$: elution is too fast, which is the case for PCBs N°0 and N°1; $1 < k' < 5$: optimal elution for PCBs N°2, N°4, N°5, N°7, N°12, N°14, N°15, N°28, and N°52; $k' > 5$: elution is too slow for PCBs N°77, N°101, N°138, N°153, N°156, N°180 and N°209. The obtained capacity factors can be directly related to the chemical structures of the PCBs, determining the molecular interactions with the non-polar stationary phase. Absence of chlorines will thus lead to a high elution rate ($k' < 1$) as it is the case for PCB N°0, which represents an apolar neutral molecule. The presence of only one chlorine in the ortho position already increases k' from 0.53 (PCB N°0) to 0.96 (PCB N°1), close to 1 (case of optimal elution). In the case of PCB molecules with an adjacent k' factor >5, the number of chlorine varies between 4 and 10. Indeed, these relatively high numbers generate more molecular interactions between PCBs and the stationary phase. These 'heavy' indicator PCBs, exhibiting long retention times, represent good separation characteristics on the GC column.

The selectivity factor α (ratio of the distribution coefficients) was calculated in relation to the peaks of neighbouring PCBs. This factor makes it possible to estimate the separating power of the used column. It was found that α values of low-chlorinated PCBs were slightly higher compared to the corresponding data of highly chlorinated compounds; this is probably related to the mass effect of the PCBs which depends essentially on the number of chlorines.

The efficiency of the chromatographic column, which is directly proportional to the number of theoretical plateaus (N), depends on the degree of peak broadening of PCB peaks (ω), occurring when the PCB compound moves through the column. This broadening depends on the residence time of each PCB molecule. The resolution of the column (Rs) was also calculated to

Table 2. Retention parameters for PCB molecules from model mixtures (mod) and separated PCB fractions (sf) from MO/PCB mixtures.

Type of PCB	t_R (minute)	t_R' (minute)	k'	á	ù	N	Rs
	Retention time mod/sf	Reduced retention time mod/sf	Capacity factor mod/sf	Selectivity factor mod/sf	Width of the base peak mod/sf	Number of theoretical plates mod/sf	Column resolution mod/sf
PCB N°0	7.63/7.62	2.63/2.58	0.53/0.51		0.29/0.28	11468/11850	
PCB N°1	9.88/9.84	4.84/4.8	0.96/0.95	1.83/1.86	0.18/0.17	46905/50586	9.31/9.76
PCB N°2	11.88/11.83	6.88/6.79	1.38/1.35	1.43/1.41	0.20/0.20	53734/55979	10.78/10.61
PCB N°4	13.67/13.59	8.67/8.55	1.73/1.70	1.26/1.26	0.31/0.30	31112/32615	6.95/7.03
PCB N°5	16.02/15.90	11.02/10.86	2.20/2.15	1.27/1.27	0.62/0.58	10546/1024	5.03/5.24
PCB N°7	17.92/17.75	12.92/12.71	2.58/2.52	1.17/1.17	0.41/0.39	29833/32973	3.66/3.81
PCB N°12	19.76/19.59	14.76/14.91	2.95/2.89	1.14/1.14	0.46/0.43	28893/33054	4.18/4.48
PCB N°14	23.47/23.24	18.47/18.2	3.69/3.61	1.25/1.25	0.51/0.50	33885/34019	7.61/7.81
PCB N°15	24.68/24.34	19.68/19.3	3.94/3.83	1.07/1.06	0.63/0.62	24554/24344	2.12/2
PCB N°28	28.07/28.05	23.07/23.01	4.61/4.57	1.17/1.19	0.14/0.14	599610/651562	8.75/9.72
PCB N°52	29/29.01	24/23.97	4.8/4.76	1.04/1.04	0.13/0.12	861184/919696	6.89/7.38
PCB N°77	30.47/30.46	25.47/25.42	5.09/5.04	1.06/1.06	0.13/0.13	815075/865041	11.31/11.5
PCB N°101	30.93/30,93	25.93/25.89	5.19/5.14	1.02/1.09	0.17/0.13	499809/919814	2.97/3.61
PCB N°138	31.46/31.32	26.46/26.28	5.29/5.21	1.02/1.02	0.11/0.11	1197407/1297113	3.66/3.59
PCB N°153	31.74/31.70	26.74/26.66	5.35/5.28	1.01/1.01	0.12/0.12	1031606/1062743	2.33/3.60
PCB N°156	32.22/32.20	27.22/27.16	5.44/5.39	1.02/1.02	0.14/0.14	789034/822725	3.41/3.77
PCB N°180	32.41/32.38	27.39/27.34	5.48/5.42	1.01/1.01	0.12/0.12	1057306/1091013	1.49/1.35
PCB N°209	34.60/34.58	29.6/29.56	5.92/5.85	1.08/1.08	0.14/0.13	1051005/1098049	16.93/17.19

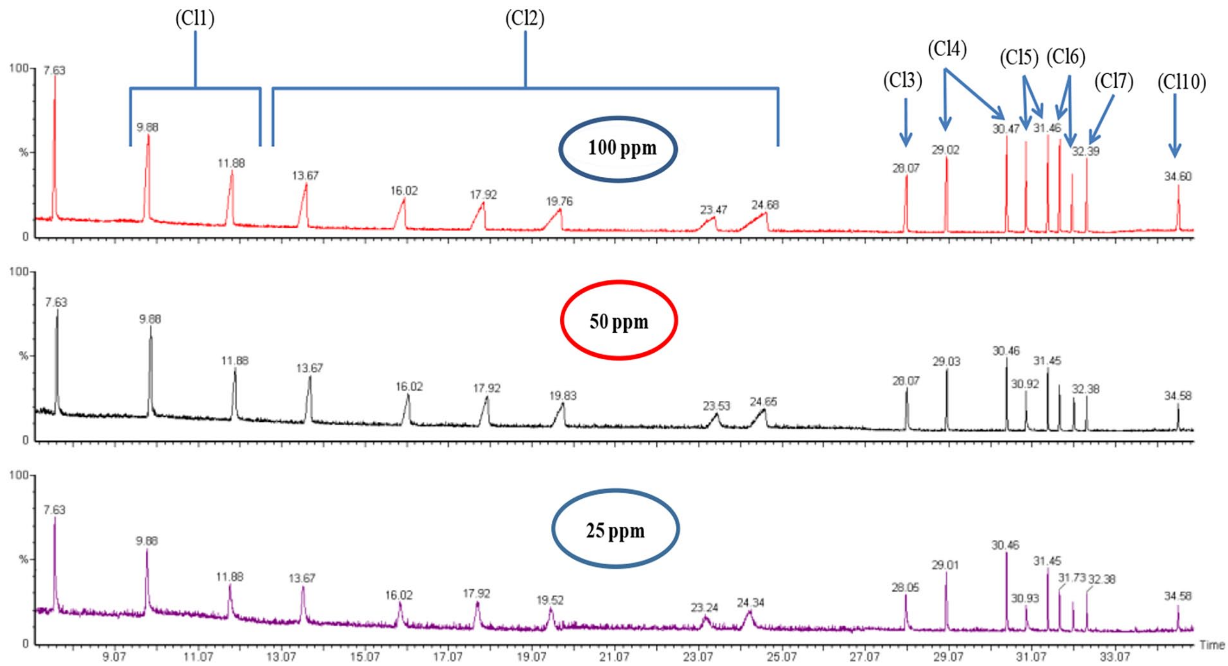
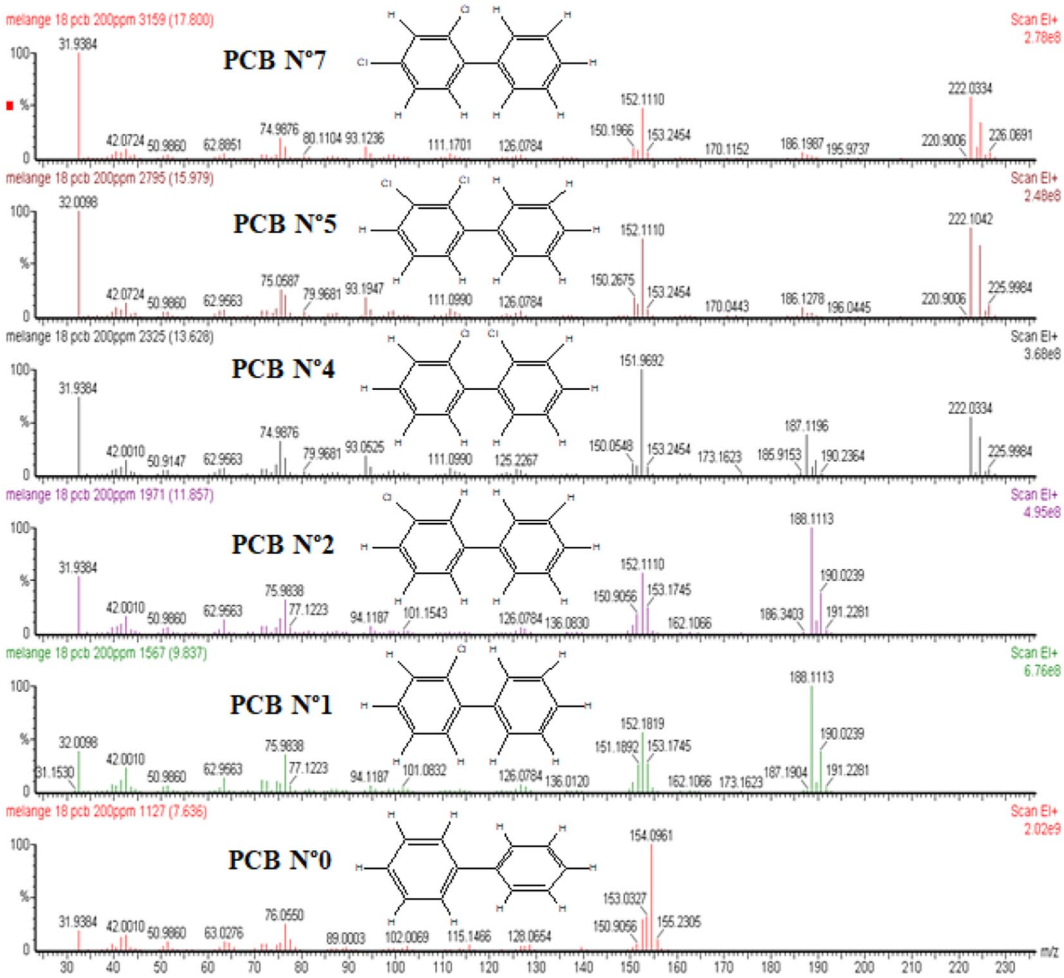


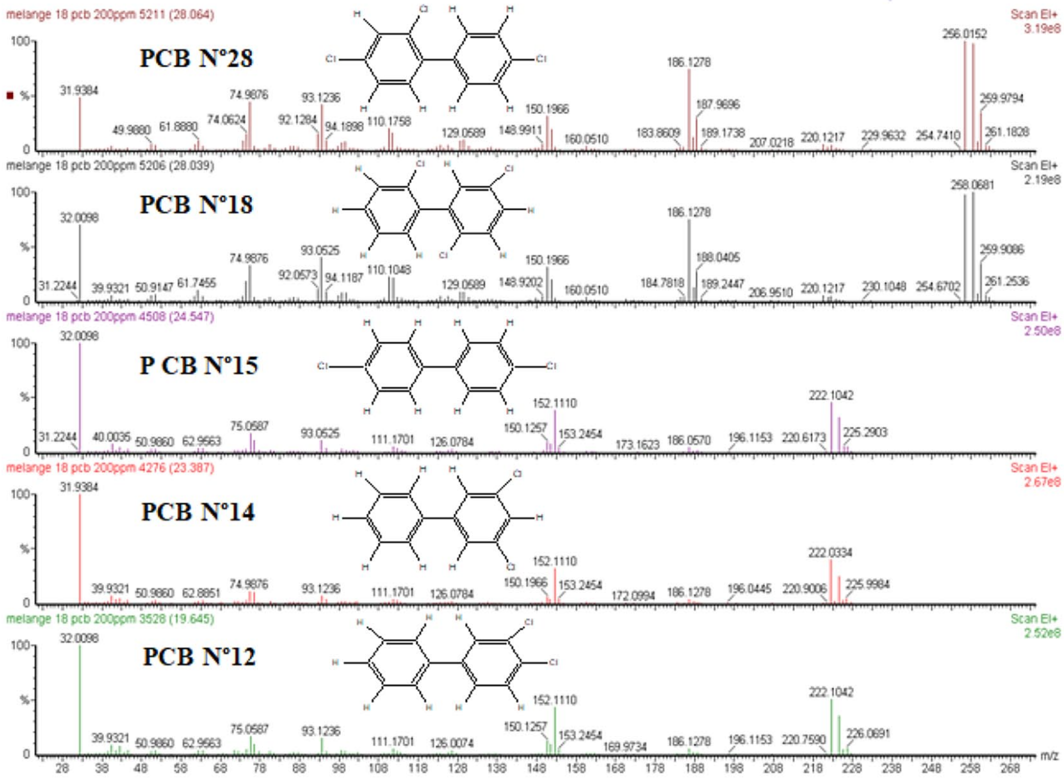
Figure 4. GC chromatograms of model mixtures including 18 PCBs with different concentrations.
GC: gas chromatography; PCB: polychlorinated biphenyl.

measure the ability to separate PCBs that have neighbouring peaks. Three situations were highlighted (Table 2): If Rs > 1.5, neighbouring PCBs were completely separated; the situation Rs ≈ 1 corresponds to incomplete separation of adjacent PCBs, and if Rs < 0.75, bordering PCBs were poorly separated. The results shown in Table 2 of the Rs calculated from PCB model mixtures and separated PCB fractions from MO/PCB blends confirm the correct choice of the stationary phase of GC.

It can be deduced that all the results obtained from the model mixture (18 PCB molecules) and the PCB fraction separated from the model MO/18 PCB blend were almost identical, thus approving the separation method described here.

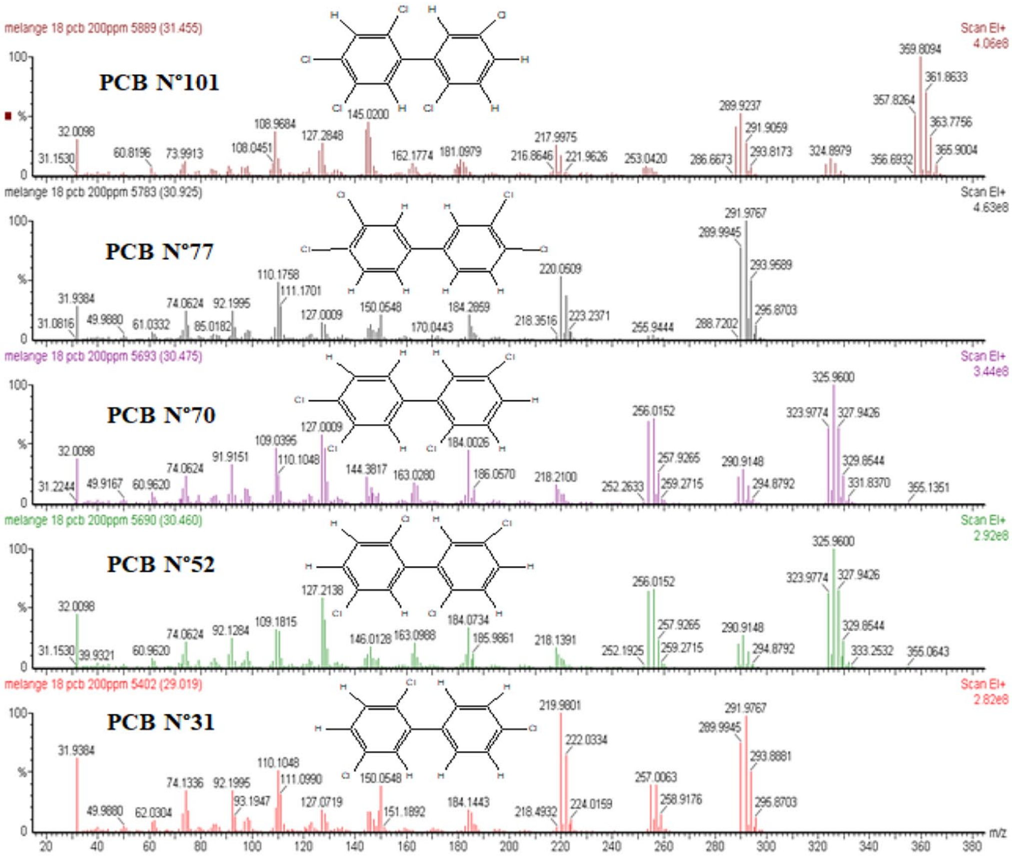


(a)

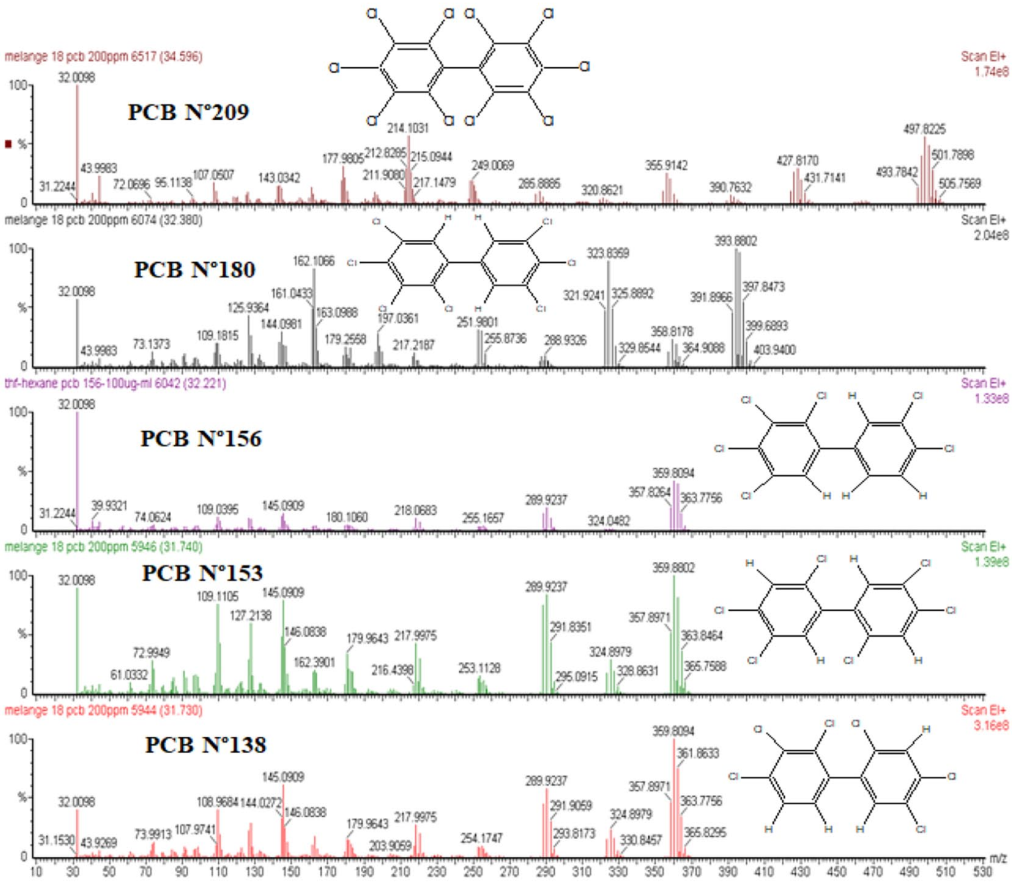


(b)

Figure 5. (continued)



(c)



(d)

Figure 5. Mass spectra of the 18 PCBs separated from the model mixture: (a) PCBs N°1, 2, 3, 4, 5, 7; (b) PCBs N°12, 14, 15, 18, 28; (c) PCBs N°31, 52, 70, 77, 101; and (d) PCBs N°138, 153, 156, 180, 209.
PCBs: polychlorinated biphenyls.

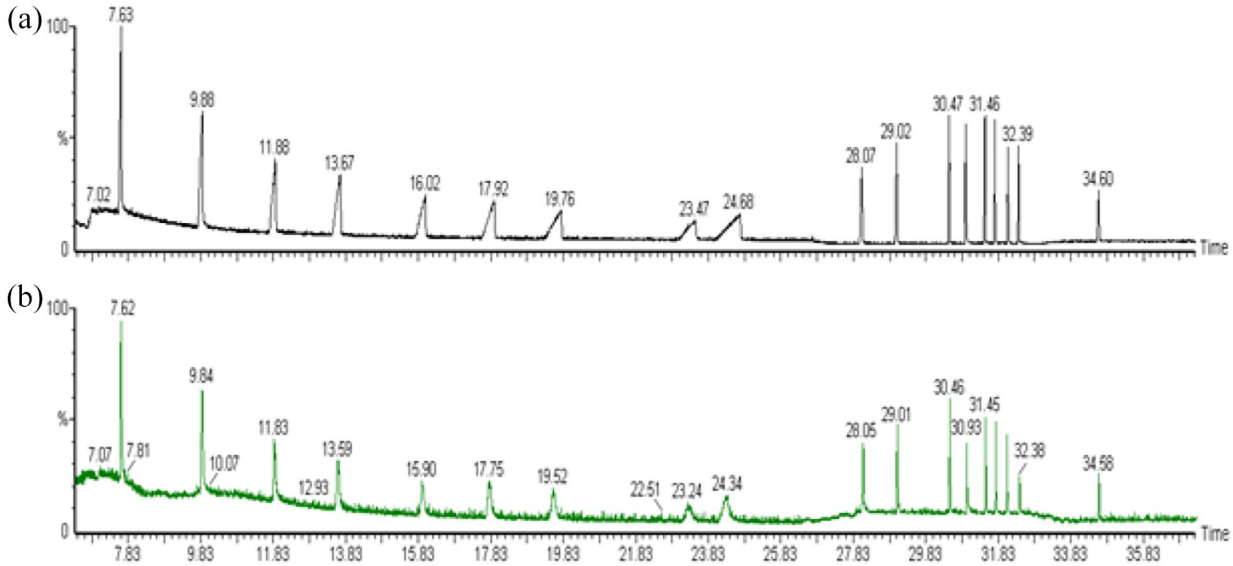


Figure 6. GC chromatograms obtained from (a) a model mixture of 18 PCB congeners (200 ppm) and (b) the PCB fraction separated from the model MO/18 PCB blend via SCC.
GC: gas chromatography; MO: mineral oil; PCB: polychlorinated biphenyl; SCC: silica column chromatography.

The correlation coefficients of the PCBs calibration curves (Supplemental Figure S1) show a good linearity (between 0.992 and 0.999). The LOD and LOQ values were determined from the data of the calibration curves of PCBs (Table 3). These values confirm the reliability of the separation method described above, showing that the pre-treatment used is consistent for complex matrices such as transformer oils.

The chromatographic separation procedure described above was also applied on a sample denominated *MO contaminated*, containing unknown number and quantities of PCBs. In particular, fractions F4–F6 were analysed (Figure 7), which do not belong to *MO virgin*. The results in terms of identified and quantitatively determined indicator PCBs are presented in Table 4. The concentrations of the different PCB congeners were determined using multiple calibration curves, following the same procedure as mentioned above. It can be seen that the concentration of PCBs in *MO contaminated* greatly exceeds the limit imposed by current legislation (50 ppm PCB), with a total PCB concentration of 219 ppm. The results presented in Table 4 correspond to the analysis of fraction F6, which contains qualitatively the same indicator PCB molecules but at their highest concentration, compared to the other fractions F4 and F5.

Table 3. Linearity, LOD and LOQ obtained for each PCB calibration curve.

PCB	Linearity	LOD (ppm)	LOQ (ppm)
PCB N°0	0.997	9	30
PCB N°1	0.988	15	45
PCB N°2	0.999	4	14
PCB N°4	0.998	7	2
PCB N°5	0.996	10	32
PCB N°7	0.995	13	40
PCB N°12	0.999	5	17
PCB N°14	0.997	10	30
PCB N°15	0.998	7	22
PCB N°18	0.995	12	38
PCB N°28	0.999	2	7
PCB N°31	0.992	13	40
PCB N°52	0.998	7	21
PCB N°70	0.999	6	17
PCB N°77	0.999	6	17
PCB N°101	0.995	11	35
PCB N°138	0.999	2	7
PCB N°153	0.994	13	39
PCB N°156	0.999	3	10
PCB N°180	0.995	12	38
PCB N°209	0.993	14	45

LOD: limit of detection; LOQ: limit of quantification; PCB: polychlorinated biphenyl.

Conclusion

A new, simplified and efficient method for separating PCB molecules from contaminated transformer MOs was established, allowing to identify these toxic molecules and to determine their concentrations. A chromatographic separation method by silica column was developed and applied on model systems composed of known quantities of PCB molecules mixed with PCB-free MO. An unknown sample of PCB-contaminated MO was investigated as well. GC-MS was applied as a powerful analytical technique to evaluate the efficiency of the separation method in terms of the qualitative and quantitative analyses of the different PCB-containing fractions. Indeed, these data confirmed the reliability and efficiency of the proposed separation process.

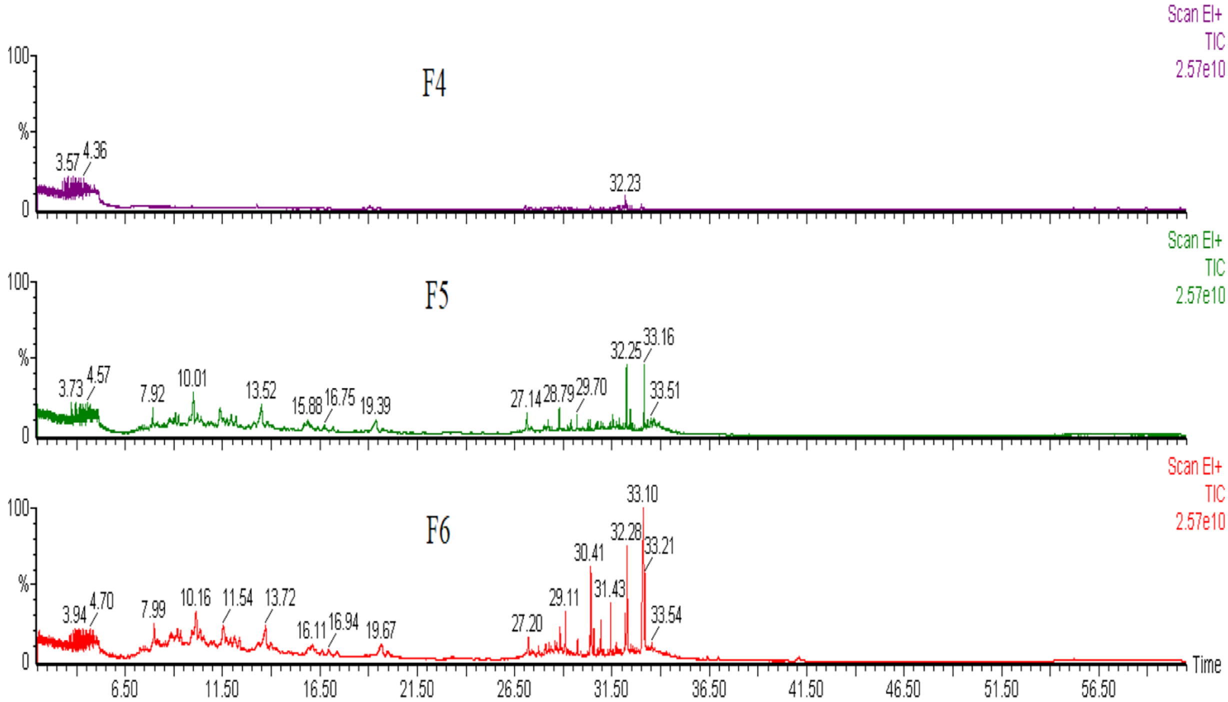


Figure 7. GC chromatograms corresponding to the fractions 4–6 (F4, F5 and F6) of a sample containing an unknown number and quantity of PCBs (*MO contaminated*).
GC: gas chromatography; MO: mineral oil; PCBs: polychlorinated biphenyls.

Table 4. Identification and quantification of *indicator PCBs* detected in the unknown *MO-contaminated* sample. The results presented here correspond to the analysis of fraction F6.

Type of indicator PCB	t_R (minute)	Concentration (ppm)
PCB N°156	32.36	52
PCB N°138	31.44	27
PCB N°77	29.1	42
PCB N°52	28.01	23
PCB N°31	24.56	10
PCB N°12	19.67	13
PCB N°7	16.11	7
PCB N°4	13.7	9
PCB N°2	11.8	8
PCB N°1	10.1	13
PCB N°0	7.9	11

MO: mineral oil; PCBs: polychlorinated biphenyls.

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ORCID iDs

Chems Eddine Gherdaoui https://orcid.org/0000-0001-9915-0022
Philippe Supiot https://orcid.org/0000-0003-0352-6422
Ulrich Maschke https://orcid.org/0000-0001-7970-1966

Supplemental material

Supplemental material for this article is available online.

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