SPME EXTRACTION OF THE PCB'S CONTAINING TRANSFORMER OILS

Constantin TOADER[1], Nicoleta GRIGORIU[2], Aurelia MEGHEA[3]

Lucrarea prezintă o metodă de determinare de înaltă rezoluție a bifenililor policloruraţi, utilizaţi ca aditivi ai uleiurilor de transformator, cunoscute drept matrici complexe. Metoda analitică este reprezentată de tehnica GC-MS. În vederea creşterii performanţelor analitice privind detecţia şi separarea compuşilor de interes s-a propus o metodă de preconcentrare bazată pe microextracţia în fază solidă, urmată de purificarea prin adsorbţie pe fluorisil. S-a demonstrat că metoda propusă este mai rapidă, mai eficientă şi versatilă în comparaţie cu alte procedee.

This paper aims to establish a high resolution method for determination of polychlorinated biphenyls used as additives in transformer's oil, known as complex matrices. The method applied for this purpose was hyphenated technique CG-MS. In order to increase the analytical performance in detection and separation of compounds of interest, a preconcentration method based on solid phase microextraction followed by a clean-up fluorisil adsorbtion has been proposed. It was demonstrated that the proposed method is faster, more efficient and versatile as compared to other procedures.

Keywords: Polychlorinated biphenyl (PCB), solid phase microextraction, Gas Chromatography with Mass Spectrometry (GC/MS), fluorisil

1. Introduction

For many reasons polychlorobiphenyl's (PCB's) are considered among the most hazardous chemicals, both for environment and health [1, 2]. They are very persistent, this characteristic meaning a low biodegradability and high level of bioaccumulation. During slow PCB's degradation, the secondary products formed possess an increased toxicity as compared to parent molecules. PCB's can induce cancer and different malformations by inhalation or skin absorption [3]. For these reasons they are considered as main contaminants having low exposure limits [3-4] and their production at macro industrial scale is forbidden in Japan since 1970, in US since 1977, in France since 1983 [2]. As a consequence, many advanced methods have been developed for monitoring their emissions, and adequate

[1] Eng., Scientific Research Centre of CBRN & Ecology, Bucharest, Romania
[2] Eng. Ph.D., Scientific Research Centre of CBRN & Ecology, Bucharest, Romania
[3] Professor, Department of Applied Physical Chemistry and Electrochemistry, University POLITEHNICA of Bucharest, Romania, e-mail: a.meghea@gmail.com

destruction techniques have been proposed. Since such type of pollutants are present in very complex matrices and at very low concentrations (of micrograms or nanograms per liter), a high sensitivity of the method to be used is necessary. Concerning their physical properties it should be mentioned that PCB's are oil form liquids with high density and viscosity and very low electrical conductivity associated with high thermal stability [5]. These properties determine their use in different industrial applications, particularly as components of transformer dielectric fluids [2].

The aim of this work consists in determination of PCB's content in transformer oil by using a high resolution technique coupled with a preconcentration method based on solid phase microextraction (SPME) of the compounds of interest.

Knowledge of this information is very important for assurance of electric power in conditions of operator's autonomy and terrestrial isolation.

2. Experimental

2.1. Calibration procedure

Transformer oils have a PCB's content comprised between 0 and 60%.

For the quantitative determinations prior the analysis, the calibration curve should be obtained by using standard solutions of known concentrations. The initial mixture contains several PCB's isomers with two, three and four chlorine atoms.

Five reference solutions were prepared as follows: stock solution 1 contained 0.6798 g PCB in 25 mL of hexane; other four solutions needed for calibration were prepared by successive dilutions starting from stock solution 1. The obtained calibration curve is presented in Fig. 1.

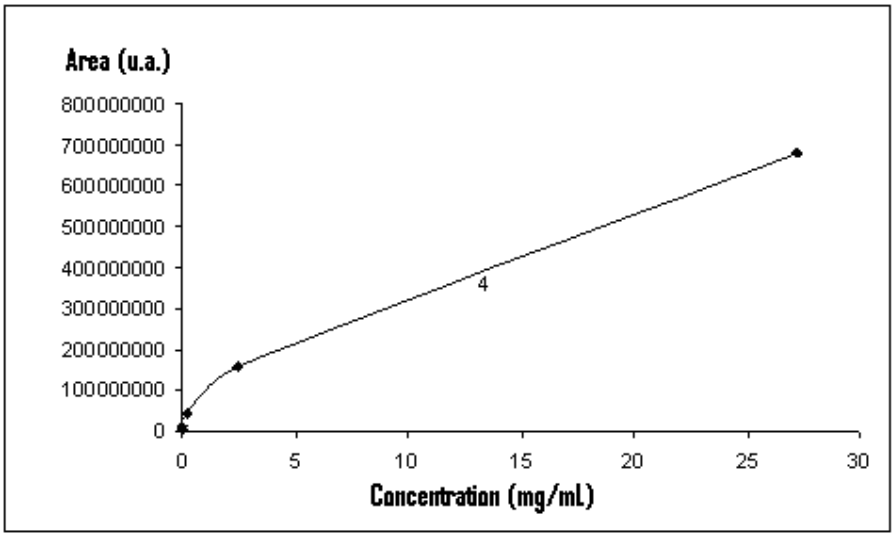


Fig. 1. Calibration curve for determination of PCB concentration

2.2. Analytical equipment and experimental parameters

Organic pollutants determination by GC/MS hyphenated method assumes adopting a specific strategy for identification which is dependent on the sample matrix and its concentration level. Thus, if the studied compounds are present in the separated samples at concentrations higher than 1 μg/mL then we can operate at low resolution mass-spectrometry (LR/MS) conditions in the ionization modes EI and CI. When the compounds under analysis are present in complex matrices at 0.01 – 1 μg/mL concentrations it is necessary to use the ionization mode SIM, high resolution mass-spectrometry (HRMS) and tandem MS-MS.

A gas chromatograph/mass spectrometer [6] Varian Saturn 3900/2100T type was used in these experiments. The gas chromatograph is provided with a split-splitless system with Factor Four VF-5ms capillary column, d_I = 0.25 mm, L = 30 m, stationary phase film = 0.25 μm.

The working temperature range on column was 60^{o}C (1 min) – 15^{o}C/ min – 300^{o}C (13 min). Injector temperature has 250 ^{o}C. Helium gas ultra pure quality 6.0 with split 2 mL/min for 4 min, after 25 mL/min has been used.

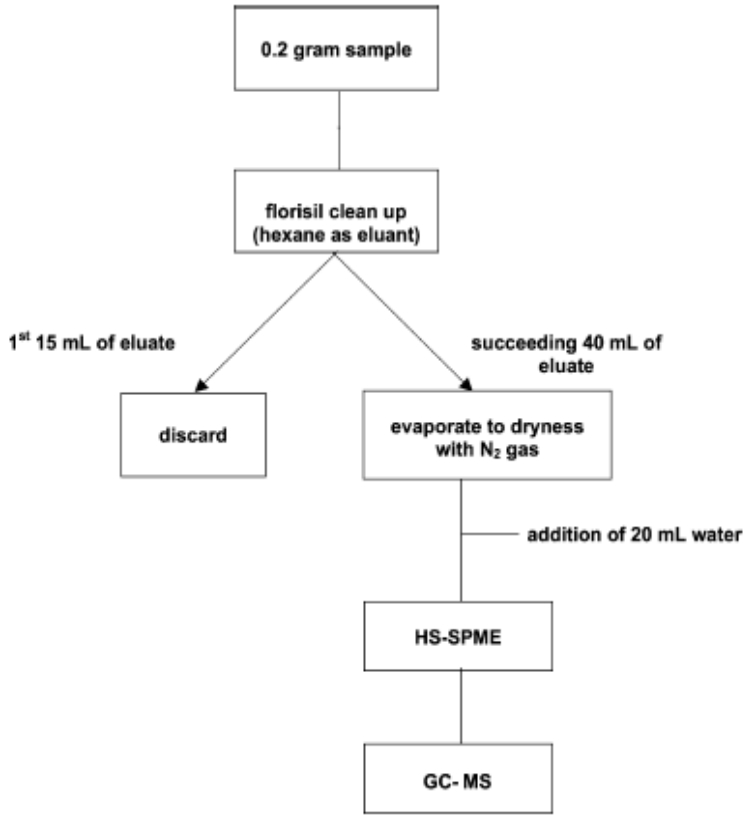
For each calibration solution and for experimental samples the same volume (1μL) was injected in the vaporization head of GC-MS coupling. Corresponding chromatograms were obtained working on the same sensitivity of apparatus (10 pg/μL i.e. 0.01 ng/L referring to hexachlorobenzene).

2.3. Extraction method of the PCB's from the transformer oils

The fluorisil cartridge [8] has been conditioned with 15 mL of n-hexane. Amounts of 0.2 grams of the oil samples that contain PCB's are past through the cartridge and 1.5 mL of n-hexane was added for the homogeneity of the mixture. The analyts of interest were eluated with 40 mL of n-hexane. Two types of fibers have been used for the SPME extraction [7], polydimethylsiloxane-divinilbenzene (PDMS-DVB) of 65 μm and polydimethylsiloxane (PDMS) of 100 μm. Each fiber was conditioned in accordance with the tehnical specifications.

The collected sample from the fluorisil cartridge was dried in a slow nitrogen stream, and then 20 mL of ultrapure water has been added. The solution was heated at 90^{o}C for 40 minutes. The SPME fiber was introduced through the vessel cap in the space untill the liquid (headspace) for adsorption of the analyt of interest for 30 minutes.

The main steps of the SPME extraction [9] method are shown in the scheme 1.



Scheme 1. The SPME extraction of the PCB's containing transformer oils

3. Results and discussion

The GC total ion chromatogram of the original oil sample is compared to the same sample that was subjected to the new extraction method, and the result was shown in Fig. 2. One can observe the efficiency of the method used from this image, as the masked compound are clearly removed from the original sample and the interest analyts are detected and identified by the existing library spectra.

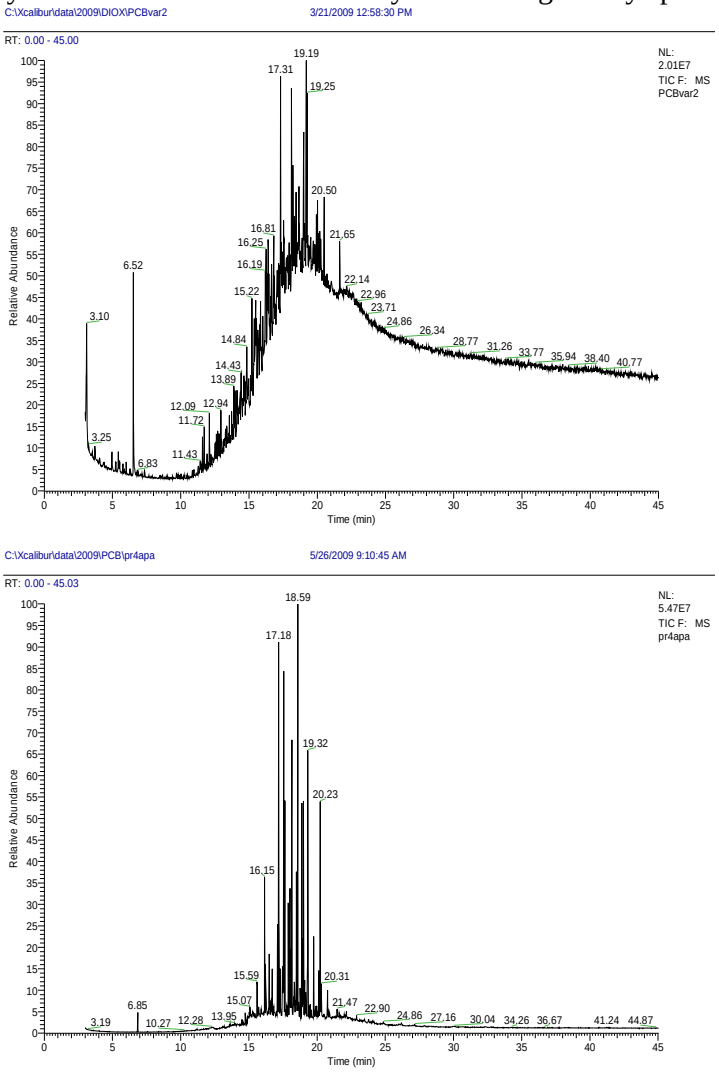


Fig. 2. The original oil sample, untreated (upper chromatogram) and the purified sample (lower chromatogram)

The comparison of the PCB's from the transformer oil sample with the PCB's standard solution can be seen in Fig. 3.

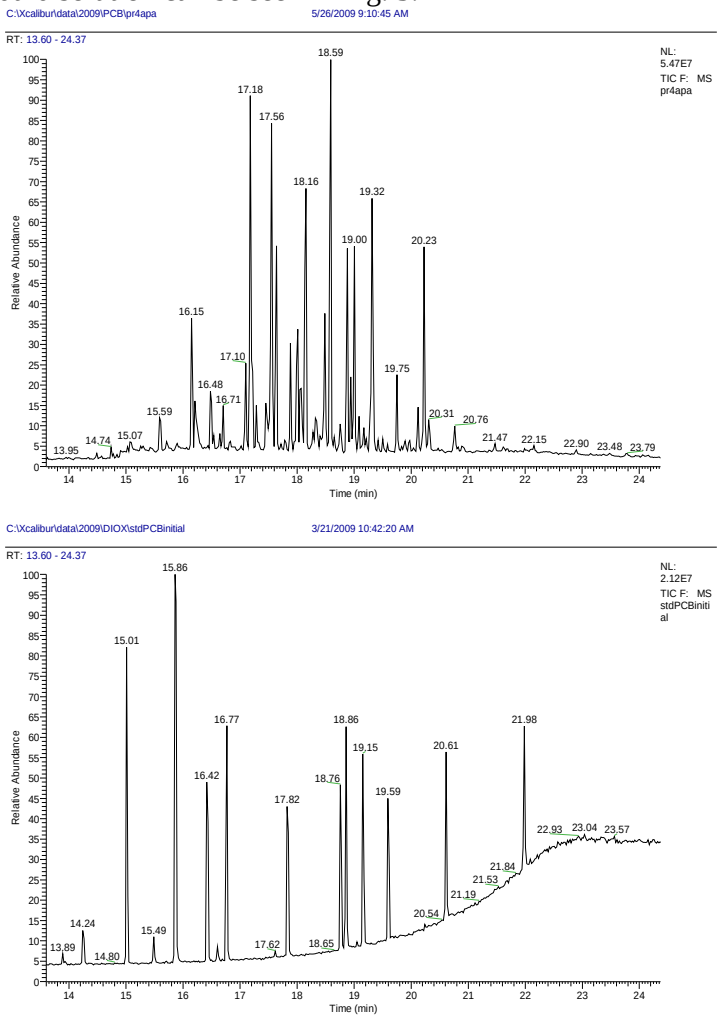


Fig. 3. The PCB's from the SPME extraction compared to the PCB's standard solution

By various experiments, the SPME extraction method was optimized and the best results were obtained in case of the PDMS-DVB fiber. The PCB's recovery rates are substantially improved in the above mentioned fiber type. The ultra-pure solvents used in the preparation stages of the samples and different parameters of the analytical instrument used conducted to higher desorption degree of the analyts of interest. The optimum conditions were reached at 260 ^{o}C in the chromatograph injection valve for 3 minutes of fiber adsorption.

The validation of the developed method consisted in testing a transformer oil blank sample and comparing to a matrix contaminated with PCB's. The detection limit was evaluated using repeatable seven analyses at a 20 - 100 ng/g spiking level of the transformer oil.

The data regarding the recovery degree of the PCB's after the extraction method are presented in the table 1.

Table 1

Recovery degree of the PCB's

PCB	Certified values of PCB's (µg/kg)	Experimental value of PCB's (µg/kg)	Recovery degree (%)
Dichlorobiphenyl	68 ± 8	88	129
Trichlorobiphenyl	149 ± 21	153	102
Tetrachlorobiphenyl	372 ± 18	418	112
Pentachlorobiphenyl	460 ± 40	408	89
Hexachlorobiphenyl	940 ± 40	1054	112
Heptachlorobiphenyl	282 ± 23	305	208

The preconcentration by SPME method developed for PCB's detection by GC/MS technique has been proven to be a faster, more efficient and versatile as compared to other existing procedures. The advantages of this method are:

- is faster – it reduces the preparation time of the samples to about 70%;
- is efficient and reusable – the fibers can be reused for more than 100 extractions;
- is cost effective – the solvent consumption is minimal;
- is versatile – can be adaptable for all GC and HPLC systems.

4. Conclusion

The concentration determination of the PCB's containing samples and also the identification of the different types of the PCB's was performed by the GC/MS technique coupled with SPME pre-concentration. The spectra libraries used in the identification of the compounds were represented by NIST and WILEY.

A new extraction technique based on the *solid phase microextraction* (SPME), followed by a clean-up on fluorisil adsorbant has been successfully developed. This is an efficient analysis method, with low consumption of solvents, low experimental time, without any diminuation in the accuracy and the precision of the method.

It was demonstrated that the SPME extraction method seems to be a faster, more efficient and versatile method for PCB's determination by GC/MS technique compared to the existing procedures.

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