ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
MATHEMATICS, PHYSICS, THEORETICAL MECHANICS
FASCICLE II, YEAR XIV (XLV) 2022, No. 1
DOI: https://doi.org/10.35219/ann-ugal-math-phys-mec.2022.1.06

Application of the gas-chromatographic analysis method for the characterization of oils in high capacity industrial electrical equipment

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Abstract
The article aims to highlight one of the highest environmental issues, caused by pollution with persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs). This form of environmental pollution with a negative impact on human health would not be possible without the use of high voltage industrial electrical equipment with dielectric fluids infested with various PCB isomers. In order to carry out the experimental program, samples of dielectric fluids both from Romania and Indonesia were investigated. The PCBs-containing samples were characterized using GC-ECD technique, employing an Agilent 7890 gas chromatograph equipped with a 15 mCi ^{63}Ni µECD detector. PCBs concentrations were calculated using the standard calibration method based on the internal standard according to the corresponding normative documents. Ongoing work is carried out to adapt the technique for the analysis of PCBs in soils contaminated with oil products.

Keywords: persistent organic compounds, gas chromatography, industrial electrical equipment.

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are a class of 209 congeners, widely used in various applications, including dielectric fluids in transformers and capacitors, heat transfer fluids, lubricants and cutting oils, and as additives in pesticides, hydraulic fluids, paints, adhesives, etc.

The complex mixtures of PCBs were marketed between 1929 and early 1970s. Commercial names of PCBs are known by a variety of commercial names such as Aroclor (USA), Sovol (Russia), Chlophen (Germany), Phenoclor (France), Kaneclor (Japan) [1,2]. PCBs spreading in the environment represents a serious problem due to their persistent and toxic properties. Toxic effects are due to PCBs hydrophobicity, which makes them bioaccumulate in the fatty tissues of animals and humans [2, 3]. In 1999, the law on limiting PCBs concentrations in transformer and capacitors oil was changed from 50 to 2 mg/L for liquid waste.

Under the Stockholm Convention on Persistent Organic Pollutants (POPs), which entered into force on May 7, 2004, the Korean environment ministry launched a new study on the PCBs concentration in existing transformers in the national electricity circuit and an initiative to set up a transformer oil management project and remove PCBs content by the end of 2015. In view to the new regulation, the Ministry of the Environment reviewed the official waste test method by adding the quality

control concept to regulate the waste management [4]. Faced with the initiative of the South Korean state, the Indonesian state developed a program for the management of PCB-infected oils from high voltage electrical equipment, that began in 2014 and continues even today.

Germany has adopted the strictest program to remove these PCBs contaminated equipment from the national electrical system and to temporarily store it in decommissioned mines. Romania and Serbia have a common program for the disposal of oils contaminated with PCBs and decontamination of industrial transformers and capacitors. Improper storage of industrial capacitors and transformers has led to soil contamination with oils containing PCBs.

Non-compliant techniques for dismantling electronic waste have led to severe PCBs contamination of soils in China. The most polluted areas are Guiyu in Guangdong province and Taizhou in Zhejiang province. Soil is the main carrier of PCBs, and the remediation of soils contaminated with PCBs has become an urgent problem in China. Remediation technologies for PCBs removal include mainly excavation and incineration, microwave irradiation, thermal desorption, photocatalysis, oxidation or chemical reduction, and biological treatment. However, many of them have disadvantages for the reclamation of soil contaminated with PCBs. For example, excavations and incineration involve not only enormous costs, but give rise to highly toxic products [5].

A microbiological study [6] was applied to determine if PCBs in soils could be destroyed by bioremediation. Thus, different concentrations of PCB 28 were used, in a less chlorinated and more biodegradable composition. The result showed that the microbes began to develop after ten months of testing even though the number of bacteria was the lowest in the first three months. Besides the problem of soil decontamination, another problem of PCBs contamination has emerged: the decontamination of the transformer oil having a low PCBs concentration. Treating these transformation oils by classical techniques would be inappropriate from an economic point of view because, for the depletion of small amounts of PCBs, all the dielectric fluids would be destroyed. A much better way would be to clean the transformer oil so it can be reused [7].

The aim of this work was to apply the optimized gas chromatographic method with electron capture detector (GC-ECD) [2] for the quantification of PCB congeners in oil samples from high voltage industrial electrical equipment and to compare the results with the legislated norms [8].

2. EXPERIMENTAL

2.1. Sampling and sample preparation

To achieve the experimental program, oil samples particularly infested with PCBs were collected from high voltage industrial electrical equipment originating from Romania and Indonesia.

Samples of contaminated oil were taken in small containers, with appropriate tools for sampling, including chains, stoppers, as well as clean dishes, thoroughly dried to prevent contamination with foreign substances or materials. Individual samples (samples from the middle, bottom and surface) were put in glass tubes and the mixed parts formed a composite sample, which was appropriately labeled and sent to the laboratory of SETCAR SA Braila, Romania.

The temperature of the environment in which samples are stored during transport in the laboratory should be between 1 and 5 °C, in the absence of sunlight (storage time is normally 24 hours). Generally, for specimen preservation, it is recommended that samples to be stored at a temperature lower than -20 °C.

2.2. Equipment and reagents

For analyses, the following equipment and materials were used: Gas Chromatograph 7890 A Agilent, rotary evaporation for concentration, vacuum pump, laboratory glassware, glass receptacles for taking samples, chromatographic columns, quartz wool, purified water, acetone, solvent extraction: hexane, decane ($C_{10}H_{22}$) or dodecane ($C_{12}H_{26}$), dry alumina, alumina deactivated: alumina/silver nitrate, silica.

2.3. GC-ECD method

The oil samples prepared by Solid Phase Extraction (SPE) were characterized using GC-ECD technique [2], employing an Agilent 7890 gas chromatograph equipped with a 15 mCi ^{63}Ni µECD detector. PCBs concentrations were calculated using the standard calibration method based on the internal standard according to the corresponding normative documents.

GC determinations were made according to the working standards, depending on the matrix from which the determination is made [2,9]. It is recommended that the extraction be carried out in the sample container. At the extraction, a sample volume of 0.25 g is currently used in the case of oil samples.

The following steps were carried out:

- Extract the solvent over the sample and shake for at least 10 minutes. Transfer the contents to a separation funnel and leave to stand for phase separation. Pass the bottom aqueous phase back into the sample container.
- Repeat the extraction twice with equal portions. Dry the extract using the following procedure: pass the extract through a drying column containing 5-7 g anhydrous sodium sulfate, pre-washed with solvent and collecting the eluate. It is recommended to wash the column further with 10 ml up to 20 ml of solvent to obtain a good recovery.
- Collect the washing solvent. Purification and separation are applied to remove relatively polar substances and / or other undesirable substances that can influence the appearance of unknown peaks that overlap the polychlorinated biphenyls.

To achieve the desired results one or both of the following procedures are used: purification on a column of alumina-alumina / silver nitrate to remove polar compounds and purification on a silica gel column for the separation of polychlorinated biphenyls from most pesticides. In the case of oil samples the following procedure is performed: ~ 0.25 g of oil in a 10 ml volumetric flask is brought to the mark with extraction solvent.

The balloon passage was quantitatively transferred through the columns for purification and separation with alumina-alumina / nitrogen silver and silica gel as described above.

3. RESULTS AND DISCUSSION

After the qualitative and quantitative analysis applied by means of the gas chromatographic method, high values were recorded for contents of all the identified polychlorinated biphenyls. Figures 1 and 2 illustrate the most important PCBs congeners identified as a result of the analysis of oil samples from Romania and Indonesia, respectively.

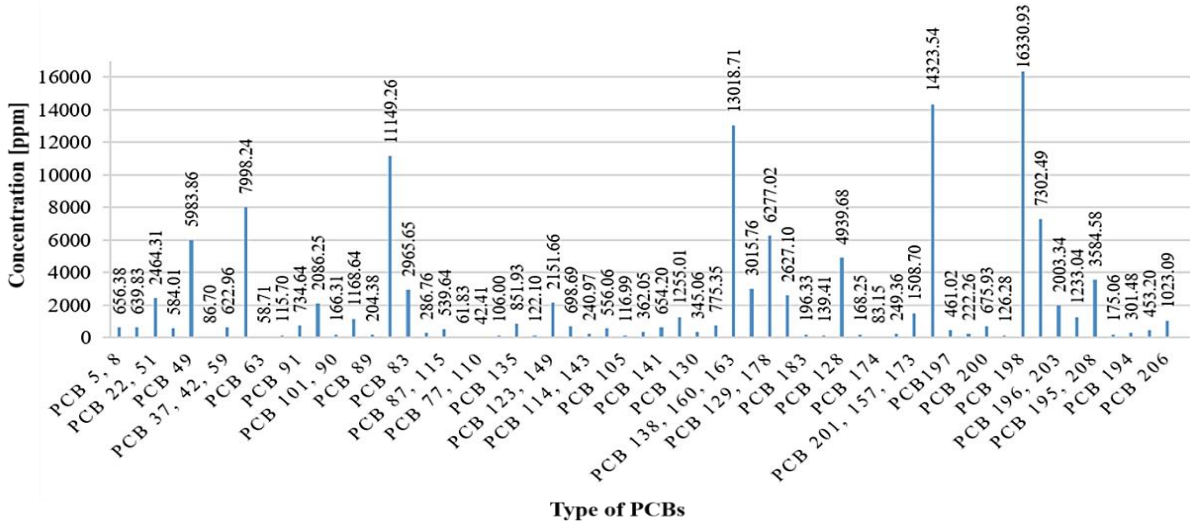

Fig. 1. The PCBs concentrations obtained for the oil sample collected in Romania

With regard to the oil sample from Romania, a total number of 84 biphenyl polychlorinated congeners were identified and, in a very large proportion, they exceeded the limit value imposed by the Stockholm Convention, the European Commission and the Romanian legislation, *i.e.* 50 ppm [8].

As can be seen in the Figure 1, the PCB congeners have values between 16330.93 and 42.41 ppm. Other examples of congeners, having concentrations from medium to large, are: PCB 22, 51 – 2464.31 ppm, PCB 52, 69 – 584.01 ppm, PCB 49 – 5983.86 ppm, PCB 96 – 7998.24 ppm, PCB 66, 95 – 2086.25 ppm, PCB 56, 60 – 1168.64 ppm, PCB 89 – 204.38 ppm, PCB 99 – 11149.26 ppm, PCB 83 – 2965.65 ppm, PCB 97 – 286.76 ppm, PCB 135 – 851.93 ppm, PCB 114, 143 – 240.97 ppm, PCB 138, 160, 163 – 13018 ppm, PCB 129, 157, 173 – 1508.70 ppm, PCB 172 - 14323 ppm, PCB 198 – 16330.93 ppm, PCB 196, 203 – 2003.34 ppm, PCB 195, 208 – 3584.58 ppm, PCB 207 – 175.06 ppm, PCB 206 – 1023.09 ppm. Some PCB isomers do not exceed the limit of 50 ppm, but there are several types of PCBs that exceed the allowed limit by 300 times.

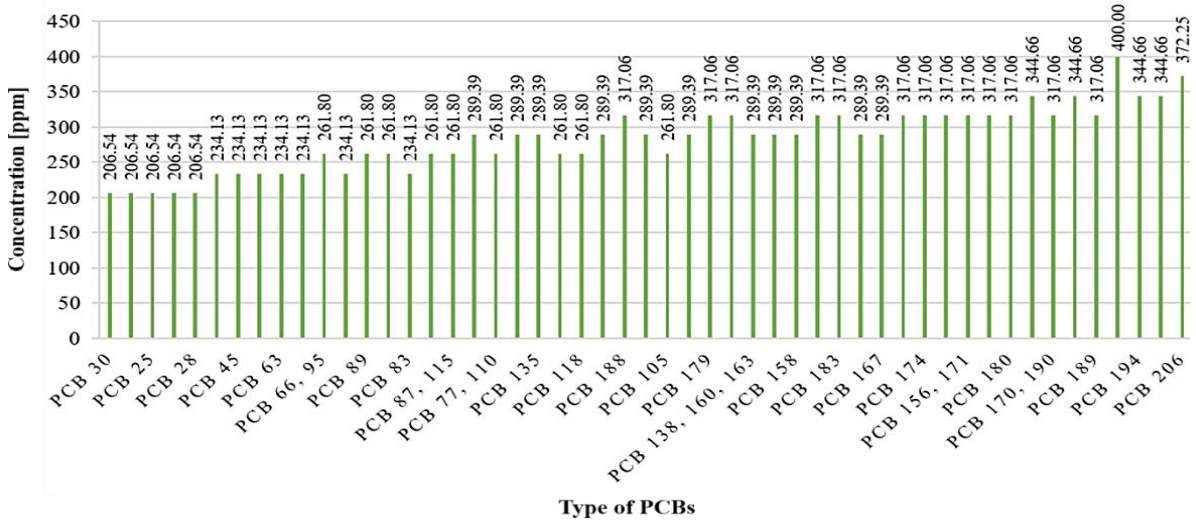

Fig. 2. The PCBs concentrations obtained for the oil sample collected in Indonesia

From the results obtained in Figure 2 it can be seen that in the sample of contaminated oil from Indonesia there was identified a lower number of congeners of polychlorinated biphenyls (72) compared to the oil sample in Romania (84). The concentrations of these 72 congeners are lower than those in the oil sample from Romania, but they exceed by far the limits allowed by the legislation.

The highest concentration was recorded for PCB 195, 208 - 400 ppm followed by PCB 206 – 372.25 ppm, PCB 205 – 344.66 ppm, PCB 189 – 317.06 ppm, PCB 158 – 289.39 ppm. , PCB 87, 115 – 261.80 ppm, etc.

Among congeners with concentrations that do not exceed the permissible limit (50 ppm) are the following: PCB 70, 74 – 234.13 ppm, PCB 47, 48, 75 – 234.13 ppm, PCB 18 - 206.54 ppm, PCB 20, 33 , 53 – 206.54 ppm etc.

The images in Figures 3 and 4 show the chromatograms obtained from the gas-chromatographic analysis for the contaminated oil samples from Romania and Indonesia, respectively.

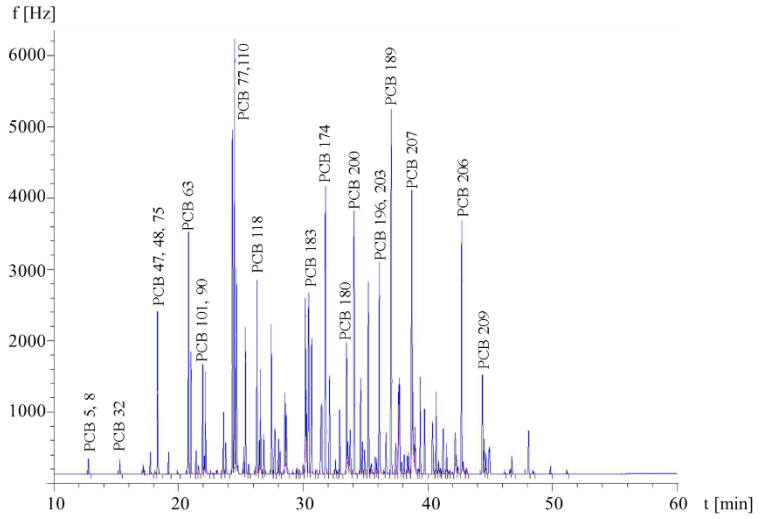

Fig. 3. Chromatogram obtained for the oil sample from Romania

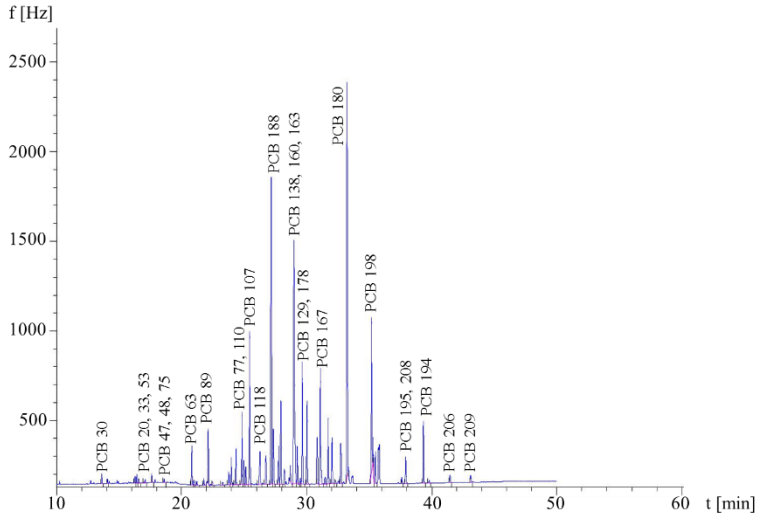

Fig. 4. Chromatogram obtained for the oil sample from Indonesia

Table 1. Comparison of calculated statistical parameters for PCBs concentrations in oils

Calculated Statistical Parameters	Total PCB content of analyzed transformer oil samples [ppm]		
	Oil sample from Romania (this work)	Oil sample from Indonesia (this work)	Oil sample from Republic of Moldova [9]
Average	2157.50	248	2.247
Minim	42.41	206.54	1.986
Maxim	16330.93	400	2.682

Table 1 shows a comparison of calculated statistical parameters (average of total concentrations, minimum concentration value and maximum concentration value) for three different transformer oil samples from Romania, Indonesia (this work) and the Republic of Moldova [9]. If we refer to the average of the total concentrations, it can be said that the value obtained in the case of the oil sample from Romania is approximately 9 times higher than the value obtained for the samples from Indonesia and 960 times higher than the value reported for samples from the Republic of Moldova.

The maximum PCB concentration obtained for the samples from Romania is 41 times higher than the specific value of PCBs in the samples from Indonesia and 6090 times higher than the specific value obtained in the Republic of Moldova. The last calculated statistical parameter - the minimum PCB concentration - shows that the minimum value for the oil samples from Romania is 6 times lower than that of Indonesian samples, but it is 20 times higher than that of the Republic of Moldova.

4. CONCLUSIONS

A first conclusion is that the high performance gas chromatographic analytical technique (GC-ECD) can be successfully applied for the separation and identification of all 209 congeners of polychlorinated biphenyls.

This study shows that in Romania the dielectric fluids used for high voltage industrial electrical equipment are contaminated with PCBs in a greater extent than in the case of industrial equipment used in Indonesia. The concentration of PCB 198 obtained from the oil sample in Romania is 40 times higher than the concentration of PCB 195 and 208 obtained from the oil sample in Indonesia. The fact that the concentration values of PCB compounds were registered even 326 times higher in relation to the limit allowed by the world and national legislation, draws attention to the solution of the problems related to the pollution with these persistent organic compounds.

The GC-ECD method can be employed in analytical laboratories for the investigation of the organic pollutant content in the complex matrix of oils.

ACKNOWLEDGEMENT

The work of the authors (A.E., O.B.) is financed by Dunarea de Jos University of Galati, through the internal grant with contract no. RF3621/30.09.2021. The author (F.S.) is grateful for the technical support provided by SETCAR S.A. Braila, through the cooperation agreement with INPOLDE center.

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