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DETERMINATION OF PCB TYPES AND CONCENTRATIONS IN INDUSTRIAL TRANSFORMER OIL SAMPLES.

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ABSTRACT

This paper aims to present how the types and concentrations of PCBs contained in a sample of oil from high voltage industrial transformers can be determined. The chromatographic method (GC-ECD) was applied to determine the PCB concentrations in the collected oil sample. For the implementation of the GC-ECD method, an Agilent - 7890 gas chromatograph was used, equipped with a µECD detector (ionizing source: Ni63, A = 15 mCi) capable of ionizing and identifying the concentrations of chlorinated organic substances in the analyzed samples. The experimental program started by collecting an oil sample from an industrial transformer from the company ELEROM S.A., Neamt county, Romania and temporarily stored, for final disposal, in the dedicated storage facilities of the company SetCar S.A. Braila, Romania. The high PCB content in the oils from high-voltage industrial electrical equipment classifies them as hazardous waste with a negative impact on environmental factors and human health and must be managed according to the laws in force.

KEYWORDS: PCB, high voltage industrial transformer, GC-ECD method,

1. INTRODUCTION

Polychlorinated biphenyls (PCBs) are synthetic aromatic compounds known under several commercial names such as Pyralene, Aroclor, etc., representing a group of 209 isomers each consisting of two benzene molecules where they add, in different positions, between 1 and 10 chlorine atoms [1], [2].

The total production of PCBs worldwide during the period 1929-1976 was approximately 61 megatons, of which more than 90% of this amount was generated by the Monsanto company, USA, under the trade name of Aroclor [3]. PCBs have been used mostly as additives for paints, inks and for cooling, dielectric and hydraulic fluids [3], [4].

Oils containing polychlorinated biphenyls were originally used for use in electrical industrial equipment such as transformers because they have exceptional dielectric properties and are non-flammable. Due to the fact that these substances are toxic, it have increased the stability regarding the reaction with chemical agents (acids, bases, oxidants, etc.) and easily accumulate in the adipose tissue of animals and humans, they have been declared extremely dangerous [5].

The toxicity of PCBs has placed them on the list of chlorinated organic substances that must be completely eliminated from high-voltage industrial electrical equipment, and by 2028 all waste containing PCBs must be completely eliminated. This decision was made worldwide according to the Stockholm Convention [6], [7].

Currently, it is considered that PCB production has been stopped worldwide, but concentrations of such persistent organochlorine substances can be found in various matrices anywhere in the world [8].

In most cases, PCB concentrations from various samples are analyzed using equipment equipped with a capillary column, inside this column there is usually a layer of fused silica. This analytical technique is called gas chromatography (GC). The most common

detectors attached to this technique are those with electron capture (ECD) [1].

2. MATERIALS AND METHODS

The experimental program consisted of taking samples of PCB-contaminated oil from inside a high-voltage industrial transformer, forming a homogenized oil sample and analyzing it using the GC-EDC method.

The industrial transformer, from the company ELEROM S.A., Neamt county, Romania, was transferred to the company SetCar S.A., Braila, Romania, for temporary storage and final disposal (Fig. 1).

Fig. 1. Temporary storage of high-voltage industrial transformer (source: [9])

The final disposal is represented by several technical operations (Fig. 2) such as: emptying the oil transformer, dismantling it, decontamination of ferrous and non-ferrous parts, respectively their economic recovery.

Fig. 2. The dismantling operation of the industrial transformer coil (source: [10])

The main reason why this experimental program was developed is to quantify the degree of PCB contamination of industrial transformer oils. Laboratory analyzes are applied according to quality standards recognized by a nationally accredited entity.

Transformer oil samples are taken with the help of sampling tools such as: glass pipettes or other mechanical instruments (syringes) and vials with covers made of glass. It is very important that all sampling utensils are very clean, dry or single use (Fig. 3). Compliance with this aspect leads to the avoidance of sample contamination with other unwanted substances.

Fig. 3. The method of sampling PCB-contaminated oil from an industrial transformer (source: [12])

Using glass pipettes, individual samples can be taken, usually three samples are taken (from the surface of the oil level, from the middle and from the lowest level) [11].

For the preparation of oil samples, the following high-purity laboratory reagents are used: organic solvents (hexane), dried and deactivated alumina, silver nitrate, silica, quartz wool, ultrapure water and acetone.

The application of the GC-ECD method was carried out using the following equipment: vaporizer with rotating mechanism for sample concentration, vacuum pump, laboratory utensils and glass vessels, respectively the Agilent 7890 gas chromatograph equipped with a chromatographic capillary column and µECD detector with a Ni-63 source, which has an activity of 15 mCi (Fig. 4). The concentrations of all PCB types identified from the analyzed oil sample were obtained using the calibration method based on the internal standard (Aroclor) and the procedures specified in the national regulations [11].

Fig. 4. Agilent 7890 gas chromatograph property of SetCar S.A. Braila (source: [9])

3. RESULTS AND DISCUSSION

After performing the qualitative and quantitative analysis applying the GC-ECD method, quite high PCB concentration values were recorded for all identified isomer types. Table 1 shows all types of PCBs and their concentrations, identified as a result of the analysis of industrial transformer oil samples from ELEROM S.A.

The results of the analysis, presented in table 1, indicated that a total number of 11 polychlorinated biphenyl isomers were identified. The concentration values of all types of identified PCBs considerably exceed the limit value (50 ppm [13]) imposed by the Stockholm Convention, European and Romanian legislation.

Table 1. Determination of PCB types and their concentrations in the analyzed oil sample

Retention Time [min.]	**PCBs type**	**Concentration of PCB [ppm]**
20.007	PCB 96	36.79
24.521	PCB 77, 110	546.60
36.123	PCB 196, 203	691.48
37.065	PCB 189	232.60
38.718	PCB 207	257.05
39.399	PCB 194	515.54
39.745	PCB 205	662.67
41.507	PCB 206	991.27
44.375	PCB 209	137.04

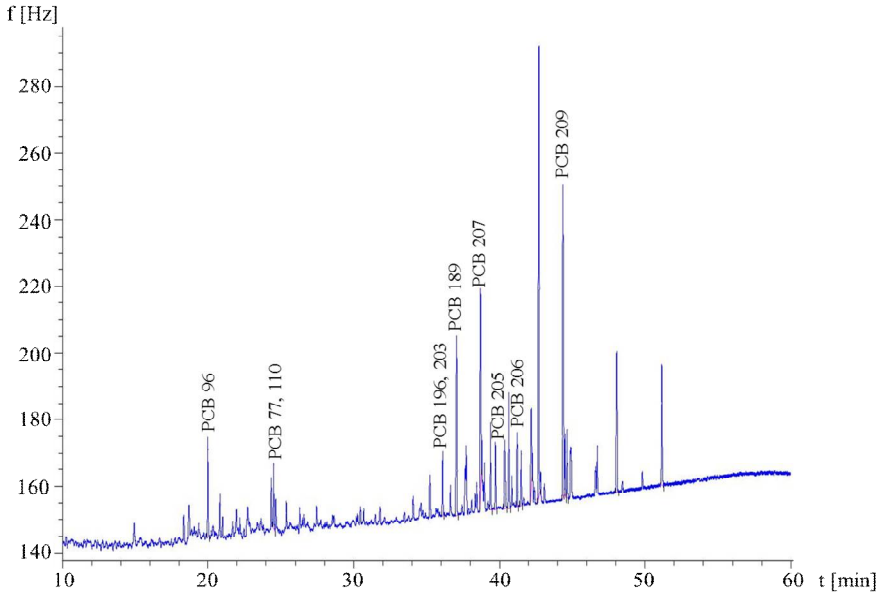

Fig. 5. The chromatogram obtained after the analysis of the contaminated oil sample

Table 2. Comparison of the results of this research and the results of another similar research

PCBs type	**Concentration of PCB in this work [ppm]**	**Concentration of PCB obtained in a sample from Romania [ppm]** [11]	**Concentration of PCB obtained in a sample from Indonesia [ppm]** [11]
PCB 96	36.79	7998.24	-
PCB 77, 110	546.60	42.41	261.80
PCB 196, 203	691.48	2003.34	-
PCB 189	232.60	1233.04	317.06
PCB 207	257.05	175.06	-
PCB 194	515.54	301.48	344.66
PCB 205	662.67	453.20	344.66
PCB 206	991.27	1023.09	372.25
PCB 209	137.04	-	-

Figure 5 shows the chromatogram obtained after the analysis of the PCBs contaminated oil sample. The results obtained in this research were compared with the results obtained in another similar research. This comparison is presented in table 2.

From the comparison of the results (Tab. 2), the following remarks can be formulated:

The concentration of PCB 96 (360.79 ppm) is extremely low compared to the concentration of PCB 96 determined in the oil sample from Romania (360.79 ppm [11]);

The concentration of PCB 77 and 110 (546.6 ppm) is much higher than the concentration of PCB 77 and 110 determined in the oil sample from Romania (42.41 ppm [11]) and significantly higher than the concentration determined in the oil sample from Indonesia (261.8 ppm [11]);

PCB 196 and 203 has a concentration (691.48 ppm) approximately 3 times lower than the concentration of the same type of PCB determined in the oil sample from Romania (2003.34 ppm [11]);

PCB 189 has a very low concentration (232.6 ppm) compared to the concentration of PCB 189 determined in the oil sample from Romania (1233.04 ppm [11]), respectively lower than the concentration determined in the oil sample from Indonesia (317.06 ppm [11]);

The concentration of PCB 207 (257.05 ppm) is higher than the concentration of the same type of PCB determined in the oil sample from Romania (157.06 ppm [11]);

PCB 194 recorded a higher concentration (515.54 ppm) than the concentrations of PCB 194 identified in oil samples from Romania (301.48 ppm [11]) and from Indonesia (344.66 ppm [11]);

The PCB 205 concentration value (662.67 ppm) is higher than the PCB 205 concentration values determined in the oil samples from Romania (453.2 ppm [11]) and from Indonesia (344.66 ppm [11]);

PCB 206 has a concentration (991.27 ppm) slightly lower than the concentration of PCB 206 determined in the oil sample from Romania (1023.09 ppm [11]), but significantly higher than the concentration of PCB 206 determined in the sample of oil from Indonesia (372.25 ppm [11]);

PCB 209 was identified only in the sample analyzed in this work and recorded a concentration (137.04 ppm) approximately three times higher than the normal limit (50 ppm [13]).

4. CONCLUSIONS

The GC analytical technique equipped with an electron capture detector (μECD) was successfully applied for the identification of the 11 types of PCBs and their concentrations.

All determined PCB concentrations are considerably higher than the normal legal limit, and for this reason the transformer oil from ELEROM S.A. is considered a hazardous waste and must be managed according to legal procedures.

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