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RESEARCH OF POLYCHLORINATED COMPOUNDS IN USED TRANSFORMER OIL

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Abstract: We have investigated the content of total chlorine, chlorinated biphenyl isomers and aromatics content in the samples used transformer oils using various physicochemical methods (colorimetric, chromatographic techniques, UV-spectroscopy).

Keywords: polychlorinated biphenyls (PCBs), transformer oil, UV spectroscopy, colorimetric and chromatographic methods of analysis.

1. Introduction

Polychlorinated biphenyls (PCBs) are among the persistent organic pollutants (POPs) and as a result of the degradation of the environment can be a source of toxic polychlorodibenzodioxins (PCDD) and dichlorbenzofuranov (PCDF). PCBs have an embryotoxic and potential carcinogenic effects and mutagenic. PCB danger lies in their ability to transfer the food chain and accumulate in the blood and lipids. According to the Stockholm Convention, they "should be banned for use, their production should be stopped, and all stockpiles destroyed." Given the high toxicity and the risk to the environment, plans for disposal of PCB-containing compounds are developed in all countries. Azerbaijan acceded to the Stockholm Convention in 2004 and has committed to disposing of PCB oils. With this in mind there is a need to explore the possibility of using physical and chemical methods for the monitoring of PCB containing equipment.

The aim of this work is to examine the possibility of methods for determining PCBs in transformer oil and the preparation of recommendations for their use for monitoring transformers.

In this work used transformer oil was studied by UV spectroscopy, gas chromatography and colorimetry.

There are a number of studies on transformer oil, which carried out spectral studies of oxidized sulfur and aromatic compounds [2-6]. But they are mainly dedicated to study UV spectroscopy of unused oil. During operation, the concentration of aromatic compounds is increased, which leads to faster oxidation and moisture absorption from the air, which entails deterioration of electrical properties. The situation is complicated in the case of cross-contamination of oil with chlorinated biphenyls, which undergoes degradation during operation time of the transformer.

2. Methods

In this work Dexsil L2000 were used in order to determine the chlorine, a gas chromatograph Agilent Technologies 7820A, UV - Varian spectroscopy - Cary-50 to get absorption spectra.

Colorimetric method for the determination of total chlorine. Analysis of transformer oil on chlorine was conducted by Dexsil L2000 analyzer. Samples were taken from transformers from Khachmaz regional power grid. Before analysis of transformer oil organic chlorine was

transferred to an inorganic sample. Pipetted into a test tube was added 5 ml of oil and tightly closed lid. Split the lower part of the ampoule and vial shaken thoroughly for 10 seconds. Then split the upper part of the ampoule and vial again shaken for 10 seconds. Then waited an additional 50 seconds, giving time for the reaction was shaken intermittently several times (for a total of one minute). Using a 5 ml pipette, 5 ml of extract was added. Tightly closed lid and thoroughly shaken until the foam has disappeared and the solution became lighter. Holding the tube upright, remove any air, partially parted the black cover. Closed tube and again shaken for 20 seconds. Then the air is removed from the tube, close the lid, set the vial upside down and allowed to stand for two minutes. In the pre-numbered 20 ml ampules, the solution was released from the tube, squeezing her hand gently before the first drop of oil. The solutions were cooled down for five minutes, and then analyzed the samples prepared for the total content of inorganic chlorine.

About 100 of transformer oil samples were studied, which were in operation 5-15 years. The chlorine concentration in 10 samples of oil exceeding 50 mg / kg. The analysis results are shown in Table 1.

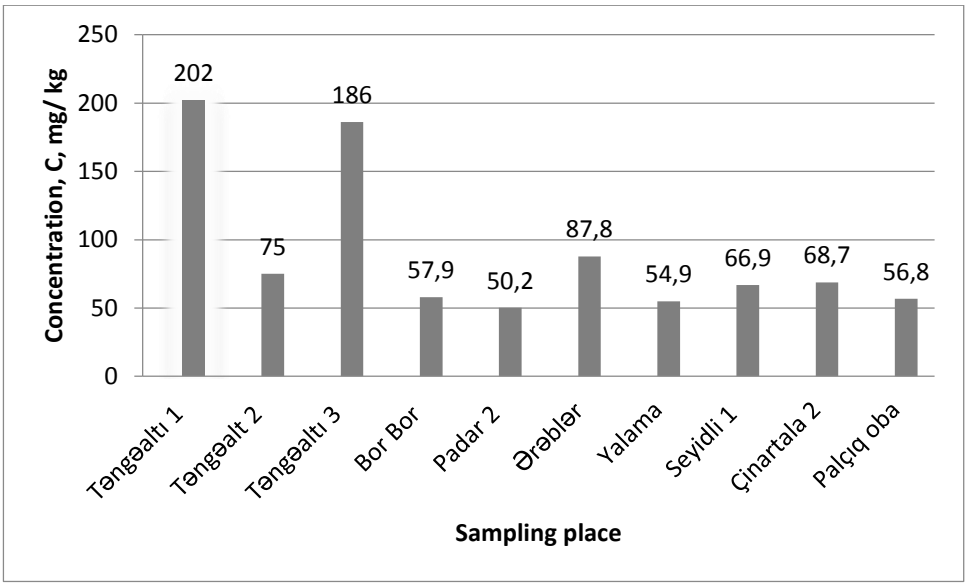

Table 1. *Chlorine concentrations exceeding 50 ppm in different places of sampling.*

Chromatographic analysis. Transformer oil, wherein the chlorine content was more than 50 ppm, further was analyzed on chromatograph Agilent Technologies 7820A.

Analysis of transformer oil containing PCBs was carried out based on the method according to the Environmental Protection Agency of the US media (Determination of Pesticides and PCBs in Industrial and Municipal Wastewaters. EPA 600 / 4-82-023.National Technical Information Service. PB82-214222 / Spring field. Virginia 22161 / April 1982). Approximately 0.1-0.5g sample was weighed on an analytical balance (sensitivity of ~ 0.0006 g), then dissolved in hexane and purified. For this purpose, 20 g florisil (previously dried at 130° C for 16 hours), also prepared column (diameter 22 mm) to remove water from the oil (if present) is added ~ 5 g of dehydrated sodium sulfate (previously dried at 400°C for 4 hours). The column was washed with 60 ml of hexane. Then the sample was passed through the column, which was first washed with 200 ml of a solution of 6% diethyl ether in hexane and collected in a round bottom flask. The speed of the filtering process to be 5 ml / min. The solvent presented in sample was evaporated to 2 - 3 ml. The same process was repeated with solutions of 200 ml of diethyl ether, each in 15 and 50% by volume and the volume reduced by evaporation to 3.2 ml.

To calibrate the chromatograph was used standard, which consists of 12 PCBs congeners (CEN PCB Congener Mix 1, 10 ug / ml in heptane, Supelco). 3 solutions were prepared with different concentrations (10, 50 and 100 mg / L), and analyzed by a chromatograph.

Table 2. *Main characteristics of the GC Agilent Technologies 7820A*

Carrier gas	N_2 (obtained from the generator and purified from moister using a filter (99.95%))
The gas flow rate	1.4 ml / min
Injector temperature	210°C
The column	Agilent J&W Capillary GC column (HP-5MS, 30 m x 0,250 mm x 0,25 um) Column Agilent J & WCapillary GC column (HP-5MS, 30 m x 0,250 mm x 0,25 um)
Thermostat temperature	290°C
detector	ECD (Electron Capture Detector), 300°C
Analysis time	45 min

For example, Figure 1 shows a chromatogram of the oil sample with concentration 100 mg / l, also release time of components.

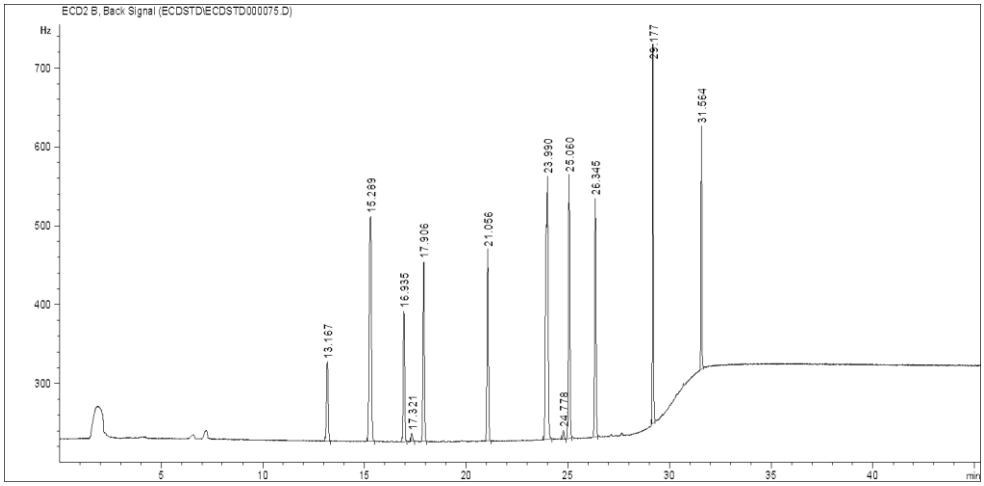

Fig.1. Standard chromatogram of 12 component PCB mixture (100 mg / l) taken with a gas chromatograph Agilent Technologies 7820A

The concentration of PCBs in the sample is calculated by:

$$C = (S \cdot D \cdot V \cdot k) / (m \cdot 1000)$$

where C - the concentration of PCBs in the sample (mg / kg); S - area of the peak; D is the

coefficient of dilution oil; V - the volume of the purified sample (ml); k - coefficient, which is calculated on the basis of calibration curve and indicates the concentration per unit area of the peak; m - mass of the sample taken for analysis (g).

Spectroscopy of oil samples. UV absorption spectra of stable layers of oils were determined with a spectrophotometer Varian-Cary -50.

For thin layer one drop of transformer oil was applied to the cell of a standard wall 10 mm, which was placed upright in the nest of a spectrophotometer. Oil flowed to the bottom gradually and by wetting forces and surface tension of the layer formed on the vertical wall of the cell. Over time, the layer thickness decreases. Stable oil layer turned a non-volatile absorption spectrum after the sample was kept for 23 hours in air. UV absorption spectra were recorded stable oil layer on a spectrophotometer Varian-Cary -50 in the wavelength range 200-400 nm.

Figure 2 shows the absorption spectra of three oil samples: (1) - oil, containing 14 ppm of PCB, (2) – unused oil TM-1500 (3) - technical oil Sovtol-10 containing 90% of isomers of PCB (basically three -, tetra and pentachlorbiphenyls).

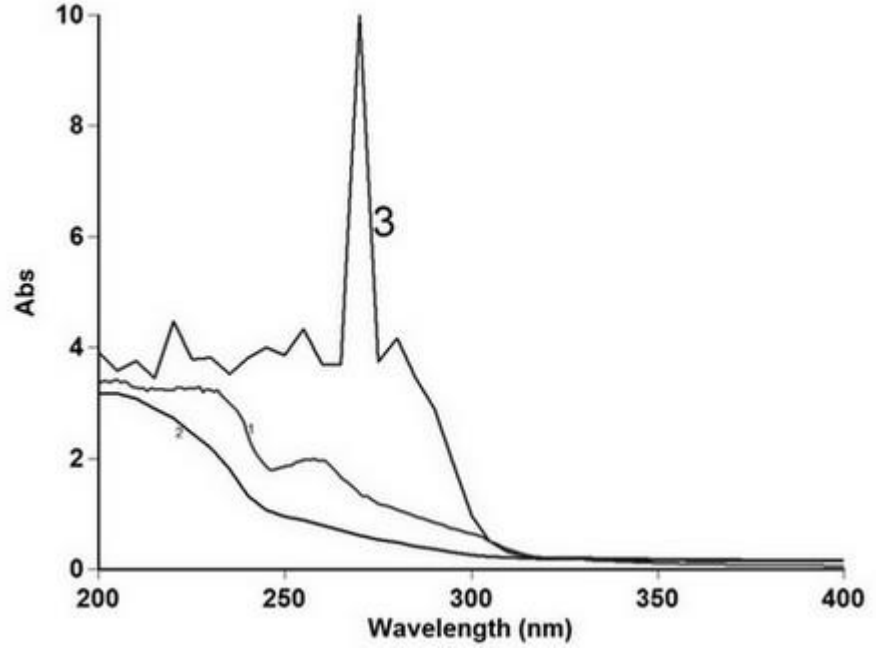

Fig. 2. Optical absorption spectra of transformer oil: 1- oil containing 14 mg / kg of PCB, 2-unused oil, 3- " Sovtol".

The absorption spectrum of the “Sovtol” samples have bands, which are characterized for PCB isomers: the main band 200-225 nm, containing 10 peaks with λ_{max} 200.0, 201.9 205.1, 207.0, 209.9, 214.0, 215.0, 220.0, 222.0, 225.0 nm; K-band 245-265 nm, containing six peaks with λ_{max} 244.9, 249.9, 255.0, 258.0, 260.0, 265.1nm and weak absorption band of 220-240 nm, containing 9 peak with λ_{max} 220.0, 222.0, 225.0, 227.1, 228.9, 230.0 , 231.9, 235.1, 240.1 nm. Unlike unused oil in used oil, new peaks are observed, particularly in 200-258 nm. In addition, appropriate used oils have a high intensity peaks. This is probably due to the formation of additional aromatic structures (polycyclic) during the operation time of oil. Increasing the concentration of aromatic compounds in the oil promotes their oxidation, and moreover, they absorb water from the air, considerably reduces its performance.

Optical absorption spectra of the transformer oil with different content of PCBs are presented in figure 3.

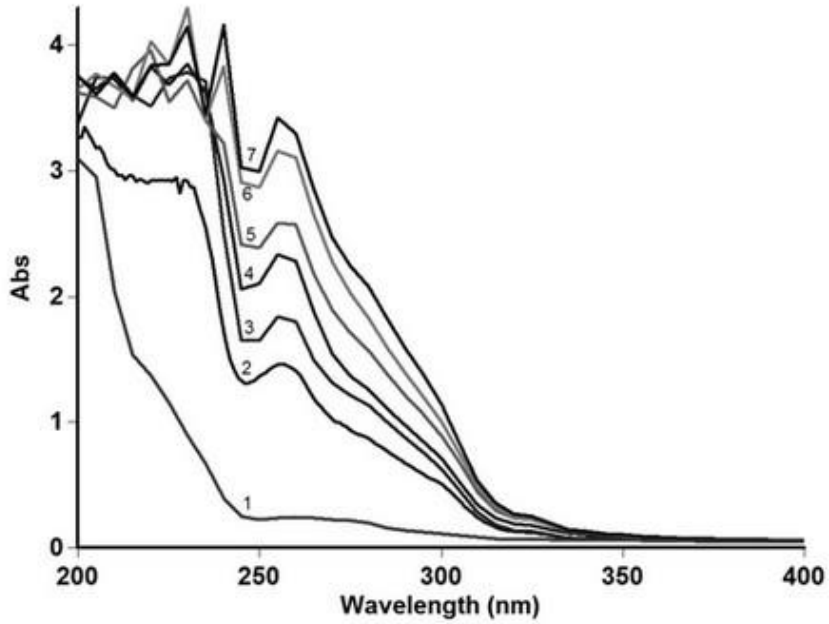

Fig. 3. Optical absorption spectra of the transformer oil, with different concentrations of PCBs: unused oil 1-, 2- oil containing 7,2 ppm of PCBs, 3- 19.3 mg / kg, 4- 44.7 mg / kg PCB, 5- 56 8 mg / kg PCB, 6-, 68.7 mg / kg PCB, 7-, 87.8 mg / kg of PCB.

As it can be seen from Figure, with increasing concentrations of PCBs increases the intensity of the respective peaks.

3. Conclusion

1. The results are shown on the "cross-'contamination of transformer oil in the distribution network. According to that about 10% of the analyzed samples contain PCBs with concentration more than 50 mg / kg. This estimate is in line with the results of the inventory carried out by the Ministry of Environment of the Republic of Azerbaijan.
2. It is shown that the use of colorimetric, chromatographic techniques and UV spectroscopy allow determining the content of total chlorine, chlorinated biphenyl isomers and aromatics content in the samples of used transformer oil. Above mentioned methods are practically used in the inventory of PCB-containing transformers in Azerbaijan.
3. The analysis of optical absorption spectra shows for increasing the concentration of aromatic compounds in the samples of used oil, which may lead to accelerated oxidation and promote the absorption of water from the air, significantly reducing the performance of the transformer oil.

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ИССЛЕДОВАНИЕ ПОЛИХЛОРИРОВАННЫХ СОЕДИНЕНИЙ В ИСПОЛЬЗУЕМОМ ТРАНСФОРМАТОРНОМ МАСЛЕ

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Резюме: Мы исследовали содержание общего хлора, изомеров хлорированных бифенилов и содержание ароматических соединений в образцах используемых трансформаторных масел с использованием различных физико-химических методов (колориметрические, хроматографические методы, УФ-спектроскопия).

Ключевые слова: Полихлорированные бифенилы (ПХБ), трансформаторное масло, УФ-спектроскопия, колориметрические и хроматографические методы анализа.

İSTİFADƏ OLUNAN TRANSFORMATOR YAĞINDA POLİXLORLAŞMIŞ BİRLƏŞMƏLƏRİN TƏDQİQİ

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Xülasə: Biz müxtəlif fiziki-kimyəvi metodlardan (kolorimetrik, xromatoqrafik metodlar, UB-spektroskopiya) istifadə etməklə transformator yağlarında istifadə olunan nümunələrdə ümumi xlorun bifenillərin xlorlaşmış izomerlərin və aromatik birləşmələrin miqdarını tədqiq etdik.

Açar sözlər: Polixlorlaşmış bifenillər (PXB), transformator yağı, UB-spektroskopiya, kolorimetrik və xromatoqrafik analiz metodları