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DETERMINATION OF POLYCHLORINATED BIPHENYL COMPOUNDS THROUGH GAS CHROMATOGRAPHY COUPLED WITH MASS SPECTROMETRY METHOD

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Lucrarea urmăreşte determinarea concentraţiei unor probe din uleiuri dielectrice contaminate cu compuşi bifenil policloruraţi (PCB), precum şi identificarea diferitelor tipuri de PCB prin metoda gaz-cromatografie cuplată cu spectrometrie de masă (GC/MS). În acest scop este utilizată metoda extracţiei ionilor moleculari din cromatogramă cu masa specifică m/z = 324, 358 şi 392.

Lucrarea prezintă prelucrarea cromatogramelor în funcţie de ionii specifici şi spectrele lor de masă. Pe baza spectrelor obţinute s-a realizat identificarea fragmentelor specifice în bibliotecile standard NIST şi WILEY.

Această metodă oferă eficienţă maximă în identificarea şi determinarea concentraţiei diferitelor tipuri de PCB în urme, din uleiurile dielectrice aşa cum s-a demonstrat experimental pe probele prelevate şi analizate.

The present paper aims to offer a Gas Chromatography with Mass Spectrometry Detection (GC/MS) method to determine the PCB concentration in dielectric oils. In addition, this method allows PCB type identification.

The respective method is based on molecular ion extraction; the specific masses m/z are 324, 358 and 392 of the ions from chromatograms.

The paper presents the processing of chromatograms according to the specific ions and their mass spectra. Based on the obtained spectra the identification of specified fragments from standard library NIST and WILEY has been performed.

This method provides an optimal efficiency in the identification and determination of the concentration to the different types of PCBs in traces, in oil capacitors, as it has been experimentally demonstrated on collected and analyzed samples.

Keywords: biphenyl polychlorinated (PCB), molecular ion/specific mass (m/z), Gas Chromatography with Electron Capture Detector (GC/ECD).

Introduction

Most transformers and capacitors use dielectric fluid based on polychlorinated biphenyl compounds (PCBs) [1, 9].

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Allthough they have some advantages and characteristics which make them usable in electric equipment (especially, due to their reduced flammability), these substances present some major disadvantages as well. These disadvantages are related to the toxic nature of PCBs and to their potential of contamination, namely their transformation into dibenzofuran [10, 16].

Their negative biological effects have been put into evidence during long periods of research and studies and now they are very well known.

Unfortunately, dielectric oils with PCBs are still widely used in transformers and capacitors, which have been introduced on the market 40 years ago; at present they must be eliminated through practical and efficient solutions [17-29].

Due to the wide use of electric equipment with fluids containing PCBs, especially of electric transformers and condensers, it was allowed, as an exception to this prohibition, in the frame policies of Stockholm Convention, to continue the use of these equipment until 2025, provided that the signatory parts of the Convention do their best to eliminate the production and use of these oils with PCBs [30-43].

Experimental

1. Materials and method

An extremely important problem is the separation and identification of persistent organic pollutants, such as PCBs, which implies two stages:

- preliminary monitoring in order to obtain information on the nature of the substances existing in the samples,
- identification through Gas Chromatography coupled with Mass Spectrometric detector (GC-MS).

In the first stage gas chromatography with specific or selective detectors, such as electron capturing detector (GC-ECD), is used for preliminary monitoring.

The system used is GC 9000, with capillary column and ECD detector which is highly sensitive as regards PCB, giving a disproportionately ample response in relation to the other compounds, which is indicative of their presence.

For the second stage the apparatus used for analyses is the gas chromatograph coupled with Varian Saturn type 3900/2100T mass spectrometer.

The gas-chromatograph is equipped with a split-splitless injector, a capillary column Factor Four VF-5ms, with d_l= 0.25mm, L=30m, film stationary phase = 0.25μm or capillary column of SE-54 type (25m X 0.32 mm inside diameter and 0.25μm film thickness) and it requires the following conditions:

- temperature regime of the column: 60^oC (1min) - 15^oC/ min - 300^oC (13min);
- injector temperature: $t_{inj} = 250^oC$;

- detector temperature: t $_{det}$ = 280°C;
- program temperature: t $_{int}$ = 40°C; isothermal one minute;
- temperature rate: 10°C/minute up to 280°C, then isothermal 10 min.
- supporting gas: helium quality 6.0 (ultra pure);
- start delay (s d): 3 min;
- splitting rate: 2 mL/minute up to 4 minutes, then 25 mL/minute.

As mobile phase, one can use helium or hydrogen with a flow rate of 1-2 mL/minute.

The mass spectrometer has a ionic trap type detector with a sensitivity of 10 pg. HCB (hexachlorobenzene). The injected sample quantity is 1-2 µL PCB solution in hexane.

Passing it over a Florisil element processed a maximal quantity of 1 mL transformer oil. After all oil has flown through the cartridge, halogenated products are driven with 1-2 mL hexane of GC quality and the solution gets diluted in a measuring bottle of 10 mL. An aliquot of 1-2 µL solution is injected in hexane and the characteristic areas are measured for PCBs.

The total of these areas is marked in a diagram with the given co-ordinates (measured area of PCBs and PCB percentage concentration), and PCB concentration is read.

2. Results and discussion

The analysis was conducted on 5 oil samples containing PCBs (I – IV) collected from the same area, but having different locations.

Sample I chromatogram is presented in Fig. 1. It shows the presence of a large series of PCBs, from trichlorobenzene to heptachlorobiphenyl.

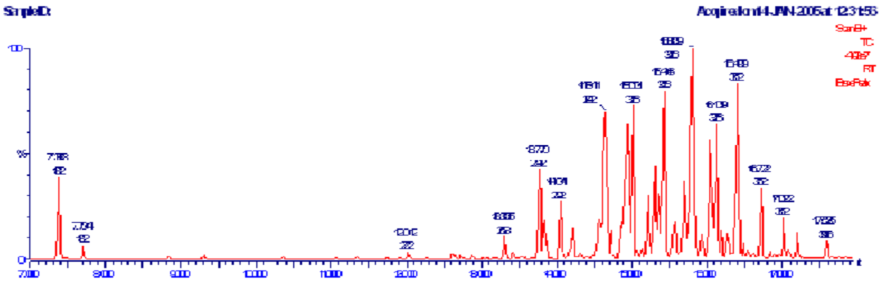


Fig.1. Chromatogram of the sample I

The sample II was collected from a condenser and its chromatogram is shown in Fig. 2. It shows that the PCBs content varies from monochlorobiphenyl to hexachlorobiphenyl, having an average chlorine concentration over 50 %.

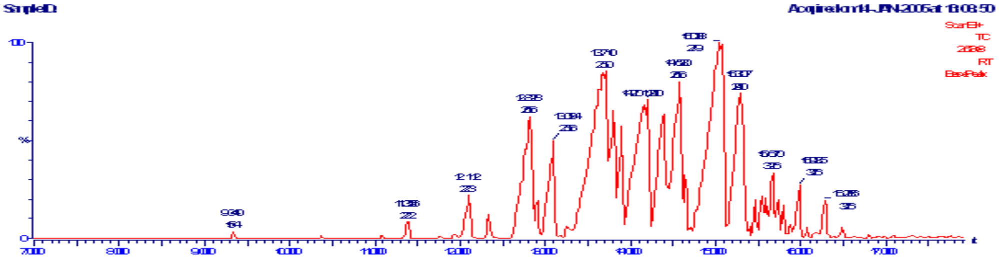


Fig.2. Chromatogram of the sample II

The sample III taken from a condenser deposited in a space of high voltage has a PCBs content varying from monochlorobiphenyl to pentachlorobiphenyl with an average concentration of chlorine lower than 45% (as shown in Fig. 3).

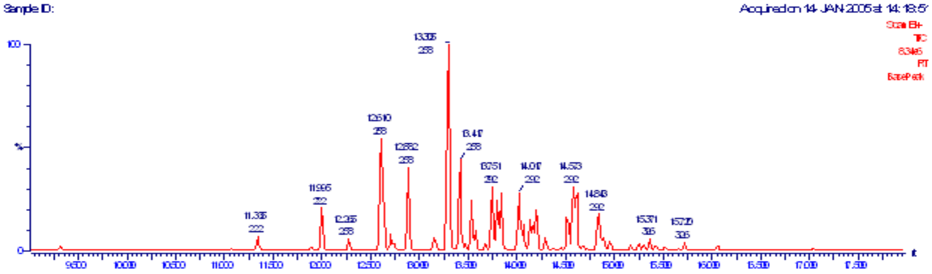


Fig.3. Chromatogram of the sample III

The condenser oil of this sample III has the following composition:

- Biphenyl Mass = 154:	0.1 %
- Monochlorobiphenyl Mass = 188:	0.1 %
- Dichlorobiphenyl Mass = 222:	1.9 %
- Trichlorobiphenyl Mass = 256:	36.8 %
- Tetrachlorobiphenyl Mass = 290:	53.5 %
- Pentachlorobiphenyl Mass = 324:	8.5 %

- Other impurities
(may be superior paraffines and phthalic esters): 1 %.

The samples chromatograms (Figs. 1-3) point out a large range of PCB compounds such as trichlorobenzene to heptachlorobiphenyls.

PCBs with a smaller number of chlorine atoms (1 to 4) are generally less persistent, more soluble in water and more flammable than PCBs with larger number of chlorine atoms (4 to 7). Moreover, they degrade more easily to form new chemical structures and are less susceptible to bio-concentration.

The European and national legislation defines “material contaminated by PCBs” any material which contains more than 50 ppm PCBs (0.005 %).

According to literature data dielectric oils contaminated with PCBs have a chlorine content between 0 % and 60 %.

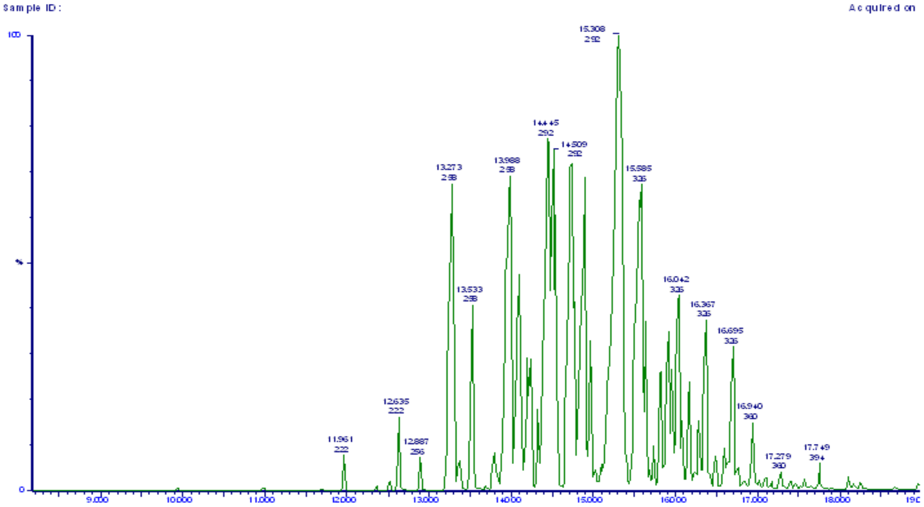


Fig.4. Processed chromatogram of sample IV from transformer oil

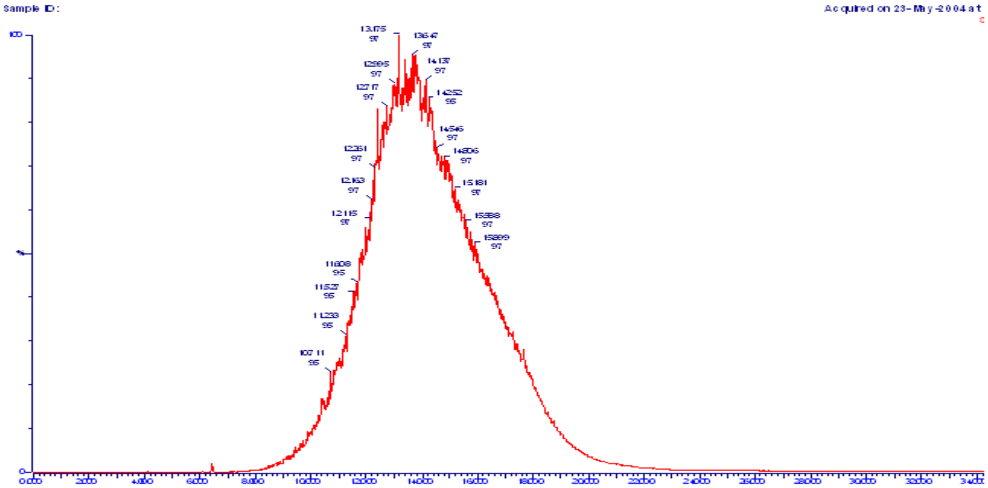


Fig.5. Chromatogram of sample V from transformer oil

The processed chromatogram of the samples shows the PCB lack in the sample V (fig.5). This leads to a Gaussian increase of the recorded chromatogram, showing the rise of paraffin content which cannot be separated by this method.

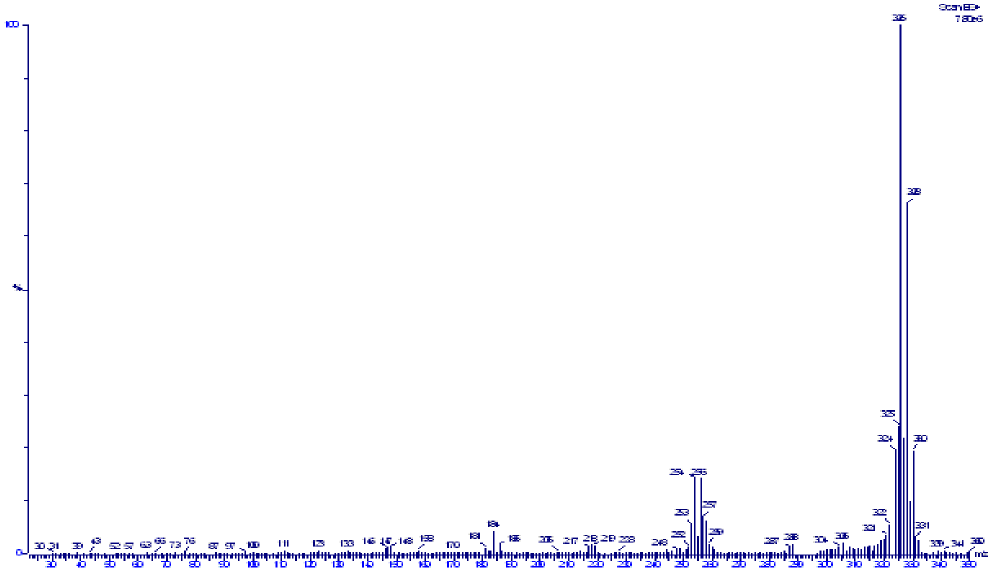


Fig.6. Mass spectrum of the sample IV from transformer oil
in relation to the specific ion m/z = 324

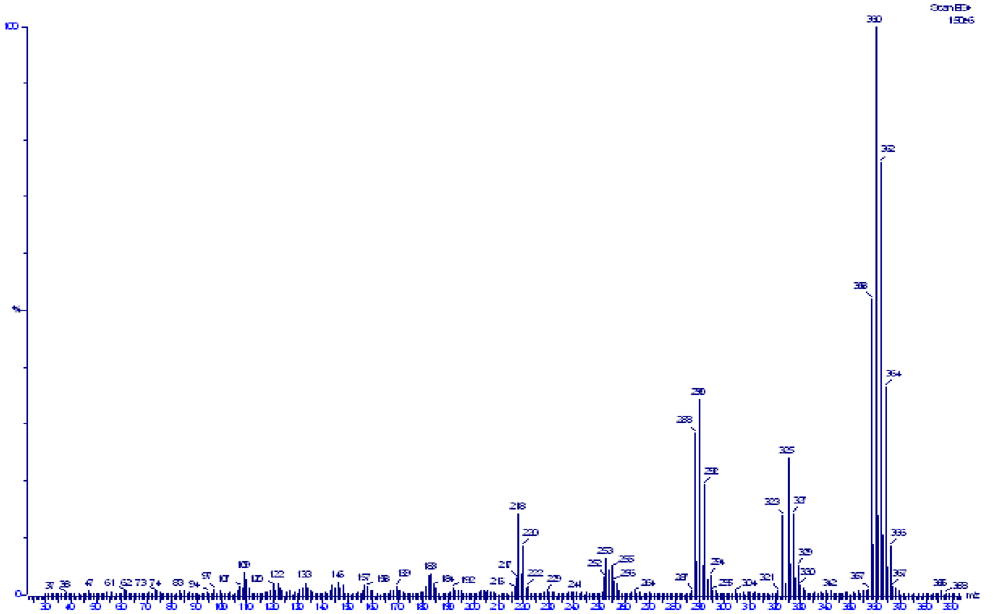


Fig.7. Mass spectrum of the sample IV from transformer oil
in relation to the specific ion m/z = 358

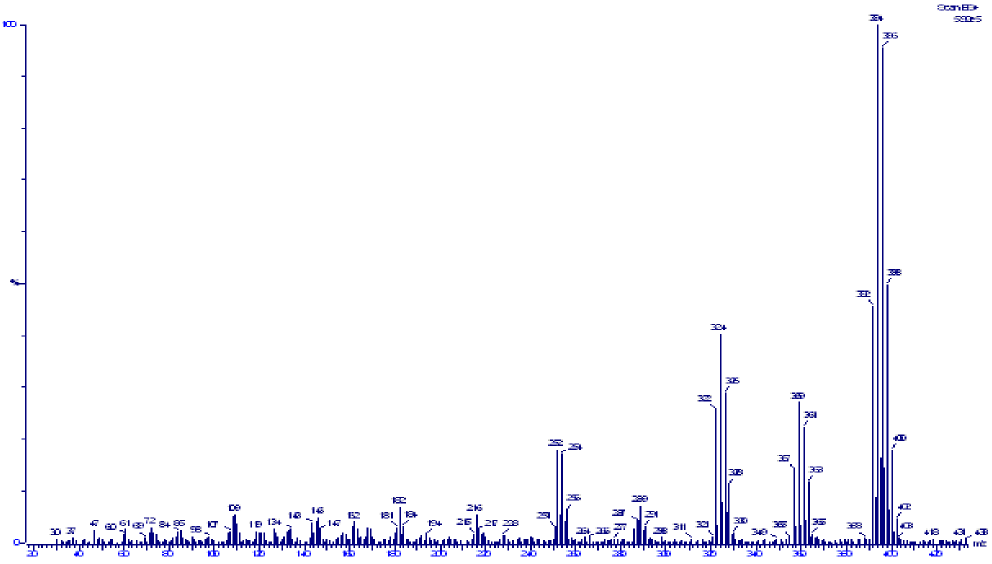


Fig.8. Mass spectrum of the sample IV from transformer oil
in relation to the specific ion m/z = 392

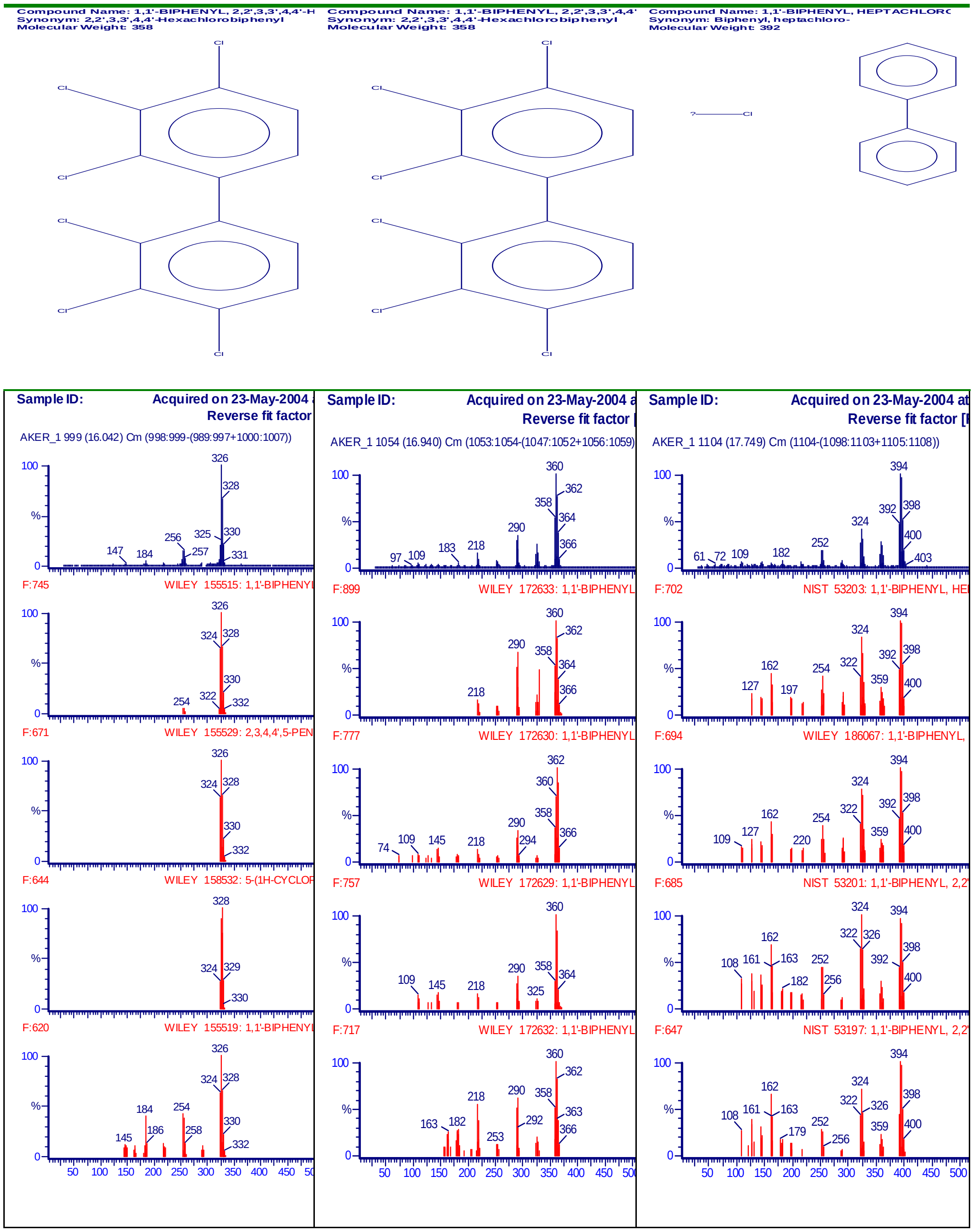
Mass spectra for 324, 358 and 392 fragments (Fig.6, 7 and 8) have been developed based on specific ions.

Fragments structures and identification of mass spectra in WILEY and NIST standard libraries (Table 1) are presented.

The method requires the use of PC–MassLab program which is a fast and precise method for determining and identifying traces of various PCB types in dielectric oils.

Table 1

Structure and identification of specific ions m/z=324, 358 and 392 in WILEY and NIST standard libraries



Compound Name: 1,1'-BIPHENYL, 2,2',3,3',4,4'-H
Synonym: 2,2',3,3',4,4'-Hexachlorobiphenyl
Molecular Weight: 358

Compound Name: 1,1'-BIPHENYL, 2,2',3,3',4,4'
Synonym: 2,2',3,3',4,4'-Hexachlorobiphenyl
Molecular Weight: 358

Compound Name: 1,1'-BIPHENYL, HEPTACHLORO
Synonym: Biphenyl, heptachloro-
Molecular Weight: 392

Sample ID: Acquired on 23-May-2004
Reverse fit factor
AKER_1 999 (16.042) Cm (998:999-(989:997+1000:1007))
F:745 WILEY 155515: 1,1'-BIPHENYL
F:671 WILEY 155529: 2,3,4,4',5-PEN
F:644 WILEY 158532: 5-(1H-CYCLOP
F:620 WILEY 155519: 1,1'-BIPHENYL

Sample ID: Acquired on 23-May-2004 a
Reverse fit factor
AKER_1 1054 (16.940) Cm (1053:1054-(1047:1052+1056:1059))
F:899 WILEY 172633: 1,1'-BIPHENYL
F:777 WILEY 172630: 1,1'-BIPHENYL
F:757 WILEY 172629: 1,1'-BIPHENYL
F:717 WILEY 172632: 1,1'-BIPHENYL

Sample ID: Acquired on 23-May-2004 at
Reverse fit factor [
AKER_1 1104 (17.749) Cm (1104-(1098:1103+1105:1108))
F:702 NIST 53203: 1,1'-BIPHENYL, HE
F:694 WILEY 186067: 1,1'-BIPHENYL,
F:685 NIST 53201: 1,1'-BIPHENYL, 2,2'
F:647 NIST 53197: 1,1'-BIPHENYL, 2,2'

The method of specific ions extraction from a chromatogram has been used for identifying and determining the concentration of different PCB types in collected and analysed samples.

This paper presents the processed chromatogram of the sample IV from transformer oil.

It is shown the presence of various PCB types in transformer oil having an average chlorine concentration lower than 50%. The fourth sample (Fig. 4) consists in a PCBs distribution ranging from monochloro- to heptachlorobiphenyl.

Global areas (in area units *u a*) of all PCB’s peaks in the chromatogram (Fig. 4) are measured in order to determinate the PCB concentration in the sample. Linear regression is used to draw the concentration diagram.

The areas and concentrations corresponding to the calibration chromatograms peaks are given in Table 2.

Table 2

Areas and concentration of calibration chromatograms peaks

Run. No	Corresponding Concentration of PCBs (mg/mL)	Area (*u a*)
1.	0.001786	11867
2.	0.003572	14964
3.	0.019644	66131
4.	0.039288	95906
5.	0.216084	404091
6.	0.432168	715706
7.	2.376923	6010577
8.	26.14615	81109154

The concentration on the 0-30 mg/mL range in relation to PCB measured areas has been plotted by the linearization method using the Microcal Origin 6.0 Demo program.

Comparing the data related to the area sum of all specific mass fragments peaks (with m/z = 324, 358, 392) for the sample IV, with the areas values corresponding to the calibration chromatograms, it has been noticed that the 78123411 u a value corresponding to a 25.21699 mg/mL concentration is less than the 81109154 *u a* value corresponding to a concentration lower than 30 mg/mL.

Conclusions

The paper presents the chromatograms of samples collected from different sites on the same area pointing out a wide range of PCB compounds ranging from trichlorobenzene to heptachlorobiphenyls.

As a result of the chromatogram processing of the sample taken from transformer oil, a wide range of different PCB concentrations has been determined and identified using an original method for specific ions extraction from the chromatogram.

Based on the molecular ions with m/z = 324, 358 and 392 specific mass, mass spectra have been obtained and the specific fragments from NIST and WILEY standard libraries have been identified.

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