Determination of polychlorinated biphenyls in waste motor and transformer oils

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1. Introduction

The discovery of PCBs in environmental samples, in the early seventies, led some industrialised countries to take legislative measures for controlling the flux of these pollutants in the environment. Established sources of polychlorinated biphenyls (PCBs) are among the other - transformers, capacitors, electric motors etc.[1)]. The materials containing more then 50 μg/g are subject to some regulations in USA and in the countries of Western Europe [2)]. Since 1993, in Poland the waste oils containing PCBs are included on the list of hazardous substances, but to the present day the flux of these pollutants is not a subject to any regulation [3)]. Recently available data [4)] have indicated that in national power plant installations about 1400t of transformer and capacitor oils are used. However, unknown is even estimated amount of the waste industrial oils (transformer, capacitor, motor etc.) occurred in the trade. The elimination of waste transformer oils containing PCBs may be hazardous when incinerated at 500-800°C, because it can lead to dibenzofuranes and dibenzodioxines formation. Uncontrolled collection and improper oil regeneration may be a potential source of PCBs and dioxins in the environment.
The aim of this study was to determine the level of total PCBs in the random samples of waste motor and transformer oils collected from different regions of Poland.

2. Materials and methods

Materials Studies were performed with the randomly selected industrial oils derived from different parts of Poland. Thirteen samples of waste motor oils were collected between March and July 1995 and the same amount of samples of transformer oils were received in September 1995. The standard solutions of PCBs 30(I.S.), 28, 52, 101, 118, 138, 153, 180; Aroclors 1242, 1254, 1260 and Clophen A 60 mixtures were prepared by adding the appropriate weight of the primary standards (Dr.Ehrenstofer, Augsburg Germany) to isooctane (Baker® Ultra-resi analysed quality). The solid phase extraction (SPE) columns used for clean-up were purchased from J.T.Baker B.V. Deventer, Holland,
Samples preparation About 1.0 g of oil (accurate weight), free from water and solid impurities, was dissolved in 10.0 ml of hexane (Baker® Ultra-resi analysed quality). For cleaning-up procedure portions of 250 μl of this solution were used. The samples were freed from impurities by liquid chromatographic preseparation. The use of hexane as elution solvent required 2 times 0.5 ml for the elution of the two SPE columns (benzene sulfonic acid/acid silicagel and neutral silicagel) and after removal of the first column, the neutral silicagel column was eluted 4 times with 0.5 ml of hexane.
The PCBs identification and quantification were performed by HRGC/ECD. A Shimadzu GC-14A gas chromatograph equipped with a ^{63}Ni electron capture detector and split injector was used. Analytical

separation of the purified extracts was carried out on a 60 m R_{Tx}-5 fused silica capillary column (5% diphenylpolysiloxane, 95% dimethylpolysiloxane), 0.25 mm i.d.; film thickness 0.25 µm (Restek Corp. USA). As a carrier gas helium was used with a flow rate of 0.6 ml/min. The injector temperature was held at 250°C and the split flow rate was 28 ml/min. Three µl of extract were injected. The detector temperature was 340°C with nitrogen as make-up gas at a flow rate 49 ml/min. The temperature program of column was 2 min. at 80°C; 40°C/min. until 130°C and 2.5°C/min. until 280°C, holding for 10 min.

3. Results and discussion

Before PCBs analysis, the linear range of the ECD detector was determined according to Wells et al. suggestions[5].

The clean-up procedure used in the present study has been tested with solutions containing transformer oil spiked with four different levels of individual congeners PCBs 28, 52, 101, 118, 138, 153 and 180 [6]. The recovery was determined to be over 90 % for all tested congeners, therefore the results were not corrected for recovery. The precision of all analytical procedures was less then 10 %.

Qualitative estimation of oil extracts was carried out on the basis of visual pattern matching (Aroclors 1242, 1254, 1260 and Clophen A 60) or specified congeners (PCBs 28, 52, 101, 118, 138, 153, 180) in the standard solutions and the samples. Fig.1 presents a typical chromatogram of oil extract.

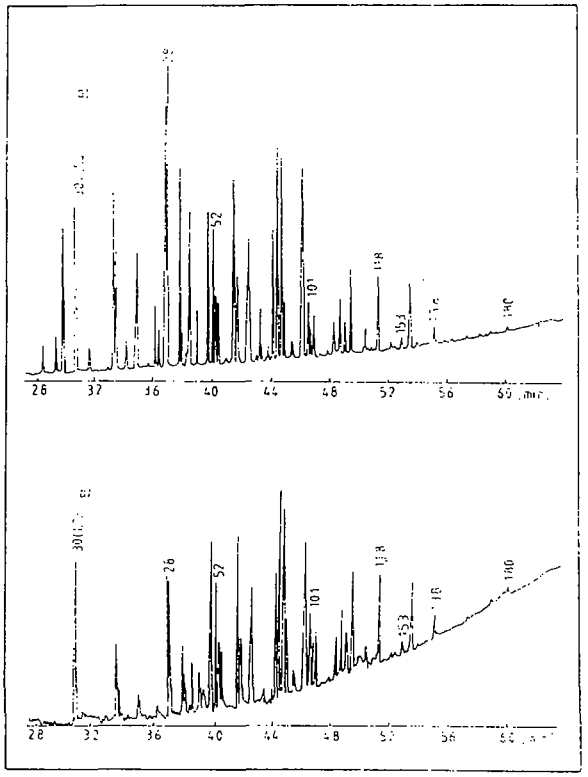

Fig.1. High resolution gas chromatograms of: a) a standard mixture of Aroclor 1242 (PCB 30 as internal standard), b) a sample of transformer oil N° 1 OLR (PCB 30 as internal standard)

The results of qualitative analysis have demonstrated that six from thirteen waste motor oils and six from thirteen transformer oils were not contaminated with PCBs. Other analysed samples contained compounds of which retention times on the chromatograms corresponded to the different types of PCBs mixtures. On the chromatograms of the samples 8 CPN, 7 EN and 1 OLR the peaks corresponding to the pure Aroclor 1254, Clophen A 60 and Aroclor 1242 were observed . Other extracts contained probably the congeners derived from different commercial mixtures (e.g. N° 10 EN corresponded to the Aroclors 1242 and 1260 mixture).Identified PCBs mixtures are shown in tab.1.

Table 1.

PCBs identification in waste motor and transformer oils from Poland

Oil N°	PCBs mixture type	Finger-print matching Σ total PCBs [µg/g]	Oil type
1 CPN	Aroclor 1242	29.71	motor oils
4 CPN	Aroclor 1242	53.42	
8 CPN	Aroclor 1254	44.19	
9 CPN	Aroclor 1242	36.72	
10 CPN	Aroclor 1254	35.11	
13 CPN	Aroclor 1254	2.88	
1 EN	Aroclor 1242	6.68	transformer oils
2 EN	Aroclor 1242	5.12	
7 EN	ClophenA60	3.51	
8 EN	Aroclor 1254	2.33	
10 EN	Aroclor 1254	2.85	
1 OLR	Aroclor 1242	30.67	

The quantification of PCBs in each sample has been carried out by a visual pattern matching and summing selected peaks to obtain a total amount (tab.1). For the sample N°1 OLR (transformer oil), additionally a sum of 6 congeners (28, 52, 101, 138, 153 and 180) was determined, according to DIN 51527 method. The concentration of individual congeners in this sample is shown in Fig.2.

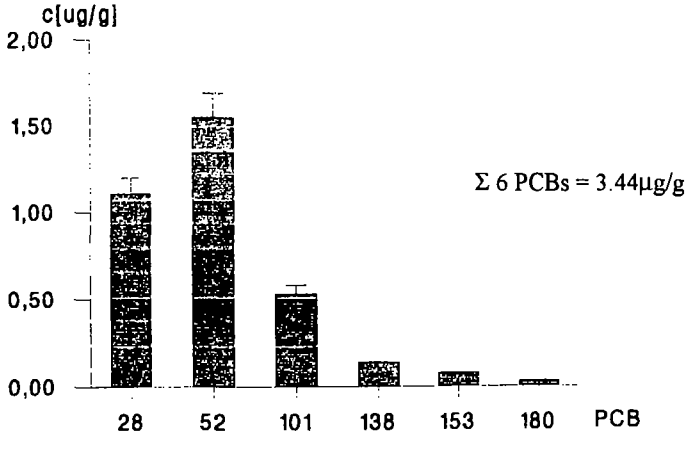

Fig.2. PCBs content in the sample of transformer oil (1 OLR)

The analysis of individual congeners confirmed the presence of Aroclor 1242 in the sample N° 1OLR, because the sum of six PCBs determined corresponded to a content of these congeners in the standard solution.
The analysed samples showed a concentration range (expressed as total PCBs content) from 2.33 µg/g in transformer oil N° 8EN , to 53.42 µg/g in motor oil N° 4 CPN.
In my studies, different PCBs mixtures were present in about 50% of analysed samples. It does not confirm the data presented by Gurgacz[4] that Polish spent transformer and motor oils do not contain the PCBs.
The determined content of PCBs in motor oils is by one order of magnitude higher than in transformer oils, except the samples N°13 CPN and N° 1OLR. It suggests that uncontrolled circulation of waste motor oils may be one of the PCBs sources in the environment in Poland.
It is worth to note that the PCBs concentrations determined both in the transformer and motor oils did not exceed 50 µg/g (except the sample N° 4 CPN) which is a generally accepted limit for the definition of special waste in the USA and most of the countries of Western Europe.
However, taking into consideration the data published by Tanabe et al.[7], concerning the PCBs concentrations in human adipose tissue in Poland (mean: 1.5 µg/g lipid weight, when e.g. in the USA 1.2 µg/g lipid weight), it seems necessary to undertake suitable measures for defining the principal sources of PCBs emission in Poland.

6. References

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