Chemosphere 73 (2008) S7–S12

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Determination of polychlorinated biphenyls in transformer oil using various adsorbents for solid phase extraction

Yun-Cheol Na [a], Kang-Jin Kim [b], Jongki Hong [c], Jung-Ju Seo [a,*]

[a] Hazardous Substance Research Team, Korea Basic Science Institute, Seoul 136-713, Republic of Korea
[b] Department of Chemistry, Korea University, Seoul 136-713, Republic of Korea
[c] College of Pharmacy, Kyung Hee University, Seoul 130-701, Republic of Korea

ARTICLE INFO

Article history:
Accepted 27 December 2006
Available online 12 May 2008

Keywords:
PCBs
Transformer oil
Gas chromatography
SPE

ABSTRACT

Various adsorbents for a solid phase extraction (SPE) method were used to study their ability to separate PCBs from transformer oil to rapidly determine their sub-ppm concentration in the transformer oil. Approximately 90% of the transformer oil could be removed from the PCBs by using a hydrophilic–lipophilic balanced copolymer (HLB) adsorbent, but the recovery of deca-chlorobiphenyl (deca-CB) used as a surrogate was only 24.5% due to lose during this cleanup process. The use of a silica adsorbent gave good results with 89.9% recovery of the deca-CB. The recovery of Aroclor 1242 and 1260 were 95.4 and 90.3% on silica, and 98.9 and 83.5% on HLB, respectively. Acid treatment was an essential step in removing the ambiguous interference peaks to help identify the PCBs. A decreased sensitivity of the electron capture detection (ECD) for PCBs was observed due to the presence of the remaining trace oil after the workup procedure. This loss in sensitivity was allowed for by using tetrachloroxylene as an internal standard, and this was found to be reliable for the criteria of quality control by employing an experiment in which LCS was spiked with 2 mg/l of Aroclor 1260 and analyzed each day over a 25 day period. The MDL for the analytical method established in this study is 0.05 mg/l.

1. Introduction

Polychlorinated biphenyls (PCBs) are chemical compounds which have been used as dielectric fluids in transformers and capacitors, as plasticizers and in hydraulic fluids (Dobson and van Esch, 1993; Berg et al., 1998). PCBs are toxic, and they accumulate in soil, sediment and biota when they are released into the environment. Although most countries have strict regulations on the use of PCBs (UNEP Chemicals, 2002), enormous amounts of PCBs did go into use before they were regulated. Indeed, they are still being used as insulators because devices such as transformers have lifetimes extending several decades. Since the Stockholm convention entered into force in May 2004, there has been a growing interest in the analysis of PCBs in transformer oils.

Many countries that have developed a classification system for PCB-containing fluids and materials have considered 50 mg/kg as the benchmark level for PCB regulation (UNEP, 1999). In accordance with PCB management, analytical test methods for determination of PCBs in insulating oil have been published as ASTM-D4059, EPA-600/4-81-045 and NIST (USEPA, 1982; ASTM International, 2000). In these methods, the oil, diluted with the appropriate solvent, is treated with acid and/or an adsorbent to remove interferences, and then analyzed by GC-ECD. However, the method detection limits (MDLs) of PCBs by these test methods are only 1–2 mg/kg because the oil is diluted 50 to 100 times to minimize the influence of the oil during the analytical procedure.

In Korea, the regulation of PCBs is strict, and liquid waste containing over 2 mg/l of PCBs is administered as a PCB-containing waste (NIER, 2004). In compliance with this criterion, a MDL of 0.05 mg/l is required for the analytical method used for PCBs in oil.

PCBs are not easily separated from oil because the physical and chemical characteristics of PCBs are very similar to those of mineral oil. The components of oil-based liquid wastes co-elute with the PCBs during a GC separation, and the baseline shifts or fluctuates due to the oil matrix. The key to lowering the MDL is to effectively remove the remaining oil during the analytical procedure. To remove the oil, a few analytical methods have been introduced to apply liquid–liquid partition using an appropriate solvent (Gordon et al., 1982; Takada et al., 2001). Although these methods are useful in identifying and determining the PCBs in oil, the separation of PCBs by liquid–liquid extraction (LLE) is dependent on the skill of the analysts. Recently, Bogdevich and Cadocinicov (2004) applied a solid phase extraction (SPE) tool for PCB sample preparation. This method provides a powerful technique to overcome the drawback of LLE. However, a procedure for removing transformer oil by SPE was not described although this is the most common interfering matrix for the determination of PCBs.

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* Corresponding author. Tel.: +82 2 920 0791; fax: +82 2 920 0789.
E-mail address: jjseo@kbsi.re.kr (J.-J. Seo).

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doi:10.1016/j.chemosphere.2006.12.102

The aim of this work was to develop a rapid sub-ppm determination method for PCBs in transformer oil. The SPE method was applied to separate the PCBs from oil and to overcome the drawbacks of column cleanup for the monitoring of multiple samples. This new method of separating PCBs from oil was studied with a variety of SPE adsorbent types. The effect of the remaining oil on the analysis of GC/ECD for quantification of PCBs was also studied.

2. Materials and methods

2.1. Reagents and materials

Silica, florisil, NH2, C8, C18 and HLB cartridges were purchased from Waters Corporation (Massachussets, USA). Aroclor 1242, 1254, 1260, deca-chlorobiphenyl, transformer oil (PCB-Free), and tetrachloro-*m*-xylene as the internal standards were purchased from Supelco (Bellefonte, PA, USA). All solvents used in this study were pesticide-free and obtained from J.T. Baker (Phillipsburg, NJ, USA). Sulfuric acid was supplied by Merck (Darmstadt, Germany), and water purified by Milli-Q system (Billerica, MA, USA) was used for liquid–liquid extraction.

2.2. SPE experiment

All adsorbents were pre-conditioned with 5 ml of elution solvent before loading the standard mixture or extracts onto the SPE column. To understand the interaction between PCBs and transformer oil on the adsorbent, elution patterns were measured. The standard mixture of 1 ml was loaded and eluent fractions (of 5 ml, 1 ml, or 0.5 ml, depending on the SPE column size) were analyzed by GC–ECD.

The samples used for recovery and method validation were eluted with *n*-hexane and 25 ml of eluent for the Si adsorbent and 9 ml eluent for the HLB adsorbent were collected after discarding 15 ml and 4 ml of an oil-containing fraction, respectively.

2.3. Instruments

To identify and quantify the PCBs, Agilent GC 6890N equipped with μ-ECD (Palo Alto, CA, USA) was used, and the column was HP-5MS (30 m × 0.25 mm, 0.25 μm thickness). The injector was operated at a 10: 1 split ratio and maintained at 250 °C. The oven temperature was held at 100 °C for 2 min, and then ramped to 160 °C at a rate of 15 °C/min, to 270 °C for 15 min at a rate of 15 °C/min. The carrier gas was helium at a flow rate of 1.5 ml/min. The ECD was maintained at 300 °C with 60 ml/min of N_2 makeup gas.

A GC/MS instrument was used to identify the transformer oil in the SPE eluent. The GC conditions applied were the same as stated above except the flowrate was adjusted 1 ml/min. The mass spectrometer (Agilent 5973N) was run in the electron ionization (EI) mode (70 eV) and scanned from 50 to 700 m/z.

2.4. Analytical procedure

For quality control, 200 ng of Aroclor standards was spiked into 100 μl of PCB-free transformer oil, then 20 ng of deca-CB (surrogate standard) was added to the oil. To remove the interferences, the oil sample was dissolved in 50 ml of *n*-hexane, and the liquid-liquid extraction was performed with 30 ml of conc-H_2SO_4 in a separatory funnel. This process was repeated until no changes in the color of the sulfuric acid layer were seen. After acid treatment, the *n*-hexane phase was washed three times with reagent grade water followed by drying with the anhydrous sodium sulfate. The extracts were concentrated to about 1 ml with a rotary evaporator before loading onto the SPE cartridge.

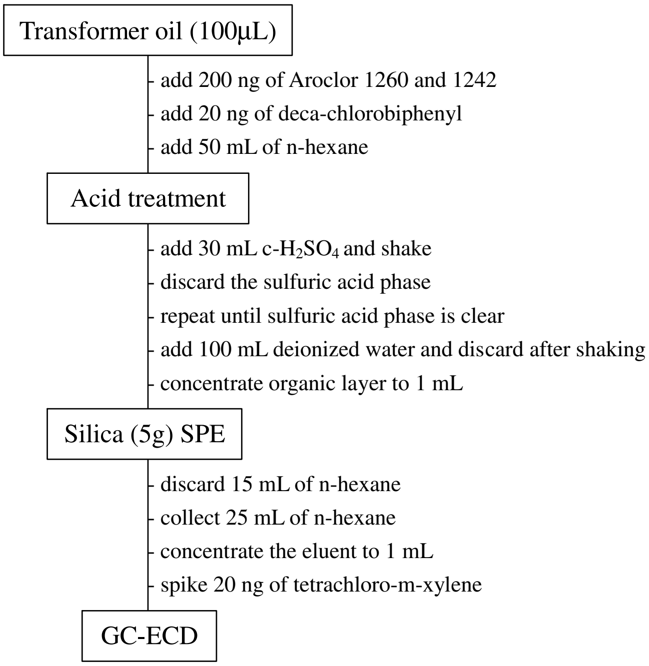

Fig. 1. Analytical procedure for determination of PCBs in transformer oil.

An aliquot of concentrated extracts was loaded into the preconditioned cartridge and then eluted with hexane. The first 15 ml of eluent was discarded, thereafter, 25 ml of eluent was collected. The eluate was concentrated to about 1 ml on a rotary evaporator. Then, 20 ng of tetrachloro-*m*-xylene was added to the sample, and analysis by GC/ECD was performed. The detailed analytical procedure is shown in Fig. 1.

3. Results and discussion

3.1. Elution pattern of PCBs and transformer oil on adsorbents

The physical and chemical properties of the transformer oil, such as solubility and polarity, are similar to that of PCBs. PCBs generally exist at a level a million times less than the transformer oil. Accordingly, the transformer oil is difficult to separate from PCBs by normal workup procedures such as liquid–liquid extraction.

In order to utilize a SPE's ability to separate PCBs from the transformer oil, various adsorbents were studied (Fig. 2). Silica, one of the polar adsorbents used in environmental clean-up, has been found to remove about 60% of oil with *n*-hexane if the first 15 ml of eluent is discarded. The elution sequence was in the following order: transformer oil, Aroclor 1260, and Aroclor 1242. This trend coincides with the polarity of the compounds, with the more highly chlorinated PCBs of Aroclor 1260 eluting faster than the lower chlorinated PCBs in Aroclor 1242. However, an increase in the polarity of the elution solvent, for example 10% diethylether in *n*-hexane, resulted in co-elution of PCBs and the oil from the polar adsorbent. Thus for silica, a nonpolar solvent is more suitable than a polar one for separating PCBs.

Florisil, which is somewhat basic, showed an elution pattern similar to that of silica, although the PCBs had longer retention times and the efficiency of separation was almost the same as that found for silica. The NH_2 polar adsorbent did not show an ability to clean up the PCBs.

When a non-polar C8 adsorbent and acetonitrile, as eluting solvent, are used for reverse phase chromatography, it was thought