

Comparison of Various Sorbent of Solid Phase Extraction for Analysis of Polychlorinated Biphenyls in Transformer Oil

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Introduction

Polychlorinated biphenyls (PCBs) are known as hazardous substances which were widely used in electrical equipments, condensers and paints^{1,2}. Due to persistence in the environmental and risk in the human, many countries have been banned the use of PCBs³ and since the Stockholm convention has entered into force on May 2004, the interest of PCBs also has been increased.

Analysis of PCBs in transformer oil by the test methods like ASTM-D4059, EPA-600/4-81-045 and NIST have been developed^{4,5}. These methods applied that diluting oil solution with solvent was treated to remove interfering substances using a combination of acid cleanup and adsorption chromatography. All the test methods, however, have background problem induced by hydrocarbon transformer oil because of their very similar physical and chemical properties with PCBs. Therefore, the detection limits (DLs) of these test methods were 1 or 2 mg/kg.

However, the DL of PCBs in transformer oil is strict as 0.05 mg/L in Korea⁶. Additionally, alkali procedure before acid treatment has to apply to effectively remove the impurity. Even if these methods can separate the interferent, the main obstacle of analysis of PCBs is caused by transformer oil and a suitable separation process of oil from PCBs is necessary to achieve sensitive detection by GC-ECD.

Conventional column cleanup using silica or florisil have been studied to separate the PCBs and some paper introduced combined column⁷. But, these are a process to consume labor, time and solvent. In this study, solid phase extraction (SPE) was used to overcome the drawback of column cleanup for monitoring of many samples. Therefore, behavior of PCBs on various sorbent types of SPE also studied to separate the transformer oil effectively.

Materials and Methods

The cartridge as silica, florisil, NH₂, C₈, C₁₈ and HLB which consist of copolymer of N-vinylpyrrolidone and divinylbenzene for SPE were purchased from Waters Corporation (Massachusetts, Ireland) and Aroclors for PCBs, deca-chlorobiphenyl (deca-CB) and tetrachloro-*m*-xylene as internal standards were purchased from Supelco (Bellefonte, PA, USA). All solvents used in this study were pesticide residue.

For identification and quantification of PCBs, Agilent GC 6890N equipped m-ECD (Palo Alto, CA, USA) was used and the column was HP-5MS (30 m × 0.25 mm, 0.25 mm thickness). GC-MS (Agilent 5973N) also, used to measure the fraction of transformer oil eluted during the SPE procedure.

The elution pattern via fractions of each cartridge collected from appropriate solvent was measured by GC-ECD for Aroclors and deca-CB, and by GC-MS for transformer oil, respectively.

To validate the method with optimized SPE condition, 100mg of transformer oil spiked with 200 ng of Aroclors and 20 ng of deca-CB as surrogate was dissolved with n-hexane followed by treatment of c-H₂SO₄ until no change in color of aqueous layer is seen. The extract after concentration was loaded into cartridge and only portion of PCBs of elute was collected. Finally, the recovery measured by GC-ECD was calculated as relative area about internal standard.

Results and Discussion

Characteristic of transformer oil is similar to PCBs in physical and chemical properties such as solubility and polarity and PCBs exist as level less million times than transformer oil. If the components of oil still remain in the aliquot after analytical pretreatment, PCBs isomers can not separate in the chromatogram as well as baseline is shifted or fluctuated due to oil.

In order to utilize the merit of SPE for removing oil, elution pattern of PCBs and oil about two eluting solvents on silica of polar sorbent was tested. Oil was separated about 60% by Silica (5g) eluted with n-hexane when the elute is discarded until fraction 3 whereas 10% diethylether in n-hexane which is little polar solvent didn't separate PCBs from transformer oil (Figure 1).

Florisil which is a little more polar property than silica was shown the similar elution pattern like silica using n-hexane. However, NH₂ sorbent absented a function as cleanup of PCBs.

With eluting solvent of acetonitrile on C8 sorbent of non-polar as reverse phase chromatography, oil could be captured for more long time on C8 sorbents so that reversed elution pattern of silica would be possible. The predicted result on C18 SPE was shown with analogous trend that oil was more retained than PCBs in sorbent but, these also were co-eluted and didn't obtained the good separation even if n-hexane was used as eluting solvent.

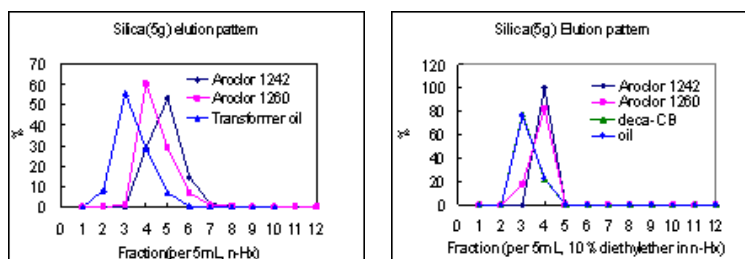
Finally, HLB sorbent which is copolymer of polar and non-polar, was tested. This HLB has been known as appropriate sorbent to separate both polar and non-polar analytes.

HLB sorbent of 200mg capacity using n-hexane solvent separated PCBs and transformer oil better than other sorbent. For more effective separation, sorbent capacity was increased to 500mg and transformer oil above about 90% could be removed when the first 4mL of n-hexane was discarded. However, deca-CB is relative non polar compound compared with other PCBs congeners. Also, early elution property on all sorbents was one drawback that deca-CB was lose when fraction contained oil was discarded.

In order to know the effect of interfering oil to analyze PCBs, the 3rd fraction of HLB which contains much oil, was measured by GC-ECD. The baseline of chromatogram of this fraction was drifted due to oil whereas chromatogram of PCBs fraction from 4 to 12 mL showed stable background and well separated all isomers.

Based on Korea test method, removing effect of impurities was tested. In the case of alkali procedure applied before sulfuric acid treatment, oil and other impurities weren't eliminated effectively because the transformer oil consist of the mixture of aliphatic, alicyclic and polynuclear aromatic hydrocarbons. Consequently, the alkali procedure was excluded in this method. Besides, acid treatment was important step to decompose the interferent, especially in the aging oil. Nevertheless, oil remained in the extract so far and cleanup procedure by the adsorption was needed for the accurate quantification of PCBs

With SPE condition of HLB sorbent resulted with the best separating ability of PCBs in this study, analytical method was validated to check recovery of PCBs in transformer oil.



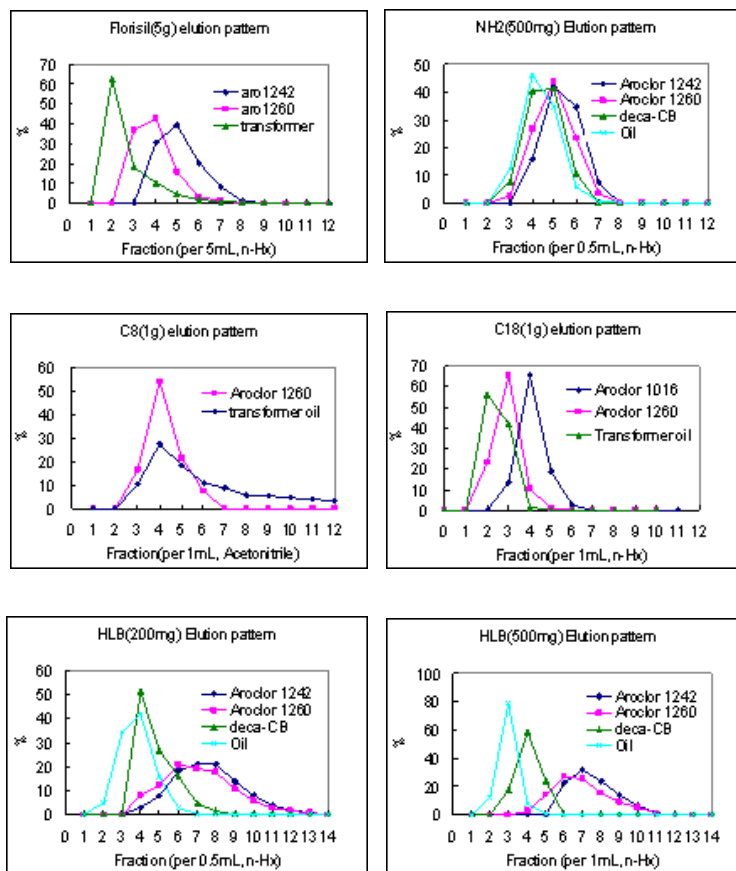


Figure 1. Elution pattern of PCBs and transformer oil by various sorbent

The recovery of sample spiked with mixture of Aroclor 1242 and 1260 into PCBs free transformer oil were 98.9% and 83.5%, respectively (Table 1). The relative low recovery of Aroclor 1260 even if the value is acceptable for quantification of PCBs, was caused by faster elution than Aroclor 1242 on SPE cleanup and little quantity of Aroclor 1260 was included in discarded oil fraction. As mention of above, recovery of deca-CB was much less to use to surrogate standard due to loss from analytical procedure, especially cleanup. The detection of PCBs by HLB method was possible to measure below 0.05 mg/L which is established value as DL in Korea

In the case of experimental included silica cleanup in place of HLB, although existing oil made some problem from chromatogram like fluctuation of baseline, the recovery was suitable value to detect the PCBs. However, it is necessary to careful attention for detection of lower level of PCBs. For analysis corresponded with strict criterion of low DL, the method using the HLB cleanup may be alternative except another surrogate must be proposed.

Table 1. Recovery of PCBs by HLB and silica cleanup method

Recovery	For HLB sorbent		For Silica sorbent	
	%	RSD	%	RSD
Aroclor 1242	98.9	10.3	95.4	0.9
Aroclor 1260	83.5	2.3	90.3	4.9
Deca-CB	24.5	9.1	89.9	3.9

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