

# THE DEVELOPMENT OF RAPID ANALYTICAL METHOD FOR POLYCHLORINATED BIPHENYLS IN TRANSFORMER OILS AND ITS APPLICATION

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## Introduction

Polychlorinated biphenyls (PCBs), which are one of persistent organic pollutants (POPs), are having been issued world-widely, especially in Stockholm convention. Due to its chemical stability and insulating characteristic, PCBs had been used in many parts of industries, especially in electric power industry<sup>1,2,3</sup>. But, as environmental adverse effect of PCBs has been known, production and usage of PCBs was banned in various advanced countries. In Korea, main source of PCBs is transformer insulating oil and its regulation level in Korea is 2ppm. Because the present regulation level is significantly low compared with other many countries, the analysis of PCBs concentration in transformer oils is extremely crucial for its well-management<sup>4</sup>. PCBs concentration analysis should be performed by Waste Official Test Method (WOTM) in Korea. But because WOTM required relatively high cost, long time, well-trained analyst and etc, it is difficult to analyze PCBs in large amount of transformer oils rapidly and quickly. Because of this problem, the number of transformers in storage places is being increased, and there is of great concerns about secondary environmental contamination. So it is getting necessary to develop a new method to analyze PCBs in transformer oils rapidly and simply. In some countries several rapid and simple analytical methods are having been used<sup>5</sup>, but it is almost impossible to apply them to Korea due to huge difference of regulation level. Therefore, in this study, development of a new rapid method for PCBs analysis was presented by comparing several pre-treatment and quantification procedures through modification of WOTM.

## Materials and methods

In this study, total 9 pre-treatment methods and 3 quantification methods were evaluated, respectively, which were modified based on WOTM. The main factors of modification in pre-treatment procedure were omission or

replacing of alkali decomposition, omission of sulfuric acid treatment, simplification of silica-gel column clean-up and etc; reducing the number of quantitative peaks, solving the complexity in calculating Aroclor mixture ratio in quantification procedure<sup>6</sup>. Comparing these several pre-treatment and quantification methods, we tried to establish the optimized analytical procedure (include both pre-treatment and quantification). Then, to evaluate the applicability of this rapid method, total 200 transformer oil samples were selected according to the concentration distribution of PCBs in Korea<sup>7</sup>. Finally, these transformer oil samples were analyzed with both rapid method and WOTM, and comparison of analytical result was performed.

## **Results and discussion**

### ***Establishment of pre-treatment and quantification procedures***

The most important point to consider in pre-treatment is removal of oily material. Because of the nature of rapid analytical methods, removal of oily material wasn't performed perfectly. Some method showed bad chromatogram that it is impossible to perform calculation of recovery rate as well as both qualification and quantification. Although many pre-treatment methods didn't make good chromatograms, Method 1 and 9 showed relatively satisfactory result in qualifying and quantifying to some extent. The recovery rate of these two pre-treatment methods was also good. In terms of peak separation, Method 9 showed the best chromatogram, but this needed relatively long time for analysis than Method 1. So it was regarded that Method 9 was less proper for the aim of this study, but it can be applicable when perfect peak separation is required.

On the other hand, as a result of evaluating 3 quantification methods by differentiating the number of quantitative peaks, there wasn't large difference from the analytical result of WOTM. It means the number of quantitative peaks doesn't cause large difference in analytical result. And, to simplify the quantification procedure, Aroclor mixture ratio of calibration standard was manufactured to Ar1242:1254:1260=1:1:1 though it is different from mixture ration of transformer oil samples. But, this also didn't make significantly different results. Among the 3 quantification methods, Method 1, which is using 13 quantitative peaks described in WOTM, was regarded to be most proper for rapid method. But, Method 1 showed relatively underestimated analytical result than WOTM and so did other 2 methods. Although this might be negligible, it is regarded very careful consideration would be necessary for the application to transformer oils.

### ***Application to transformer oil samples***

With selected pre-treatment and quantification procedure as mentioned above, the rapid analytical method was established. And total 200 transformer oil samples were analyzed with both this rapid method and WOTM. As a result, there wasn't large difference in analytical results of these two methods. Especially, relatively high correlation coefficient was shown for the oil samples around present regulation level (2ppm). Consequently, the

established rapid method made satisfactory recovery rate and analytical result compared with WOTM, and we could reduce time required for PCBs analysis to 1/3 of WOTM.

### Acknowledgement

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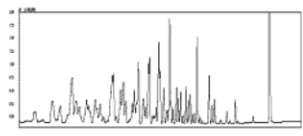
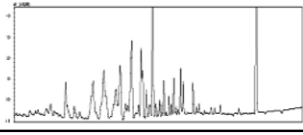
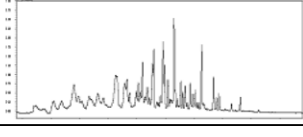
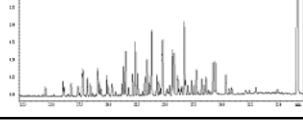
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**Table 1: Comparison of several pre-treatment methods**

| No. | Chromatogram | Q.L. | Q.N. | R.R. | Pre-treatment condition   |
|-----|--------------|------|------|------|---|
| 1   |              | ○    | ○    | ○    | <ul style="list-style-type: none"> <li>• Adding sample and 1.5N-KOH in vial, shaking for 20min, then neutralization</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g)</li> <li>• Elution : n-Hex 100mL</li> </ul>                                    |
| 2   |              | △    | △    | ×    | <ul style="list-style-type: none"> <li>• Adding Florisil 0.3g and sample in vial, then adsorption</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g)</li> <li>• Elution : n-Hex 120mL</li> </ul>  |
| 3   |              | △    | △    | ×    | <ul style="list-style-type: none"> <li>• Adding Florisil 1.0g and sample in vial, then adsorption</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g)</li> <li>• Elution : n-Hex 120mL</li> </ul>  |
| 4   |              | △    | △    | ×    | <ul style="list-style-type: none"> <li>• Adding sample and 1.5N-KOH in vial, shaking for 20min, then neutralization</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g, Florisil: 4g)</li> <li>• Elution : n-Hex 120mL, 150mL</li> </ul>               |
| 5   |              | ×    | ×    | ×    | <ul style="list-style-type: none"> <li>• Dissolving of sample with n-Hex in concentration tube, then injection in clean-up column</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g, Florisil: 4g)</li> <li>• Elution : n-Hex 120mL, 150mL</li> </ul> |

**Table 1: Comparison of several pre-treatment methods (continued)**

| No. | Chromatogram  | Q.L. | Q.N. | R.R. | Pre-treatment condition   |
|-----|---|------|------|------|---|
| 6   |  | △    | △    | ×    | <ul style="list-style-type: none"> <li>• Adding sample and 1.5N-KOH in vial, shaking for 20min, then neutralization</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g, Florisil: 4g)</li> <li>• Elution : n-Hex 120mL, 150mL</li> </ul>               |
| 7   |  | △    | △    | ×    | <ul style="list-style-type: none"> <li>• Dissolving of sample with n-Hex in concentration tube, then injection in clean-up column</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g, Florisil: 4g)</li> <li>• Elution : n-Hex 120mL, 150mL</li> </ul> |
| 8   |  | △    | △    | —    | <ul style="list-style-type: none"> <li>• SPE (Isolute NH<sub>2</sub>) (commercial product)</li> <li>• Activation of solution : n-Hex 5mL</li> <li>• Elution : n-Hex 20mL</li> </ul>   |
| 9   |  | ○    | ○    | ○    | <ul style="list-style-type: none"> <li>• Dimethyl Sulfoxide (DMSO 2mL, 2 times) in concentration tube → separation, reverse extraction</li> <li>• Multi-layer silica-gel column (44% sulfuric acid silica-gel: 25g, neutral silica-gel: 2g)</li> <li>• Elution : n-Hex 100mL</li> </ul>                 |

\* Q.L.: Qualification, Q.N.: Quantification, R.R.: Recovery rate

**Figure 1: Comparison of analytical result between WOTM and rapid method**

