Analysis Method of PCBs in transformer oil and distribution characteristic of PCB-congeners before and after chemical treatment of waste transformer oil contaminated PCBs

Geum Ju SONG, Joung Ho Joo, A Yeoung Lee

Institute of Environmental and Energy Technology, Pohang University of Science and Technology, San 32 Hyoja-Dong, Nam-Gu, Pohang, Kyungbuk, Republic of Korea

Abstract

In this study, the clean-up method of polychlorinated biphenyls (PCBs) in waste transformer oil were compared Korea Standard Test Method (KSTM) with Japanese Industrial Standard (JIS) and the PCBs concentrations in waste transformer oil were compared by gas chromatography/electron capture detector (GC/ECD) for analysis of peak patter with by high resolution gas chromatography/ high resolution mass spectrometer (HRGC/HRMS) for analysis of 209 congeners. And also the distribution characteristic of PCBs congeners before and after chemical treatment of waste transformer oil contaminated PCBs was investigated. The clean-up method without reverse extraction using dimethylsulfoxide (DMSO) was more effective than the clean-up method with reverse extraction using DMSO. After than the alkali dissolve, sulfuric acid, silica-gel and florisil column were used for clean-up. The PCBs concentrations in waste transformer oil were 6-23% higher by HRGC/HRMS for analysis of 209 congeners than by GC/ECD for analysis of peak patter. The distribution characteristic of PCBs congeners before chemical treatment of waste transformer oil contaminated PCBs showed Cl5-Cl7 compounds higher than Cl2-Cl4 compounds, but after chemical treatment of waste transformer oil contaminated PCBs showed Cl2-Cl4 compounds higher than Cl5-Cl7 compounds usually. Therefore it could be find out that the congener distribution of PCBs before and after chemical treatment of waste transformer oil contaminated PCBs was very different.

Introduction

Since 1929, PCBs were used as transformer oil in the world-wide. But the PCBs were banned to use as transformer oil after recognition as a toxic substance. 209 compounds exist as PCB congeners but only 130 compounds were produced as manufactured goods and used 1,300,000 ton. The management and control of transformer- or transformer oil contaminated PCBs were not easy, because usually the transformer is reused, which was contaminated the PCBs. Therefore, it is difficult to find the adequately management and control methods. Recently, the concern of management- or treatment methods for products- and waste containing PCBs is rose in the World. In Korea many investigations are carried out to find the safe management- and treatment methods. The high temperature incineration was permitted by Waste Management Law, but it was not carried out because of public relation and concerns. The washing- and chemical treatment is permitted by POPs Management Law since 2008. Nowadays we test all incineration facilities having written permission to solve the problems and to get the trust of public. For the permit as washing- or chemical treatment facility the safety of final material after treatment should be proved with analysis result of 209 congeners. Therefore, the analysis

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method of 209 congeners in transformer oil and any other samples such as off-gas, solid waste, wastewater from incinerator or washing- or chemical treatment facility are investigated. In this paper, the analysis methods were compared with KSTM and JIS by HRGC/HRMS and the concentrations of PCBs by GC/ECD for analysis of peak patter and by   HRGC/HRMS for all congeners were compared. And also the distribution characteristic of congeners before and after chemical treatment for PCBs was investigated.

Materials and Methods

The sampling and analysis of PCBs was based on the KSTM and was referred to the JIS and USEPA method. At the first, using standard materials containing all congeners of PCBs (1668A-0.01X-SET, Accustandard) the analysis method was compared with KSTM and JIS for HRGC/HRMS. Each step for clean-up was estimated by recovery efficiency and the final sample after clean-up was analyzed using HRGC/HRMS with DB5-MS column to invest the characteristic of separated each congener. According to the investigated method using standard materials the PCBs in waste transformer oils before- and after chemical treatment were analyzed to compare the concentration and distribution characteristics of PCBs.

Results and Discussion

At the result of compare with KSTM and JIS for HRGC/HRMS using standard materials containing all congeners of PCBs (1668A-0.01X-SET, Accustandard); the method without reverse extraction using DMSO (KSTM) was more effective than the method with reverse extraction using DMSO (JIS). The recovery efficiency of method without reverse extraction using DMSO was 12% higher than the recovery efficiency of method with reverse extraction using DMSO. And also the detected concentration was 10% higher. After than for the clean-up the alkali dissolve, sulfuric acid, silica-gel and florisil column were used. The final sample after clean-up was analyzed by HRGC/HRMS with DB-5MS and separated the 166 peaks. Figure 1 showed the mass chromatograms.
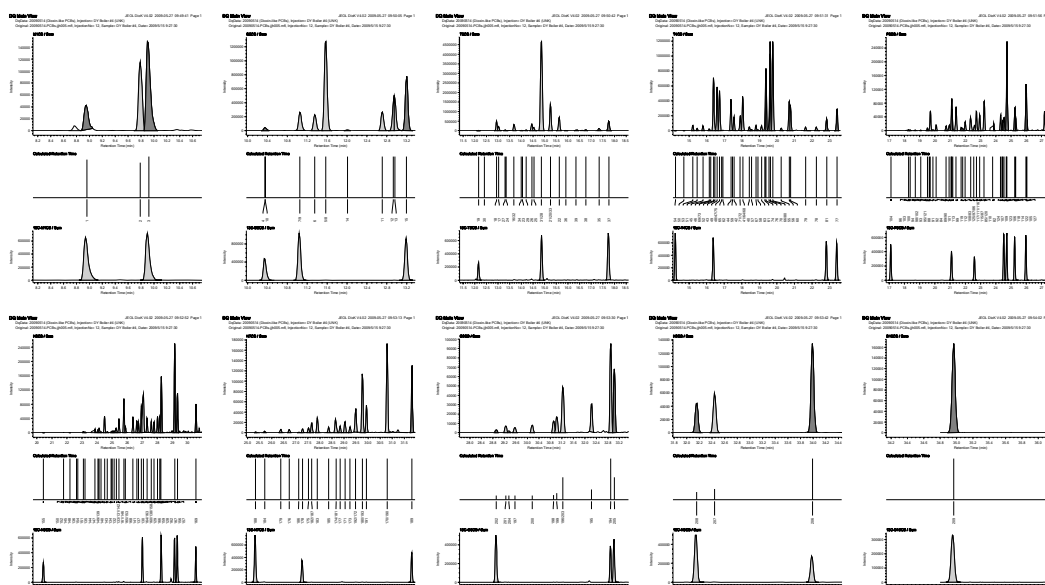

Figure 2. Mass chromatograms of PCBs.

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The Cl1 compounds and Cl9 compounds were separated all congeners distinctly, but the other Cl2-Cl8 compounds were not separated all congeners distinctly. The retention time (RT) of separated peaks and overlapped peaks showed the similar with another studies. The samples analyzed by GC/ECD, which were known the concentration, were analyzed with the result of clean-up and HRGC/HRMS. The concentrations of PCBs analyzed by HRGC/HRMS were 6-23% higher than the concentrations of PCBs analyzed by GC/ECD. The samples before chemical treatment was high the Cl5-Cl7 homologues but the samples after chemical treatment was high the Cl2-Cl4 homologues. The distribution of congener showed very different. After chemical treatment of waste transformer oil contaminated PCBs the concentration of each congener was varied. The concentration rate of congener 4, 6, 10, 17, 20, 21, 22, 37, 56, 60, 66, 76, 80, 89, 90, 105, 146, 161, 163, 164, 170, 190, 197, 199, 200, 207 and 208 decreased over 2 times and the concentration rate of congener 11, 12, 13, 25, 26, 35, 43, 49, 52, 53, 84, 91, 93, 94, 135, 136, 175, 193, 202, 203, 205 and 209 increased over 2 times. Therefore, it was concluded, that the reverse extraction using DMSO would be not carried out for the recovery efficiency by clean-up and with one column the each congener of PCBs could be not separated. And also KSTM should be reexamined, because the existed KSTM using GC/ECD and new KSTM using HRGC/HRMS showed the very different results, especially for the sample after chemical treatment to safe the management and treatment of waste transformer oil contaminated PCBs.

References

1. The Ministry of Environment of Korea. Korea Standard Test Method of POPs 2008.

2. The Ministry of Environment of Korea. Korea Standard Test Method of Waste 2004.

3. National Institute of Environmental Research. A study on the appropriated management of polychlorinated biphenyls containing wastes 2003.

4. G. M. Frame, J. W. Cochran, and S. S. Boewadt. J.High Res. Chromatogr. 1996;19;657-668.

5. K.S. Kim, K. K. Kim and J. G. Kim. Analytical Science & Technology 2006;19;352-364.

6. G. M. Frame. J. Anal. Chem. 1997;357;701-713.

7. T. H. Michael, P. Haglund and K. P. Nailwaid. Organohalogen Compounds 1998;35;111-114.

8. W. Vetter, B. Luckas and J. Buijten. J. of Chromatogr. A 1998;799;249-258.