DEVELOPMENT OF CLEANUP METHOD FOR THE ANALYSIS OF BROMINATED DIOXIN USING MULTILAYERED SILICA GEL CHROMATOGRAPHY

Hwang Seung-Ryul, Kim Kum-Hee, Park Sun-Ku, Kim Sam-Cwan, Kwon Myung-Hee, Kim Sue-Jin, Kang Yeong-Yeol, Kim Dong-Hoon, Son Ji-Hwan

National Institute of Environmental Research, Environmental Research Complex, Kyungseo-Dong, Seo-Ku, Inchon, 404-708, Republic of Korea

Abstract

Silica gel column chromatography, including multilayered silica gel is one of cleanup methods used in pretreatment step to perform trace organic analysis in environmental samples such as flue gas, ash, soil etc. However, in case of brominated dioxin and furan, the recovery of isotope labeled congeners spiked as surrogate has been reduced at the range of 4 ~ 10 % in multilayered silica gel column chromatography. It is needed to improve the lack of recovery for the analysis of environmental samples and found that 10 % $AgNO_3$ impregnated silica gel used to remove sulfur impurity in multilayered silica gel cause recovery problem. So we attempted to perform multilayered silica gel column cleanup except 10 % $AgNO_3$ impregnated silica gel and acquired the result satisfied the recovery range 50 ~ 120 % .

Introduction

Environmental pollutant polybrominated dibenzo-*p*-dioxins (PBDDs) and dibenzofurans (PBDFs) have similar molecular structure and physico-chemical properties as their chlorinated analogues. It is well known that an important source of PBDDs/PBDFs is thermal processes and manufacturing of brominated flame retardants (BFRs). Although there is only limited information for toxicity of PBDDs/PBDFs, recently the evidence of dioxin-like toxicity is increasing.[1] Currently there are a few standard analytical methods for the determination of PBDDs/PBDFs and most of the methods reported literature could not identify congeners completely compared with chlorinated dioxins and furans.[2,3,4,5] In 2002, Ministry of the Environment of Japan has established analytical method for PBDDs/PBDFs to survey the environmental concentrations.[6] In this study, cleanup method using multi-layered silica gel column was modified to develop the analytical procedure for PBDDs/PBDFs involved in Japanese official method.

Materials and Method

All solvents were pesticide residue analysis grade and obtained from WAKO Pure Chemicals Corporation. Cleanup columns were prepared with 4 g of copper and two kinds of multi-layered silica gel columns packed

with Na_2SO_4 6g, silica gel 0.9g, 22% H_2SO_4 silica gel 3 g, silica gel 0.9 g, 44% H_2SO_4 silica gel 3 g, silica gel 0.9 g, 2% KOH silica gel 3 g, silica gel 0.9 g and Na_2SO_4 6 g, 10% $AgNO_3$ silica gel 3 g, silica gel 0.9 g.

On the top of column 0.5 ng of labeled PBDDs/PBDFs standard, EDF-4153 (Cambridge Isotope Laboratory) and 0.5 ng of labeled PCDDs/PCDFs standard, EDF-8999 (Cambridge Isotope Laboratory) were spiked and eluted with 150 mL of *n*-hexane. The collected eluent was concentrated to a volume of 50 µL and spiked with 0.5 ng of labeled PBDDs/PBDFs standard, EDF-4154 (Cambridge Isotope Laboratory) and 0.5 ng of labeled PCDDs/PCDFs standard, EDF-2521 (Cambridge Isotope Laboratory).

The final sample was analyzed by high-resolution gas chromatography/high-resolution mass spectrometry(HRGC/HRMS) using Waters Autospec Ultima HRMS equipped with Agillant 6890 GC above 10,000 resolution with a Dioxin II capillary column (30 m × 0.25 mm inner diameter × 0.25 µm). Column temperature was held at 160 °C for 2 min, ramped at 40 °C / min to 240 °C, ramped at 5 °C / min to 280 °C and then programmed 10 °C / min to 300 °C held for 24 min.

Results and Discussion

Previously reported in literatures analytical methods for PBDDs/PBDFs are similar to those of polychlorinated biphenyls(PCBs), polychlorinated dibenzo-*p*-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs). The procedure for the analysis of PBDDs/PBDFs includes sample extraction, cleanup and instrumental analysis by HRGC/HRMS.

Cleanup step is a process to remove interferences from sample extract, in trace level analysis it is very important to achieve satisfactory recovery in complex matrices. Most of analytical methods for PBDD/PBDFs including official method published by Ministry of the Environment of Japan, multi-layered silica gel column chromatography suggested as one of effective cleanup methods to remove a variety of organic interferences and organic sulfur simultaneously. Sometimes recovery of labeled PBDD/PBDFs standard have been decreased in the process of multi-layered silica gel cleanup. As shown in Fig. 1. Both blank and sample analysis labeled 1,2,3,7,8-PBDF and labeled 1,2,3,7,8,9-HBDD disappeared on the chromatograms analyzed by HRGC/HRMS. This result has never been observed in the case of other organic pollutants such as PCBs, PCDDs/PCDFs.

In general, according to electornegativity aromatic carbon-bromine bonds are weaker than similar carbon-chlorine bonds and reductive substitution of halogens in aromatic structures becomes easier as the size of halogen atoms increases. So it is suggested that carbon-bromine bond of PBDDs/PBDFs have been decomposed in the process of multi-layered silica gel cleanup due to decreased carbon-bromine bond strength compared with carbon-chlorine bond of PCDDs/PCDFs.

In the analysis of PBDDs/PBDFs, to dissolve this problems a variety of cleanup methods have been tested to find out the reason for the decreased recovery of labeled PBDDs/PBDFs in the cleanup process. When column cleanup was performed with $AgNO_3$ silica gel, the results were the same as multi-layered silica gel column and

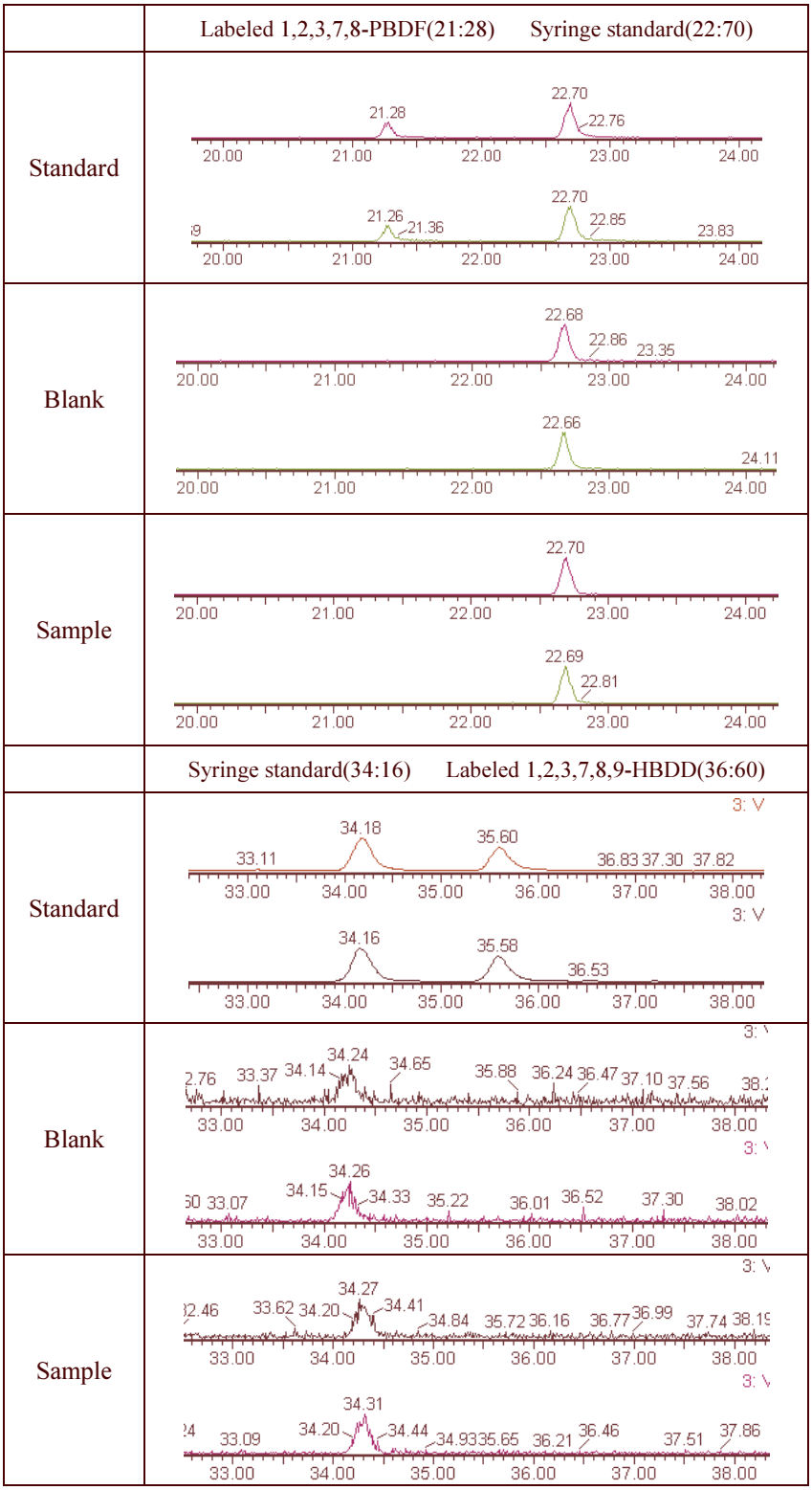

Figure 1. Chromatograms of PBDDs/PBDFs congeners analyzed by HRGC/HRMS.

all labeled PBDDs/PBDFs could not detected. For the further investigation, we carried out multi-layered silica gel column except $AgNO_3$ silica gel and obtained recoveries of labeled PBDDs/PBDFs in the range 30 ~ 150 % and recoveries of labeled PCDDs/PCDFs in the range 50 ~ 120 % .

Instead of $AgNO_3$ silica gel, copper column as a cleanup method to remove organic sulfur was tested using labeled PBDDs/PBDFs standard, the results were the same as $AgNO_3$ silica gel cleanup. So it is also impossible to introduce activated copper column and required to develop cleanup method for the elimination of organic sulfur to overcome the interfering effect in HRGC/HRMS analysis.

It is concluded that multi-layered silica gel cleanup method except $AgNO_3$ silica gel was developed as a efficient method for the analysis of PBDDs/PBDFs.

References

1. WHO, Environmental Health Criteria 205, **1998**.
2. J. Onodera, J-W Choi, K. Kitamura, S. Hashimoto, H. Ito, N. Suzuki, S. Sakai and M. Morita, *Chemosphere*, 2003;53:637.
3. US EPA Method TO-9A, **1999.**
4. Bert van Bavel, Ingrid Ericsson, Helen Bjonfoth, Jessika Hagberg, Gunilla Lindstrom, *Organohalogen Compounds*, **2004;66:107.**
5. N. Hanari, T. Okazawa, K. Guruge, J. Falandysz, N. Yamashita, *Organohalogen Compounds* 2004;66:207.
6. www.nies.go.jp/edc/japanese/sokuteil-7.html.