Organohalogen Compounds, Volume 60, Pages 76-79 (2003)

EXAMINATION OF EXTRACTION METHOD FOR DIOXINS IN CHARCOAL

Kouji Takiguchi[1], Hiroaki Mochizuki[1], Daisuke Nakajima[2], Yuka Ezoe[2],
Shozo Asada[1], Sumio Goto[2], Shinichi Sakai[2]

[1]Japan Quality Assurance Organization, 14-12 Dezuminato, Chuou-ku, Chiba-Shi, Chiba, 260-0023, Japan
[2]National Institute for Environmental Studies, 16-2 Onogawa, Tsukuba-Shi, Ibaraki, 305-8506 Japan

Introduction

Charcoal has many physical characters. Especially making good use the adsorptive, charcoal is used exhaust gas treatment, water treatment, deodorant, etc. by the adsorptive.[1)] Furthermore, charcoal is easily obtained by carbonizing scrap woods. Therefore it is thought that charcoal is useful as one of recycle method of scrap woods. However, it is important to avoid exposure to danger from recycled products that may contain hazardous substances such as PCBs and dioxins. Charcoal permit chemical materials to adsorb strongly and so extraction process was very important to estimate chemical material in charcoal.

We provide a comparative study of five solvents (toluene, acetone, dichloromethane, ethanol and methanol) to extract of the dioxins from charcoal and we report on some findings we have made by examining.

Methods and Materials

Charcoal Sample: Charcoal sample was purchased the commercial black coal for fuel. Charcoal sample was homogenized by blender and was sifted sieve (2 mm mesh).

Extraction: Charcoal sample was extracted by Soxhlet extraction of 16 hours. Extract solvents were used toluene, acetone, dichloromethane, methanol, and ethanol. Obtained extract was concentrated and diluted by n-hexane. Each solution was spiked with ^{13}C 2, 3, 7, 8-substitued PCDDs/PCDFs and Co-PCBs isomers. On and after this process, analysis was carried out according to the JIS (Japan Industrial Standards)-method.[2)]

Cleanup: Following processes were carried out as cleanup process--- multi-layer silica gel column treatment (multi-layer silica gel column: SPELCO), silica gel column treatment (silica gel 60 (granular): Kanto chemical co., Inc.), and activated carbon column treatment (activated carbon distributing silica gel: Kanto chemical co., Inc.). Obtained solution was concentrated under nitrogen flow and addition of syringe standards and n-nonane.

HRGC-HRMS measurement: HRGC-HRMS measurement was carried out at 10,000 or more resolution by the EI-SIM method. HRGC-HRMS systems were Autospec Ultima MS (Micromass UK Ltd.) equipped with a HP6890 GC (Agilent Technologies), JMS-700 MS (JEOL ltd.) equipped with a HP6890 GC (Agilent Technologies) and JMS-700 MS (JEOL ltd.) equipped with a HP5890 GC (Agilent).

Following capillary columns were used: CP-Sil88 for DIOXIN (0.25 mm i.d. * 60 m Length * 0.1 μm stationary phase, Varian Inc.), Rh-17ms (0.32 mm i.d. * 30 m Length * 0.15 μm stationary phase, Inventex co. ltd.) and HT-8 (0.22 mm i.d. * 50 m Length * 0.1 μm stationary phase, SGE Japan Inc.).

Results and Discussion

Determination results that were obtained in the way described above are shown Table 1and Fig. 1. Isomer substituted by chlorine at 2, 3, 7, 8-positions was detected only OCDD of toluene-Soxhlet extract and acetone Soxhlet extract.

It was seemed that total concentrations were different from each solvent. Total concentration of acetone Soxhlet extract was the highest among five extracts and secondary was ethanol Soxhlet extract. PCDFs and HpCDDs homologue concentration were scarcely detected about any solvents. In PCDDs concentrations, low-chlorinated PCDDs concentrations were higher than high-chlorinated PCDDs concentrations. Contribution of Homologue concentration to total PCDDs + PCDFs concentration was shown in Fig. 2. Contribution of TeCDDs homologue concentration was occupied about 40-70% of the whole, and contribution of PeCDDs homologue concentration was occupied about 20-30% of the whole. Moreover, contribution of HxCDDs homologue concentration was observed only in methanol Soxhlet extract. It was seemed that contribution of OCDD homologue concentration was seen about 30% in only toluene Soxhlet extract, but OCDD homologue concentration was similar to OCDD concentration of acetone Soxhlet extract.

Table1 Homologue Concentrations of PCDDs/PCDFs and Co-PCBs in Charcoal Sample

	Extraction Solvent				
congener	**toluene (*n* = 4)**	**acetone (*n* = 5)**	**dicloro-methane (*n* = 5)**	**ethanol (*n* = 5)**	**methanol (*n* = 5)**
TeCDDs	**4.2 ± 0.6**	**22 ± 2**	**10 ± 3**	**20 ± 2**	**14 ± 7**
PeCDDs	**1.6 ± 0.4**	**10 ± 1.2**	**5.0 ± 2.5**	**10 ± 1**	**5.7 ± 3.5**
HxCDDs	**0.90 ± 0.10**	**2.9 ± 0.76**	**3.5 ± 2.0**	**2.3 ± 0.1**	**N. D.**
HpCDDs	**N. D.**	**N. D.**	**N. D.**	**N. D.**	**N. D.**
OCDD	**2.8 ± 1.0**	**2.3 ± 0.8**	**N. D.**	**N. D.**	**N. D.**
Total PCDDs	**9.4 ± 0.4**	**37 ± 4**	**19 ± 7**	**33 ± 3**	**19 ± 7**
TeCDFs	**N. D.**	**3.8 ± 1.3**	**N. D.**	**0.91 ± 0.01**	**N. D.**
PeCDFs	**N. D.**	**N. D.**	**N. D.**	**N. D.**	**N. D.**
HxCDFs	**N. D.**	**3.3 ± 0.6**	**N. D.**	**N. D.**	**N. D.**
HpCDFs	**N. D.**	**N. D.**	**N. D.**	**N. D.**	**N. D.**
OCDF	**N. D.**	**N. D.**	**N. D.**	**N. D.**	**N. D.**
Total PCDFs	**N. D.**	**7.1 ± 2.3**	**N. D.**	**0.91 ± 0.50**	**N. D.**
Total (PCDDs + PCDFs)	**9.4 ± 0.4**	**44 ± 4**	**19 ± 2**	**34 ± 3**	**19 ± 7**
Total non-orthoCo-PCBs	**2.1 ± 0.2**	**2.4 ± 0.3**	**2.0 ± 0.1**	**2.1 ± 0.3**	**2.0 ± 0.4**
Total mono-ortho Co-PCBs	**17 ± 2**	**19 ± 6**	**15 ± 3**	**15 ± 1**	**17 ± 2**
Total(dioxin + Co-PCBs)	**29 ± 2**	**65 ± 8**	**36 ± 7**	**50 ± 3**	**38 ± 8**

unit : pg / g
N. D. : Not Detected

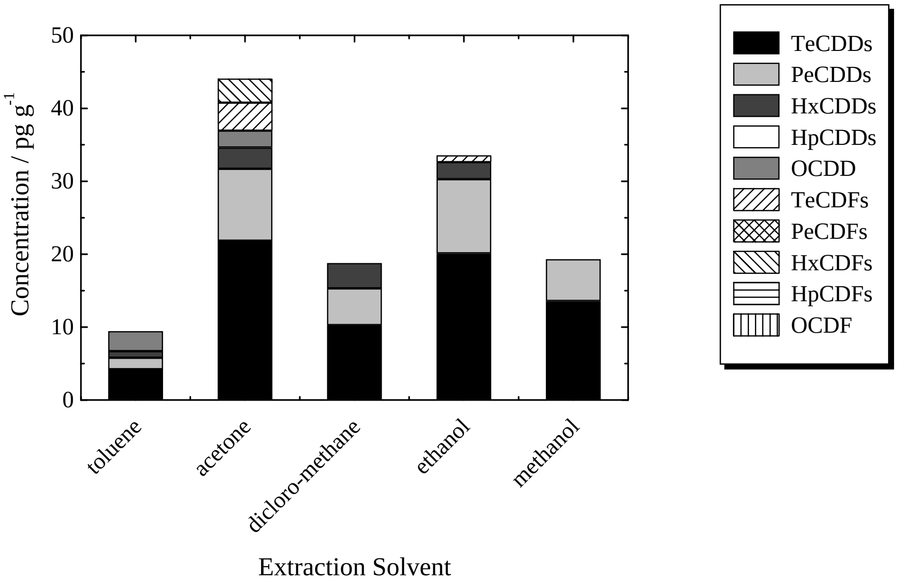

Fig. 1 Homologue Concentrations of PCDDs/PCDFs in Charcoal sample

From above results, acetone could be extracted dioxin most efficiency from charcoal sample in this experiment.

It was reported that when Soxhlet extraction was carried out over 16 hours, amount of extracted dioxins from fly ash splayed activated carbon was increased[3)]. Therefore we assumed that extraction of dioxins from charcoal sample was not carried out sufficiently, so that we were carried out 72 hours extraction examination of acetone Soxhlet. However, it seemed that amount of extracted dioxins was not increased. With above result, it was considered that extraction of dioxins in charcoal sample was carried out sufficiently by acetone Soxhlet of 16 hours.

Acknowledgements

We should like to express our grateful thanks to Y. Nomura, H. Asai, S. Kumagai, H. Maeda and H. Shimono of Chiba testing laboratory, Japan Quality Assurance Organization Chiba testing laboratory.

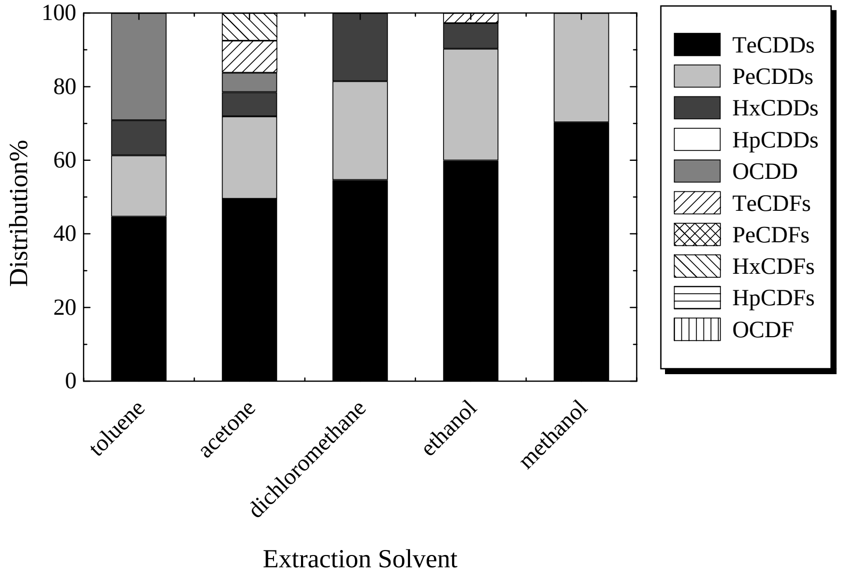

Fig.2 Contribution of homologue to total PCDDs/PCDFs concentration in charcoal sample

References
1. K. Matsunaga, Kagoshima prefectural institute of industrial technology News (1996), 35, 3-4
2. Japanese Standards Association (1999) JIS K 0311 Method for determination of tetra- through octa-chlorodibenzo-p-dioxins, tetra- through octa-chlorodibenzo-furans and coplanar polychlorobiphenyls
3. Y. Kennmochi, K. Tsutsumi (2000) 9th Symposium on Environmental Chemistry Abstracts (Japan Society for Environmental Chemistry), 139