New Preconcentration System Based on Steam Distillation for Dioxin Analogs[1]

Takeru Iwamura,* Junji Hirayama, and Jun-ichi Iwamura†
Research and Development Department, Laboratory of Creative Science Co. Ltd., Mishono-cho, Yao, Osaka 581-0818
†*The Junior College of Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502*

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Polychlorinated aromatic compounds such as polychlorinated dibenzo-*p*-dioxins, and dibenzofurans were successfully and quantitatively recovered using a steam distillation-azeotropy system without the complex procedures.

Polychlorinated aromatic compounds such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and biphenyls are highly toxic and stable pollutants. Because of their extreme toxicity and widespread occurrence in the environment, these compounds are among the most intensively studied persistent pollutants.[2] In the standard analytical procedure for organochlorine compounds, the sample preparation for GC or GC-MS analysis of complex mixtures still involves complex procedures such as liquid-liquid extraction, Soxhlet extraction, column chromatography, and so on.[3,4] For this reason, dynamic monitoring of polychlorinated aromatic compounds is very difficult under the present circumstances. Accordingly, it is important to establish a quick and simple sample preparation method. In this regard we investigated the steam distillation method. Therefore, we have investigated technical development on the basis of water. We have developed equipment for recovering waste cleaning solvent and distillation sludge from the dry cleaning process.[5,6] This equipment was based on the steam distillation method. In recent years, steam distillation-extraction, in which the compounds are first distilled and then extracted into organic solvent, has attracted much attention.[7–9] Ramos et al. reported the recovery of dioxin analogs using steam distillation-solvent extraction.[10] Unfortunately, the recovery of these compounds was uneven, and the recovery of octachlorinated compounds has not been so high (39.1–55.9%). We expected that the recovery of these compounds might be improved by using electron-donating solvent. The benzene ring of polychlorinated aromatic compounds such as OCDF will be electron poor because of the presence of the chlorine atoms as the electron-withdrawing group. Therefore, using electron-donating solvent might accelerate the azeotropic distillation.

We first examined the recovery of 2,3,7,8-tetrachlorodibenzofuran (TCDD) and 1,2,3,4,6,7,9-octachlorodibenzofuran (OCDF) under steam distillation-azeotropy system. The recovery experiments were carried out using Kalov® (Figure 1).[11] The heating steam (ca 120 °C) and toluene (10 mL/min) as azeotropy solvent flowed into a kiln containing 1.0 mL of organochlorine compound (1.0 ppm) and 1.0 L of distilled water. Heating of the kiln was unnecessary. Water vapor containing toluene and organochlorine compound condensed on the cool condenser surface, they were mixed in a separating funnel. The water phase was extracted by distilled toluene as the organic phase. The extracted organic phase was evaporated to dryness. The concentrated organochlorine compound was then dissolved by 1.0 mL of an internal standard solution (2-fluorofluorene hexane solution).

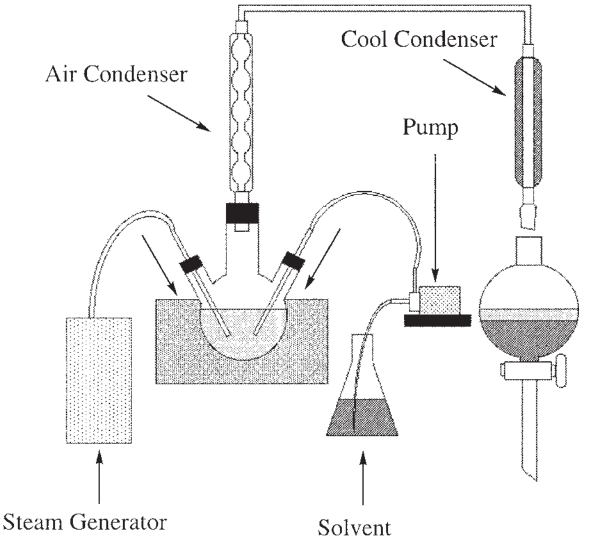

Figure 1. Mimetic diagram of Kalov® for steam distillation-azeotropy equipment.

Prepared samples were analyzed with a GC-MS spectrometer. The result was that the recovery of TCDD reached 97% within 4 h. In the case of OCDF, the recovery reached 102% within 6 h. Tetrachlorinated and octachlorinated compound were successfully and quantitatively recovered (Figure 2).

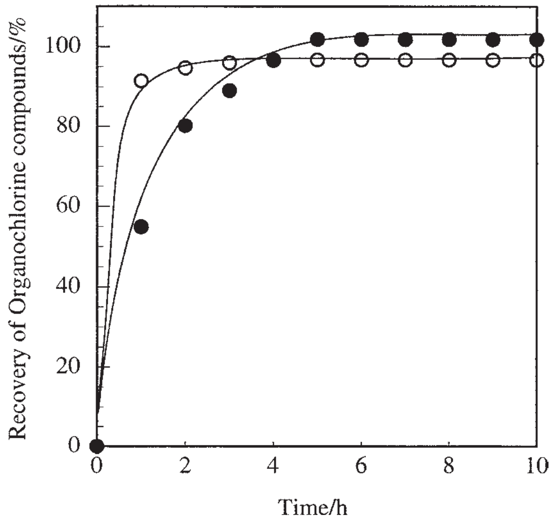

Figure 2. Plot of recovery versus time for steam azeotropy of organochlorine compounds with toluene (○ TCDD; ● OCDF). Recovery determined by GC-MS analysis.

The boiling points of TCDD and OCDF are 446.5 and 537 °C, respectively. Consequently, the recovery of dibenzo-*p*-dioxins and dibenzofurans will be quantitatively for tetrachloro to octachloro compounds.

Moreover, the solvent effect for steam distillation-azeotropy was investigated with a similar method. Four kinds of azeotropy solvents (i.e. chlorobenzene, benzene, toluene, ethylbenzene) were employed (Figure 3). If the π–π interaction controlled these azeotropy systems, the aromatic solvents, which were electron rich in the benzene ring, would produce good results. Accordingly, we supposed that the order of recovery was ethylbenzene > toluene > benzene > chlorobenzene. However, the actual order of recovery was chlorobenzene (105%) > toluene (102%) > benzene (42%) > ethylbenzene (23%).

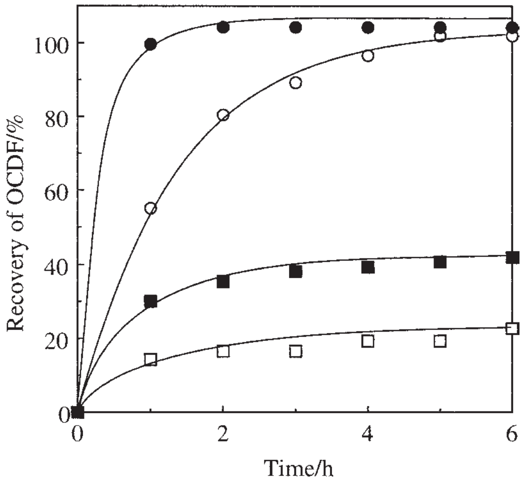

Figure 3. Plot of recovery versus time for steam distillation-azeotropy of OCDF with various solvents (● chlorobenzene; ○ toluene; ■ benzene; □ ethylbenzene). Recovery determined by GC-MS analysis.

The UV-vis spectra of OCDF in various solvents were measured to get information on polychlorinated compound-solvent interaction. Previously, Ramos et al. reported that the recovery of OCDF was 42.4% in pentane, and 55.9% in dichloromethane using steam distillation-solvent extraction.[9] Therefore, the UV-vis spectra of OCDF were measured in pentane, dichloromethane, and chlorobenzene, which gave the best result in our experiment (Figure 4).

The UV-vis spectrum of OCDF in pentane exhibited the strongest absorption with the λ_{max} at 305 nm (Figure 4a). Additionally, the hypochromic effect was observed in dichloromethane and chlorobenzene, respectively (Figure 4b, c). Above all, the absorption at 305 nm is the lowest in chlorobenzene. The absorption of 305 nm observed in pentane, shifted from 305 nm to 306 nm in dichloromethane. In chlorobenzene, the corresponding absorption was observed at 308 nm. These results confirmed that polychlorinated compound–solvent interaction was the strongest in chlorobenzene.

Moreover, the UV-vis spectra of OCDF were measured in benzene, toluene, and ethylbenzene. However, changes of the obtained spectra were small. These spectra have not been explained in our results, that is, the order of recovery was chlorobenzene > toluene > benzene > ethylbenzene.[12] At present, further investigation on this point is at an advanced stage.

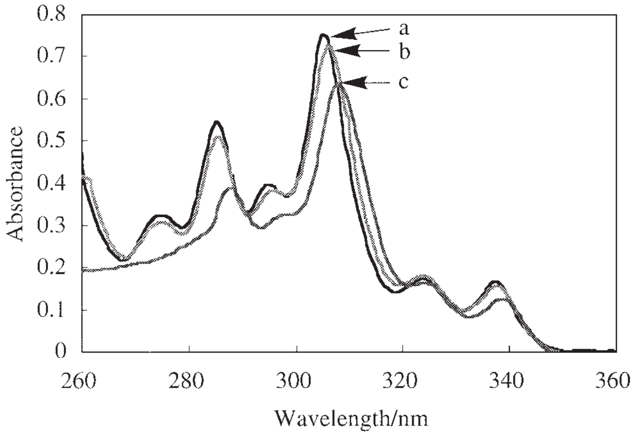

Figure 4. UV-vis Spectra of OCDF in pentane (a), dichloromethane (b), and chlorobenzene (c) (OCDF concentration; 22.54 mM).

Present analytical procedure for organochlorine compounds includes complex procedures. We believe that preconcentration by steam distillation-azeotropy system will contribute to the analysis of organochlorine compounds. Further investigations are currently under way.

References and Notes

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11 Kalov®, which produced by Laboratory of Creative Science Co., Ltd., is a steam distillation equipment for the recycling organic solvents.

12 In the case of chlorobenzene, the good result might be brought about the increase of polarizability, which is originated from the presence of chlorine atom in the aromatic solvent.