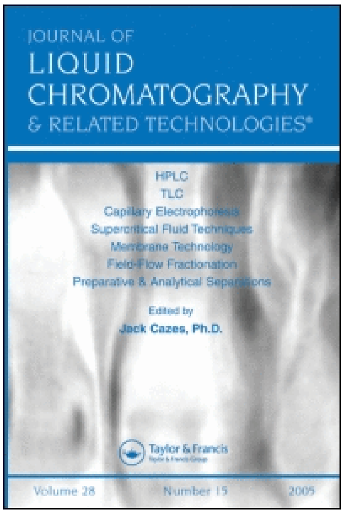

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# Microwave-Assisted Extraction (MAE) of Polychlorinated Biphenyls and Polychlorinated Dibenzo-*p*-Dioxins from Fly Ash and Sea Sediments: Effect of Water and Removal of Interferences

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## ABSTRACT

This study involved microwave-assisted extraction (MAE) of polychlorinated biphenyls (PCBs) and polychlorinated dibenzodioxins (PCDDs) from fly ash and sea sediments. The effect of the addition of water to the extracting solvent (solvation) and sample matrices (wetting) on the variation of recoveries was studied under four concentrations of a toluene–isopropyl alcohol (IPA) mixture. The results indicate that MAE, using 1–2% of solvation or 10–20% of wetting in 90 : 10 (v/v) of toluene–IPA mixture, was the most effective treatment in isolating PCBs and PCDDs from the samples. Multi-layer column chromatography on neutral and acidic silica gel with *n*-hexane was used for cleaning up the

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extracts. In addition, alumina column clean-up was performed to remove chromatographic interferences from sediment extracts. High performance liquid chromatography (HPLC) with ultraviolet (UV) detection was employed to identify and quantify the analytes.

## INTRODUCTION

Compared to instrumental analyses, sample preparation is a long and critical step in analyzing organic contaminants in the environment. The extraction of organic compounds from solid materials can be attained using several established methods. The most conventional approach is the Soxhlet extraction.[1]

Ganzler et al. first reported the use of microwave energy to improve the extraction of organic compounds.[2] Microwave-assisted extraction (MAE) has recently been reported as an effective sample preparation technique for various environmental solid samples. The main advantage of MAE is the rapid heating of solvents at a temperature above a boiling point in closed vessels. This high temperature and pressure allow quick sample extraction, with excellent efficiency. In addition, MAE uses small solvent volumes. Dupont et al. extracted polychlorinated biphenyls (PCBs) from sewage sludge efficiently using MAE.[3] Extractions could be achieved within 10 min, while recoveries compared favorably with Soxhlet values.

Eljarrat et al. developed an MAE procedure for extracting polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from sewage sludge.[4] Recoveries ranged from 30% to 70% among the 17 isomers investigated. The results obtained using MAE were consistent with the concentrations found using Soxhlet extraction. Likewise, Shu et al.[5] performed MAE of polycyclic aromatic hydrocarbons (PAHs) from sediments and river bed soil. Both the MAE and the Soxhlet extraction method yielded comparable results. On the other hands, Lopez-Avila et al.[6] suggested the use of microwave radiation in the presence of solvents to extract different organic compounds (organochlorine pesticides, PCBs, organophosphorous pesticides, and other semi-volatile compounds) from various solid matrices (soils and sediments).

Heat generation in the sample, in the microwave field, requires a dielectric compound. Higher dielectric constants trigger the release of more thermal energy and accelerates heating for a given frequency. Consequently, the effect of microwave energy strongly depends on the nature of both the solvent and the matrix. In general, the solvent chosen has a high dielectric constant; thus, it strongly absorbs microwave energy. Chee et al. reported that hexane–acetone

1 : 1 (v/v) was efficient in extracting PAHs from sediments. Likewise, recoveries were similar to those obtained using dichloromethane.[7] The best results of the MAE of sulfonylurea herbicides from soil were obtained using a dichloromethane–methanol (90 : 10, v/v) mixture.[8] Similarly, the efficiency of MAE of phenols from soils using a hexane–acetone mixture was increased with the percentage of acetone in the mixture.[9]

While organic solvents are predominant, aqueous phases may also be used in some cases. Pastor et al. reported the efficiency of the toluene–water 9 : 1 mixture to extract several compounds including PAHs, PCBs, and organochlorinated pesticides from marine sediments.[10] Efficient extraction of PAHs from sludge and wet harbor sediments was achieved using two different extractants, i.e., acetone–water (4 : 1, v/v) (100°C, 1 h) and *N*-methyl-2-pyrrolidinone (NMP) (130°C, 1 h).[11]

The matrix moisture is also found to be a critical parameter during the MAE of organic compounds from solid samples. A study by Chee et al. showed that increased moisture content from 10 to 20% (w/w) obtained the best recoveries of phthalate esters from marine sediments using an acetone–hexane (1 : 1, v/v) mixture.[12] Likewise, Letellier et al. reported that the addition of water to the matrix enhanced the extraction of PAHs from marine sediments using dichloromethane.[13] On the other hand, Camel et al. suggested that microwave heating of water allowed the migration of the compounds out of the matrix.[14] During the extraction of essential oils from plant materials, microwaves interact selectively with free water molecules present in the gland and vascular system; thus, leading to localized heating and rapidly increasing temperature to near or above the boiling point of water. As a result, the systems undergo dramatic expansion and subsequent rupture of their walls. This allows the essential oil to flow towards the organic solvent.

In an earlier study, the authors investigated MAE parameters for extracting PCBs and PCDDs from fly ash.[15] These materials were subjected to MAE in a closed-vessel microwave system. The parameters considered were: toluene–isopropyl alcohol (IPA) (100 : 0, 95 : 5, 90 : 10, 80 : 20) mixtures as the extracting solvent, temperatures (72, 85, 94, 100, and 110°C), times, solvent volumes, etc. The best results were obtained when the toluene–IPA (90 : 10, v/v) mixture was used at 100°C for 25.3 min.

This study, determined the effect of water on the efficient MAE and removal of interferences for the effective quantification of PCBs and PCDDs from fly ash and sea sediments, using toluene–IPA (100 : 0, 95 : 5, 90 : 10, 80 : 20) at 100°C for 25.3 min in a closed-vessel microwave system. For the purposes of comparison, the samples were subjected to solvation by adding water to the extracting solvent before allowing the solvent mixture to come in contact with the solid matrix. Likewise, wetting was also induced by adding water to the solid matrix before allowing the solvent mixture to come in contact with the solid matrix. In addition, the results of the fly ash extraction were compared with those of the sea sediments under the same conditions. Lastly, the removal of chromatographic interferences from fly ash was compared with that of sea sediments. The effects of solvation and wetting under varying toluene–IPA mixture concentrations on the MAE of PCBs and PCDDs from fly ash and sea sediments have rarely been compared. It should be noted, that the purpose of this investigation is to compare the effects of extraction parameters on MAE, rather than obtain quantitative recoveries.

## EXPERIMENTAL

### Reagents

All high performance liquid chromatography (HPLC) grade organic solvents (methanol, dichloromethane, *n*-hexane, toluene, and acetonitrile) used were obtained from Burdick & Jackson (Muskegon, MI). Isopropyl alcohol was obtained from Kanto Chemical (Tokyo, Japan). Silica gel (230–400 mesh, Merck, Darmstadt, Germany) and alumina (neutral, 70–230 mesh, Merck, Darmstadt, Germany) were initially rinsed with methanol twice, and then with dichloromethane twice. They were then activated at 180°C for at least 12 hours. Anhydrous sodium sulfate (Merck, Darmstadt, Germany) was used to protect the packing materials in the multi-layer silica gel and alumina column.

Polychlorinated biphenyls consisting of 2,2′,4,5′-tetrachlorinated biphenyl (T4CB) and 2,3,4,5,6-pentachlorinated biphenyl (P5CB), and PCDDs consisting of 1,2,3,4-tetrachlorinated dibenzodioxin (T4CDD), 1,2,3,4,7-pentachlorinated dibenzodioxin (P5CDD), 1,2,3,4,7,8-hexachlorinated dibenzodioxin (H6CDD), 1,2,3,4,6,7,8-heptachlorinated dibenzodioxin (H7CDD), and octachlorinated dibenzodioxin (O8CDD) were obtained from Ultra Scientific (250 Smith Street, North Kingstown, USA). A stock solution containing a mixture of 5.0 μg/mL PCBs and 0.45 μg/mL PCDDs was prepared in toluene for each compound.

### Sample Preparation

The samples, fly ash, and sea sediments, were used as a fortified sample matrix during the recovery studies. The fly ash and sea sediments were collected from the Mokdong municipal solid waste incinerator (Seoul, Korea) and Masan bay (Masan, Korea), respectively. All samples were dried at room temperature and then at 110°C in an oven to remove water content. 0.5 g of the sample was spiked at 500 ng/g level with a stock solution of T4CB and P5CB, and at 45 ng/g with T4CDD, P5CDD, H6CDD, H7CDD, and O8CDD, prior to aging at 110°C for 24 h.

Microwave-assisted extraction of PCBs and PCDDs from the samples was performed, using a MARS X microwave extraction system (CEM, Matthews, NC). The sample was transferred to Teflon-lined extraction vessels. After extraction, the vessels were allowed to cool down in room temperature before the caps were opened. The multi-layer silica gel column was used for the clean-up of the extract after filtering and concentration. For sea sediments, in particular, alumina column clean-up was performed to remove residual interferences after the multi-layer silica gel column clean-up.

Microwave-assisted extraction variables, solvation, and wetting using varying toluene–IPA mixtures, were evaluated to compare recoveries of analytes. Solvation refers to the addition of water to the extraction solvent, while wetting involves the addition of water to the sample matrices. Four varying extracting solvent concentrations of toluene–IPA, i.e., 100 : 0, 95 : 5, 90 : 10, and 80 : 20 (v/v) were heated for 25.3 min at 100°C. Extractions were then performed at four varying solvations or wettings, i.e., 0.05, 0.10, 0.25, or 0.50 mL, corresponding to the four solvent concentrations.

The extracts were cleaned up using a multi-layer silica gel column,[16,17] which had been packed according to the following order: neutral (2 g); acidic (6 g); and neutral (4 g) silica gel. The column was then eluted with 50 mL of *n*-hexane. For sea sediments, the purified extract was fractioned in a column containing alumina to collect, separately, the interferences and analytes eluted with hexane (70 mL) and a mixture (40 mL) of hexane–dichloromethane (8 : 2, v/v), respectively. The eluent was concentrated using a rotary evaporator in 2–3 mL and transferred into a 7-mL vial. Nitrogen evaporation was induced to remove *n*-hexane, with 100 μL of acetonitrile subsequently refilled for quantification using HPLC–ultraviolet (UV).

## Analysis of Extracts

The amount of PCBs and PCDDs in the liquid extracts was determined using a Kromasil KR100-5C18 column (250 × 4.6 mm, Eka Chemicals AB, Bohus, Sweden). The HPLC system used in this study was an M920 delivery pump (Young-Lin, Korea) equipped with an SPD-10A UV-visible detector (Shimadzu, Japan) and C-R6A integrator (Shimadzu). The injected volume was 20 μL, with the flow rate of the mobile phase at 1.0 mL/min at 40°C. An acetonitrile–water (90 : 10, v/v) solution was used to separate the analytes in 40 min. The chromatograms were then recorded at 250 nm (AUFS = 0.005).

## RESULTS AND DISCUSSION

The relative ratios of recoveries were obtained by dividing the % recovery at 0.10 mL of solvation in 90 : 10 (v/v) of toluene–IPA by the corresponding % recovery in the tables. Averages were expressed in means with standard deviation for the three replicates.

### Microwave-Assisted Extraction of Polychlorinated Biphenyls and Polychlorinated Dibenzodioxins from Fly Ash and Sea Sediments

Tables 1 and 2 present the MAE recoveries and the relative recovery ratios of PCBs and PCDDs from fly ash and sea sediments, respectively, based on extracting solvent concentrations at 0.00 mL of water. The results depended on the content of IPA in toluene, as indicated by the averages that were proportional to the content of IPA. This observation was consistent with the earlier study, i.e., the presence of IPA in the matrix resulted in more matrix surface available for the extracting solvent (toluene).[15] The previous study used toluene–IPA (90 : 10, v/v) mixture for the desorption of analytes and microwave heating of samples, although toluene is known to be a suitable solvent for extracting PCBs and PCDDs from solid samples.

The water contents of the matrix and extracting solvent were critical factors, since water molecules had a high dipole moment and consequently absorbed microwave energy strongly; thus, leading to the efficient heating of the sample. The influence of the water content of the matrix on the extraction efficiency (wetting) was tested as 0–100% (w/w) of water, with the influence of the water content of the extracting solvent (solvation) as 0–10% (w/w). While PCBs and PCDDs were rarely soluble in water, enhanced MAE was performed throughout solvation or wetting (Tables 1 and 2). The average ratio of relative recovery of extracted PCBs and PCDDs was increased with a quantity of water (from 0 to 20% for wetting and from 0 to 2% for solvation). However, with a greater amount of water, the recovery was decreased. At a quantity of water equal to 100%, i.e., 0.5 mL of wetting, the ratio of relative recovery was very low, because of miscibility problems in using the organic solvent, toluene, for extraction.

The relative contributions of solvation and wetting to recoveries were compared at 100 : 0 (v/v) of toluene–IPA. Results revealed that wetting extraction yielded lower recoveries compared with solvation. It may be suggested, that water in wetting acts as a barrier between toluene and matrix and, consequently, hinders the contact of toluene with analytes adsorbed in the matrix. However, the other mixtures of toluene–IPA, i.e., 95 : 5, 90 : 10, 80 : 20 (v/v), did not exhibit the same behavior. Microwave heating of the water in the matrix may lead to the formation of gas bubbles, with subsequent local

***Table 1.*** Recovery and relative ratio of recovery of PCBs and PCDDs in fly ash extracts.

| | Relative ratio of recovery | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Analytes | 0.00 | S/0.05 | W/0.05 | S/0.10 | W/0.10 | S/0.25 | W/0.25 | S/0.50 | W/0.50 |
| | | | | Toluene : IPA (v/v) 100 : 0 | | | | | |
| T4CB | 0.92 | 0.83 | 0.77 | 0.83 | 0.83 | 0.82 | 0.80 | 0.82 | 0.75 |
| P5CB | 1.01 | 0.70 | 0.53 | 0.74 | 0.72 | 0.69 | 0.72 | 0.82 | 0.60 |
| T4CDD | 0.88 | 0.90 | 0.81 | 0.91 | 0.84 | 1.04 | 0.88 | 0.91 | 0.83 |
| P5CDD | 0.88 | 0.84 | 0.79 | 0.88 | 0.83 | 0.85 | 0.72 | 0.78 | 0.70 |
| H6CDD | 0.82 | 0.86 | 0.78 | 0.93 | 0.85 | 0.86 | 0.73 | 0.83 | 0.72 |
| H7CDD | 0.87 | 0.86 | 0.82 | 0.96 | 0.90 | 0.90 | 0.79 | 0.86 | 0.80 |
| O8CDD | 0.87 | 0.81 | 0.76 | 0.94 | 0.83 | 0.84 | 0.76 | 0.82 | 0.76 |
| Average | 0.88 | 0.85 | 0.79 | 0.91 | 0.85 | 0.88 | 0.78 | 0.84 | 0.76 |
| (SD) | (0.03) | (0.02) | (0.04) | (0.03) | (0.02) | (0.05) | (0.02) | (0.07) | (0.03) |
| | | | | Toluene : IPA (v/v) 95 : 5 | | | | | |
| T4CB | 0.93 | 0.99 | 0.92 | 0.96 | 0.97 | 0.95 | 0.80 | 0.66 | 0.75 |
| P5CB | 1.04 | 0.72 | 0.86 | 0.81 | 0.94 | 0.93 | 0.79 | 0.66 | 0.75 |
| T4CDD | 0.88 | 0.93 | 1.03 | 0.89 | 0.87 | 0.76 | 0.68 | 0.45 | 0.52 |
| P5CDD | 0.89 | 1.03 | 0.87 | 0.97 | 0.94 | 0.78 | 0.65 | 0.48 | 0.64 |
| H6CDD | 0.84 | 0.99 | 0.92 | 0.86 | 0.84 | 0.73 | 0.60 | 0.49 | 0.60 |
| H7CDD | 0.89 | 1.02 | 0.98 | 0.85 | 0.88 | 0.68 | 0.52 | 0.54 | 0.58 |
| O8CDD | 0.92 | 0.98 | 1.03 | 0.96 | 0.94 | 0.73 | 0.51 | 0.57 | 0.59 |
| Average | 0.89 | 0.99 | 0.96 | 0.91 | 0.91 | 0.77 | 0.63 | 0.53 | 0.61 |
| (SD) | (0.03) | (0.02) | (0.04) | (0.02) | (0.04) | (0.01) | (0.04) | (0.05) | (0.02) |

*(continued)*

***Table 1.*** Continued.

| | Relative ratio of recovery | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Analytes | 0.00 | S/0.05 | W/0.05 | S/0.10 | W/0.10 | S/0.25 | W/0.25 | S/0.50 | W/0.50 |
| | | | | Toluene : IPA (v/v) 90 : 10 | | | | | |
| T4CB | 0.92 | 1.02 | 1.07 | 87.3 | 0.95 | 0.93 | 1.04 | 0.92 | 0.95 |
| P5CB | 0.96 | 0.91 | 0.92 | 80.6 | 0.88 | 0.86 | 1.04 | 0.99 | 0.84 |
| T4CDD | 0.89 | 0.90 | 0.97 | 86.2 | 0.98 | 0.85 | 0.93 | 0.73 | 0.85 |
| P5CDD | 0.92 | 1.02 | 1.02 | 82.9 | 0.98 | 0.83 | 0.93 | 0.75 | 0.87 |
| H6CDD | 0.88 | 1.05 | 1.03 | 83.1 | 1.02 | 0.82 | 0.93 | 0.69 | 0.86 |
| H7CDD | 0.95 | 1.00 | 1.13 | 81.5 | 1.00 | 0.86 | 0.91 | 0.68 | 0.79 |
| O8CDD | 0.92 | 0.94 | 0.92 | 82.9 | 1.08 | 0.84 | 0.89 | 0.66 | 0.78 |
| Average | 0.91 | 0.99 | 1.02 | 84.0 | 1.00 | 0.85 | 0.94 | 0.74 | 0.85 |
| (SD) | (0.03) | (0.07) | (0.05) | (3.8) | (0.04) | (0.03) | (0.02) | (0.02) | (0.04) |
| | | | | Toluene : IPA (v/v) 80 : 20 | | | | | |
| T4CB | 0.98 | 0.99 | 0.97 | 1.03 | 1.08 | 0.94 | 1.04 | 0.75 | 0.61 |
| P5CB | 1.06 | 0.93 | 0.85 | 1.00 | 1.06 | 1.01 | 1.16 | 0.95 | 0.71 |
| T4CDD | 0.86 | 1.13 | 1.07 | 1.07 | 1.16 | 0.97 | 1.01 | 0.62 | 0.43 |
| P5CDD | 0.94 | 1.04 | 1.06 | 1.01 | 1.11 | 0.86 | 0.92 | 0.55 | 0.38 |
| H6CDD | 0.86 | 1.04 | 0.96 | 1.07 | 1.09 | 0.87 | 0.91 | 0.49 | 0.38 |
| H7CDD | 0.74 | 0.88 | 0.83 | 1.05 | 1.05 | 0.75 | 0.85 | 0.54 | 0.39 |
| O8CDD | 0.70 | 0.74 | 0.66 | 1.05 | 1.01 | 0.71 | 0.66 | 0.59 | 0.32 |
| Average | 0.85 | 0.97 | 0.92 | 1.05 | 1.09 | 0.85 | 0.90 | 0.59 | 0.42 |
| (SD) | (0.03) | (0.04) | (0.02) | (0.02) | (0.05) | (0.03) | (0.01) | (0.08) | (0.02) |

*Note:* Solvation (S) or wetting (W) water volume (mL).

***Table 2.*** Recovery and relative ratio of recovery of PCBs and PCDDs in sediment extracts.

| | Relative ratio of recovery | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Analytes | 0.00 | S/0.05 | W/0.05 | S/0.10 | W/0.10 | S/0.25 | W/0.25 | S/0.50 | W/0.50 |
| | | | | Toluene : IPA (v/v) 100 : 0 | | | | | |
| T4CB | 0.81 | 0.88 | 0.76 | 1.00 | 0.90 | 1.07 | 0.89 | 0.95 | 0.57 |
| P5CB | 0.71 | 0.82 | 0.65 | 0.96 | 0.70 | 1.09 | 0.68 | 0.90 | 0.37 |
| T4CDD | 0.42 | 0.69 | 0.69 | 0.75 | 0.69 | 1.20 | 0.77 | 0.77 | 0.47 |
| P5CDD | 0.67 | 0.89 | 0.87 | 1.00 | 0.98 | 1.22 | 0.93 | 1.01 | 0.52 |
| H6CDD | 0.66 | 0.82 | 0.84 | 1.00 | 0.99 | 1.07 | 0.92 | 0.99 | 0.42 |
| H7CDD | 0.58 | 0.80 | 0.84 | 0.95 | 0.96 | 0.95 | 0.79 | 0.96 | 0.32 |
| O8CDD | 0.57 | 0.75 | 0.81 | 0.98 | 0.93 | 0.97 | 0.76 | 0.97 | 0.23 |
| Average | 0.63 | 0.81 | 0.78 | 0.95 | 0.88 | 1.08 | 0.82 | 0.93 | 0.41 |
| (SD) | (0.05) | (0.03) | (0.05) | (0.02) | (0.04) | (0.06) | (0.04) | (0.02) | (0.04) |
| | | | | Toluene : IPA (v/v) 95 : 5 | | | | | |
| T4CB | 0.51 | 0.56 | 0.91 | 0.87 | 0.94 | 0.80 | 0.72 | 0.52 | 0.58 |
| P5CB | 0.58 | 0.67 | 0.98 | 0.53 | 0.92 | 0.55 | 0.54 | 0.53 | 0.62 |
| T4CDD | 0.62 | 0.67 | 0.61 | 0.75 | 0.67 | 0.73 | 0.64 | 0.67 | 0.43 |
| P5CDD | 0.85 | 0.94 | 0.83 | 0.98 | 0.90 | 0.92 | 0.78 | 0.86 | 0.49 |
| H6CDD | 0.87 | 0.97 | 0.83 | 0.98 | 0.88 | 0.94 | 0.77 | 0.86 | 0.39 |
| H7CDD | 0.79 | 0.89 | 0.79 | 0.93 | 0.84 | 0.86 | 0.64 | 0.82 | 0.29 |
| O8CDD | 0.71 | 0.85 | 0.76 | 0.94 | 0.81 | 0.83 | 0.54 | 0.80 | 0.20 |
| Average | 0.70 | 0.79 | 0.82 | 0.85 | 0.85 | 0.81 | 0.66 | 0.72 | 0.43 |
| (SD) | (0.02) | (0.05) | (0.04) | (0.01) | (0.02) | (0.04) | (0.03) | (0.02) | (0.06) |

*(continued)*

*Table 2.* Continued.

| | Relative ratio of recovery | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Analytes | 0.00 | S/0.05 | W/0.05 | S/0.10 | W/0.10 | S/0.25 | W/0.25 | S/0.50 | W/0.50 |
| | | | | Toluene : IPA (v/v) 90 : 10 | | | | | |
| T4CB | 0.86 | 1.04 | 1.00 | 99.6 | 0.98 | 0.92 | 0.67 | 0.92 | 0.77 |
| P5CB | 0.73 | 0.87 | 0.77 | 119.6 | 0.89 | 0.83 | 0.65 | 0.86 | 0.71 |
| T4CDD | 0.61 | 1.03 | 1.03 | 92.2 | 0.89 | 1.02 | 0.87 | 0.74 | 0.75 |
| P5CDD | 0.89 | 1.04 | 1.11 | 89.2 | 1.00 | 1.03 | 0.96 | 0.91 | 0.72 |
| H6CDD | 1.07 | 1.18 | 1.06 | 92.6 | 0.99 | 1.09 | 0.98 | 1.04 | 0.64 |
| H7CDD | 0.85 | 0.95 | 1.09 | 91.6 | 0.99 | 0.90 | 0.98 | 0.85 | 0.53 |
| O8CDD | 0.73 | 0.81 | 1.03 | 92.0 | 0.99 | 0.90 | 0.90 | 0.81 | 0.43 |
| Average | 0.82 | 0.99 | 1.01 | 96.7 | 0.96 | 0.96 | 0.86 | 0.88 | 0.65 |
| (SD) | (0.05) | (0.03) | (0.08) | (2.7) | (0.04) | (0.02) | (0.03) | (0.07) | (0.04) |
| | | | | Toluene : IPA (v/v) 80 : 20 | | | | | |
| T4CB | 1.08 | 1.06 | 0.93 | 0.98 | 0.95 | 1.09 | 0.94 | 1.02 | 0.85 |
| P5CB | 1.25 | 1.25 | 0.66 | 0.93 | 0.74 | 1.19 | 0.66 | 1.04 | 0.66 |
| T4CDD | 0.78 | 0.81 | 0.92 | 0.81 | 0.78 | 0.81 | 0.98 | 0.90 | 0.86 |
| P5CDD | 0.93 | 0.93 | 1.02 | 1.02 | 1.00 | 0.97 | 0.95 | 0.95 | 0.86 |
| H6CDD | 0.87 | 0.86 | 1.03 | 1.00 | 1.03 | 0.90 | 0.98 | 0.89 | 0.88 |
| H7CDD | 0.86 | 0.85 | 1.01 | 0.95 | 1.00 | 0.86 | 0.95 | 0.81 | 0.75 |
| O8CDD | 0.89 | 0.84 | 1.02 | 0.94 | 1.00 | 0.88 | 0.92 | 0.87 | 0.66 |
| Average | 0.95 | 0.94 | 0.94 | 0.95 | 0.93 | 0.96 | 0.91 | 0.93 | 0.79 |
| (SD) | (0.03) | (0.04) | (0.05) | (0.02) | (0.04) | (0.03) | (0.02) | (0.05) | (0.07) |

*Note:* Solvation (S) or Wetting (W)/Water volume (mL).

pressure upsurge. This results in the destruction of the macrostructure of the matrix, thereby, increasing the surface available for toluene as the extracting solvent. Isopropyl alcohol dissolves in water, and triggers subsequent rupture of water-barriers, thereby, allowing toluene molecules to diffuse in the matrix and extract PCBs and PCDDs through kinetic desorption.

Therefore, water's positive and negative effects on MAE include the disintegration of the macrostructure of the matrix, that causes the enhanced impregnation of toluene through water-barriers ruptured by IPA; and the blockage of toluene from coming in contact with PCBs and PCDDs adsorbed to the matrix, respectively.

Determining the roles of water, IPA, and toluene required establishing the optimum conditions for enhanced recoveries of PCBs and PCDDs, i.e., toluene–IPA at 90 : 10 (v/v), solvation of 1–2%, and wetting of 10–20%. These ranges of solvation and wetting enabled about 10–20% increase in the recovery of the dried matrix. Water quantities should be added accurately and low enough to allow the use of extract without any drying step. Roughly the same amount of water is found in the natural fly ash (<10%) and sediments (around 20% for sands and 40% for mud). This consequently allows the use of natural sample matrices without requiring any drying or freeze-drying step prior to the extraction; thereby saving on experimentation time.

## Comparison of Microwave-Assisted Extractions from Fly Ash and Sea Sediments

The recoveries at 0.00 mL water were proportional to the content of IPA. However, higher recoveries of PCBs and PCDDs from fly ash were obtained at 10% IPA level rather than 20%. Such a result was consistent with the results of the enhanced-fluidity liquid extraction (EFLE) and pressurized fluid extraction (PFE) in the previous paper.[18] This can be explained by the strong analyte–matrix interaction, which can be resolved by using toluene instead of IPA. For sea sediments, higher concentration of IPA in toluene resulted in higher recovery (Table 2). This suggests that the interaction between sediments matrices is stronger than that of the fly ash; thus, the impregnation of toluene into matrix is more difficult for sea sediments than fly ash.

Compared to the certified values, the average recoveries obtained by MAE at 2% of water, i.e., 0.1 mL of solvation, from fly ash and sea sediments was 84.0% and 96.7%, respectively. Higher recovery from sea sediments implies that analyte–matrix interaction is weaker in sediments compared to that of fly ash, although matrix–matrix interaction is stronger in sediments.

Upon the application of 100% water (w/w), i.e., 0.5 mL of wetting, average recovery from fly ash was lowest in toluene–IPA 80 : 20 (v/v), while that of the sea sediments was highest. The organic carbon content of the matrix is known to hinder extraction, owing to strong analyte–matrix interactions that are difficult to disrupt.[19,20] Since fly ash is a carbonaceous particle adsorbing PCBs and PCDDs strongly, lowest recoveries were obtained at the highest concentration of IPA. Strong matrix–matrix interaction in sea sediments also hinders extraction. However, highest recoveries were obtained at the highest concentration of IPA. While IPA hampered desorption, the polar solvent helped toluene to gain access to the matrix by breaking down the water-barriers between them.

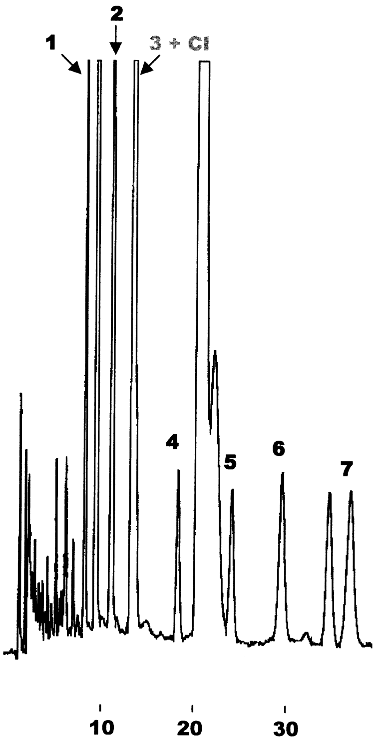

***Figure 1.*** High performance liquid chromatography–UV chromatograms of sea sediment sample extracted through MAE, followed by multi-layer silica gel column clean-up. The assignment of peaks is as follows: 1 = 2,3,4,5,6-pentachlorinated biphenyl; 2 = 2,2′,4,5′-tetrachlorinated biphenyl; 3 = 1,2,3,4-tetrachlorinated dibenzodioxin; 4 = 1,2,3,4,7-pentachlorinated dibenzodioxin; 5 = 1,2,3,4,7,8-hexachlorinated dibenzodioxin; 6 = 1,2,3,4,6,7,8-heptachlorinated dibenzodioxin; 7 = octachlorinated dibenzodioxin.

## Removal of Chromatographic Interferences

All the extracts were analyzed during the MAE process using HPLC–UV. The clean-up procedures required for the removal of the chromatographic interferences (CI) were influenced by the nature of the sample matrices. After the extractions, residual CI rendered quantification of PCBs and PCDDs inaccurate. However, the extracts obtained from fly ash could be purified through the multi-layer silica gel column clean-up. Previous studies proved that CI could be removed using multi-layer silica gel column clean-up.[18–21]

On the other hand, performance of the clean-up step for sediments resulted in the overlapping of T4CDD with CI (Fig. 1). Budzinski et al. suggested that the organic extract obtained from sediments was desulfurized on activated copper to remove sulfur interferences.[22] In this study, however, the activated copper packed in a multi-layer silica gel column could not separate the T4CDD from CI. Nonetheless, better chromatography (the more stable baseline) was obtained (Fig. 2). The additional use of alumina clean-up, as well as the multi-layer silica gel, enabled the removal of the interference (Fig. 3).

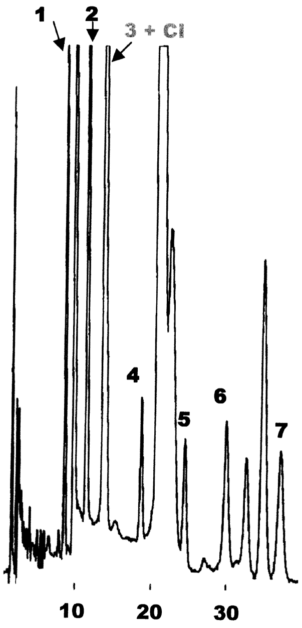

*Figure 2.* High performance liquid chromatography–UV chromatograms of sea sediment sample extracted through MAE, followed by Cu-multi-layer silica gel column clean-up (see Fig. 1 for the assignment of peaks).

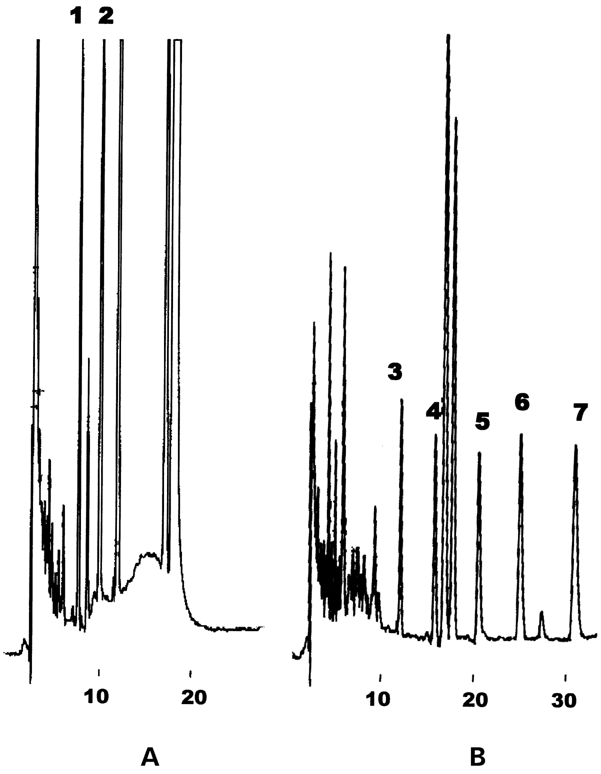

*Figure 3.* High performance liquid chromatography–UV chromatograms of sea sediment sample extracted through MAE, followed by alumina column clean-up. (A): 1st fraction, (B): 2nd fraction (see Fig. 1 for the assignment of peaks).

## CONCLUSION

In this study, the MAE conditions were studied and optimized. The study of parameters (toluene–IPA mixtures, water, and nature of matrix) revealed that the amount of water is an important parameter that should be considered. Isopropyl alcohol enabled the efficient extraction of PCBs and PCDDs from fly ash and sea sediments. However, toluene–IPA mixture, alone, was not responsible for the efficient recoveries. Among the extractants tested, the mixture water–IPA–toluene produced higher extractability. To achieve good extraction between the wider ranges of water proportion, the use of toluene–IPA 90 : 10 is, therefore, recommended. The presence of water in both matrices and extracting solvent had positive and negative effects on the recoveries. Both the addition of water to the dry matrices (wetting) and to the toluene–IPA mixture (solvation) enabled the significant increase of recoveries of PCBs and PCDDs from solid matrices, such as fly ash and sediments. The best recoveries were obtained at 0.05–0.10 mL water (10–20% wetting or 1–2% solvation level). Results indicate that the extraction conditions for an efficient MAE depends on the nature of the matrix that interacts with analytes and the content of water within the matrix. Additional alumina column clean-up, as well as multi-layer silica gel, are recommended for better chromatographic performance of PCBs and PCDDs from sea sediments. However, only multi-layer silica gel column clean-up is recommended for fly ash.

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## REFERENCES

1. Shu, Y.Y.; Lao, R.C.; Chiu, C.H.; Turle, R. Chemosphere **2000**, *41*, 1709–1716.
2. Ganzler, K.; Salgo, A.; Valko, K. J. Chromatogr. **1986**, *371*, 299–306.
3. Dupont, G.; Delteil, C.; Camel, V.; Bermond, A. Analyst **1999**, *124*, 453–458.
4. Eljarrat, E.; Caixach, J.; Rivera, J. Chemosphere **1998**, *36*, 2359–2366.
5. Shu, Y.Y.; Lao, R.C.; Chiu, C.H.; Turle, R. Chemosphere **2000**, *41*, 1709–1716.
6. Lopez-Avila, V.; Young, R.; Benedicto, J.; Ho, P.; Kim, R.; Beckert, W.F. Anal. Chem. **1995**, *67*, 2096–2102.
7. Chee, K.K.; Wong, M.K.; Lee, H.K. J. Chromatogr. A **1996**, *723*, 259–271.
8. Font, N.; Hernandez, F.; Hogendoorn, E.A.; Baumann, R.A.; Van Zoonen, P. J. Chromatogr. A **1998**, *798*, 179–186.
9. Llompart, M.P.; Lorenzo, R.A.; Cela, R.; Pare, J.R.J. Analyst **1997**, *122*, 133–137.
10. Pastor, A.; Vazquez, E.; Ciscar, R.; De La Guardia, M. Anal. Chim. Acta **1997**, *344*, 241–249.
11. Noordkamp, E.R.; Grotenhuis, J.T.C.; Rulkens, W.H. Chemosphere **1997**, *35*, 1907–1917.

12. Chee, K.K.; Wong, M.K.; Lee, H.K. Chromatographia **1996**, *42*, 378–384.
13. Letellier, M.; Budzinski, H. Analyst **1999**, *124*, 5–14.
14. Camel, V. Trends Anal. Chem. **2000**, *19* (4), 229–248.
15. Yang, J.S.; Lee, D.W.; Lee, S. J. Liq. Chrom. & Rel. Technol. **2002**, *25* (6), 899–911.
16. Yang, J.S.; Kim, J.Y.; Choi, Y.W.; Lee, D.W. Bull. Korean Chem. Soc. **1998**, *19* (6), 619–624.
17. Kim, D.H.; Yang, J.S.; Lee, D.W.; Chung, H.K. J. Liq. Chrom. & Rel. Technol. **2001**, *24* (2), 229–239.
18. Yang, J.S.; Jeong, J.H.; Lee, D.W.; Chang, Y.-S. J. Liq. Chrom. & Rel. Technol. **2001**, *24* (18), 2815–2825.
19. Yang, J.S.; Kim, W.-S.; Lee, D.W.; Yu, E.K. J. Liq. Chrom. & Rel. Technol. **2001**, *24* (7), 993–1005.
20. Yang, J.S.; Kim, D.H.; Kim, D.H.; Lee, D.W.; Chang, Y.-S. J. Liq. Chrom. & Rel. Technol. **2001**, *24* (15), 2293–2302.
21. Yang, J.S.; Lee, S.K.; Park, Y.H.; Lee, D.W. Bull. Korean Chem. Soc. **1999**, *20* (6), 689–695.
22. Budzinski, H.; Letellier, M.; Garrigues, P.; Le Menach, K. J. Chromatogr. A **1999**, *837*, 187–200.

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