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Extraction and clean-up procedure for polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fly ash from municipal solid waste incinerators

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ABSTRACT

An exhaustive extraction and a good clean-up method for analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in incinerator fly ash is presented. After Soxhlet extraction of the fly ash with benzene, a multi-step clean-up is necessary to remove all interferences from the sample. The principal problem is the separation of PCDDs and PCDFs from the polychlorinated biphenyls. There are two key conditions: the alumina activation and the polarity of the solvents used. The recovery of the PCDDs and PCDFs is good, ranging from 87.1 to 118 percent.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) have been the subject of much concern in recent years. Some of these compounds, especially the 2,3,7,8-substituted congeners, have extraordinarily toxic properties and are teratogenic, mutagenic and potentially carcinogenic [1]. Since PCDDs were found in fly ash from the Amsterdam municipal incinerator [2], investigations have been carried out [3,4] on the emissions from municipal incinerators from different parts of the world.

Because of the high toxicity of these compounds, it is necessary to have an effective method for their identification and determination at parts per trillion (ppt) levels. The determination of ppt concentrations of chemical residues generally requires the use of either highly selective sample purification procedures or very specific detectors [5,6].

We describe here an extraction and exhaustive clean-up procedure for PCDDs and PCDFs in fly ash from Spanish municipal solid waste (MSW) incinerators.

EXPERIMENTAL AND RESULTS

The chromatographic adsorbents used were basic alumina 100–200 mesh (Bio-Rad, AG10, Ref. 33197) and acid silica gel, 100–200 mesh (Bio-Rad, Biosil-A, Ref.

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131.1340). The gels were rinsed with 300 ml of dichloromethane and the dichloromethane-saturated material was dried in a glass tube furnace under a continuous purge of dry nitrogen initially at 50°C, increased to 180°C over a period of 25 min and maintained there for 90 min. The adsorbents were then activated for an additional 90 min at 300°C. The adsorbents were stored in a glass bottle in a desiccator over phosphorus pentoxide until used. Alumina needed additional activation prior to its use.

Concentrated sulphuric acid on silica (44%), 1 *M* sodium hydroxide on silica (33%) and silver nitrate on silica (10%) were prepared as described previously [7,8].

Chromatographic and extraction solvents, including *n*-hexane, dichloromethane, benzene, toluene and carbon tetrachloride were of glass-distilled pesticide grade (Merck).

Gas chromatography (GC) was performed using a Perkin-Elmer Model 8310B instrument equipped with a ^{63}Ni electron-capture detector. A fused-silica WCOT capillary column (50 m × 0.22 mm I.D.) covered with BP-5, obtained from Chrompack, was used. The chromatographic conditions were as follows: detector temperature, 350°C; injector temperature 300°C; column temperature programme, 100°C for 3 min, increased at 20°C/min to 180°C, then at 2°C/min to 250°C, held for 45 min, increase at 2°C/min to 280°C, held for 20 min. The carrier gas (nitrogen) flow-rate was 0.35 ml/min.

PCDDs and PCDFs used as reference standards for GC were obtained from Wellington Labs. (Ontario, Canada).

Fly ash samples were taken from Spanish municipal incinerators located in Cádiz, Alava, Gerona, Barcelona, Melilla, Pontevedra and Palma de Mallorca. Samples were stored in closed containers at room temperature and protected from light.

All glassware was cleaned using the following procedure: (1) rinsing with soap and tap water; (2) rinsing with acetone; (3) ultrasonic agitation for 1 h in a 2% aqueous solution of detergent; (4) rinsing with copious amounts of tap water; (5) rinsing with deionized water; and (6) heating in a general laboratory oven for 2 h at 130°C.

Extraction

A variety of methods have been used for the extraction of PCDDs and PCDFs from fly ash. Extraction efficiencies of PCDDs and PCDFs have been compared [9] using seven different extraction methods and it was concluded [9] that generally Soxhlet extraction with benzene or toluene gives the best results. We therefore tried Soxhlet extraction with benzene and toluene and, although both solvents gave good results, benzene was selected because its evaporation time is shorter than that of toluene, which reduces the preanalytical treatment time.

The fly ash was extracted with 200 ml of benzene for 36 h and the benzene extract was evaporated to dryness.

Fly ash extracts contain a complex mixture of PCDDs, PCDFs and other extractable organic compounds. These compounds include polycyclic aromatic hydrocarbons (PAHs) and numerous chlorinated compounds [10–12]. The complexity of the mixture makes the identification and determination of the individual isomers very difficult.

Clean-up

In order to avoid the above interferences, it was necessary to develop a multi-step clean-up method which is very effective at removing PAHs and clorinated compounds and also yields a high recovery and good precision for PCDDs and PCDFs.

Procedure

Removal of benzene-extractable compounds other than PCDDs and PCDFs is accomplished by passing the extract of the residue through the first (A) of the column systems (see Fig. 1) prepared as follows. A glass-wool plug is inserted into the end of the column to serve as a bed support and the following materials are then placed in sequence in the column: 1.0 g of silica (bottom layer); 2.0 g of 33% 1 *M* sodium hydroxide on silica; 1.0 g of silica; 4.0 g of 44% concentrated sulphuric acid on silica; and 1.0 g of silica (top layer). The packed column is prewashed with 30 ml of *n*-hexane and the effluent is discarded. The extract of the residue (1.5 ml) is then passed through the column followed by three 1.5-ml *n*-hexane rinses of the boiling glass vessel. Following these rinses, an additional 55 ml of *n*-hexane is passed through the column.

The total effluent is then evaporated to dryness under a stream of nitrogen. The residue is passed through a dual column system consisting of an chromatographic column draining into a bottom column (B and C, respectively, in Fig. 1) to remove common chemical interferences with PCDDs and PCDFs.

Column B is packed with 1.5 g of silica gel containing 10% (w/w) silver nitrate and column C is packed with 6 g of basic alumina. A glass-wool plug is placed at the bottom of each column (B and C) and, after depositing the reagents, the columns are prewashed with 30 ml of *n*-hexane, the washings being discarded.

The residue from column A is transferred to silver nitrate–silica column (B) using three 1.5-ml portions of *n*-hexane. A 45-ml volume of *n*-hexane is used as the eluent. The eluate is collected on the top of the basic alumina column. Now the problem is to separate the PCDDs and PCDFs from polychlorinated biphenyls (PCBs) into the alumina column. First, we tried 50 ml of *n*-hexane–carbon tetrachloride (50:50, v/v) to remove PCBs, and finally 22.5 ml of *n*-hexane–dichloromethane (50:50, v/v) for eluting PCDDs and PCDFs as described previously [6]. However,

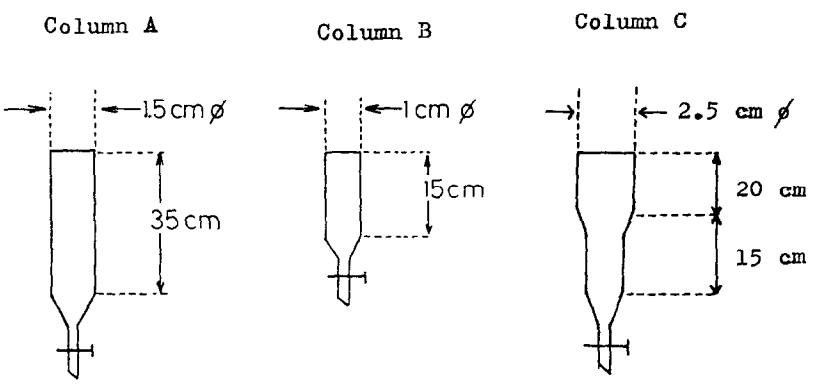

Fig. 1. Liquid chromatographic clean-up columns. ∅ = Diameter.

these solvents did not solve the problem; the PCDDs and PCDFs fraction contained too much impurities, principally PCBs. It was therefore necessary to investigate the polarity of the solvents. The solvents proposed by Albro *et al.* [13]were investigated. Two fractions of 25 ml were tried: *n*-hexane–dichloromethane (98:2, v/v) to elute PCBs and *n*-hexane–dichloromethane (80:20, v/v) to elute PCDDs and PCDFs. The two fractions contained too much impurities and the separation was poor.

In view of these results, the alumina activation was investigated. Three experiments were designed with (1) alumina activated at 600°C for 16 h [14], (2) alumina activated at 130°C for 8 h [15] and (3) alumina activated at 130°C for 18 h [13,16]. For all three experiments 6 g of basic alumina and 10 ml of solvent per gram of alumina were used. The fractionation scheme is shown in Fig. 2.

The best results for the removal of all impurties were obtained using alumina using alumina activated at 130°C for 18 h. The results confirmed the significance of the alumina activation conditions. This is important for removing all impurities and for obtaining a good separation of PCDDs and PCDFs from PCBs. Up to this stage of our investigations we have only achieved the first objective. The polarity of the solvents was then investigated using alumina activated at 130°C for 18 h.

Three different experiments were carried out in order to establish the influence of solvent polarity and the amount of solvent on the production of the different fractions (Fig. 3). For this investigation a mixture of known standards containing

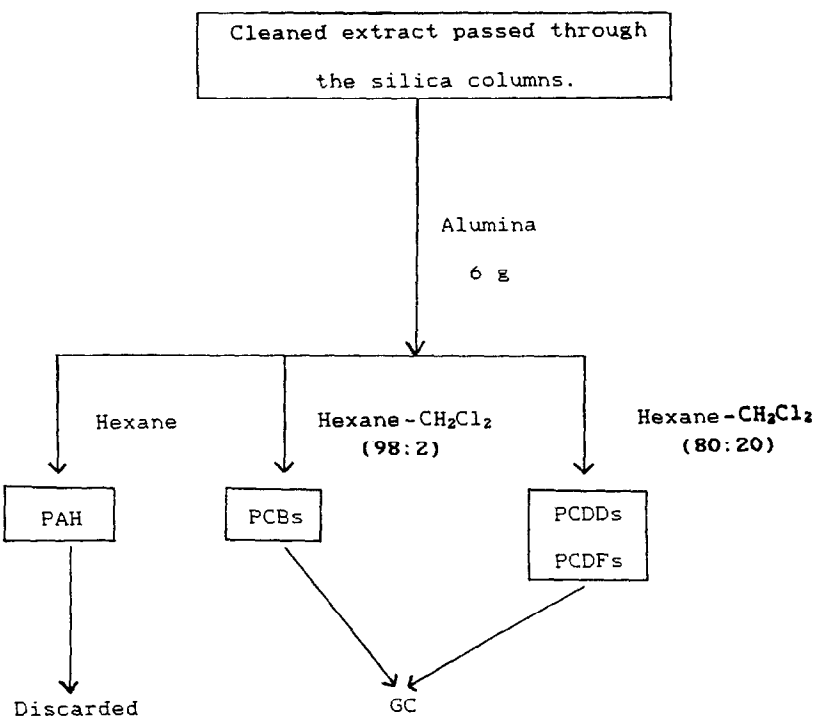

Fig. 2. Fractionation scheme.

Experiment	1	2	3
Fraction 1	Hexane-CCl_4 (50:50) 50 ml	Hexane-CCl_4 (50:50) 40 ml	Hexane-CCl_4 (75:25) 50 ml
Fraction 2	Hexane-CH_2Cl_2 (80:20) 50 ml	Hexane-CH_2Cl_2 (80:20) 40 ml	Hexane-CH_2Cl_2 (80:20) 50 ml

Fig. 3. Scheme of three experiments to study the effects of polarity and amount of solvent. Fraction 1 for PCBs and fraction 2 for PCDDs and PCDFs.

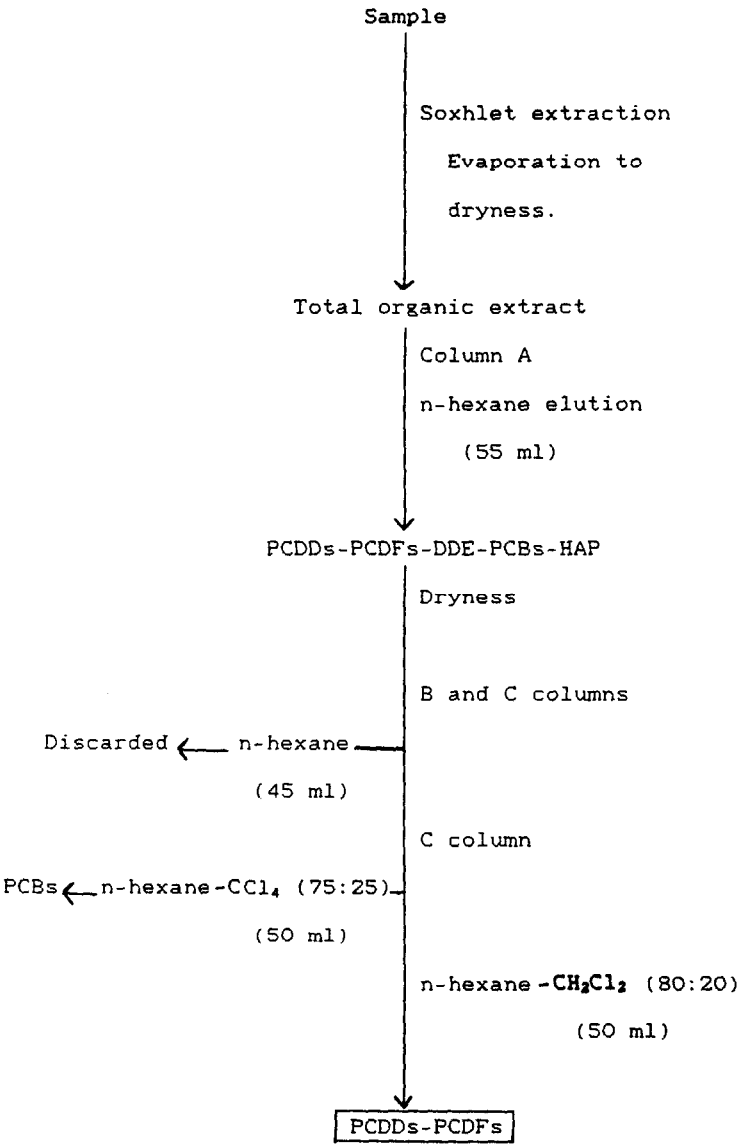

Fig. 4. Definitive procedure for extraction and clean-up.

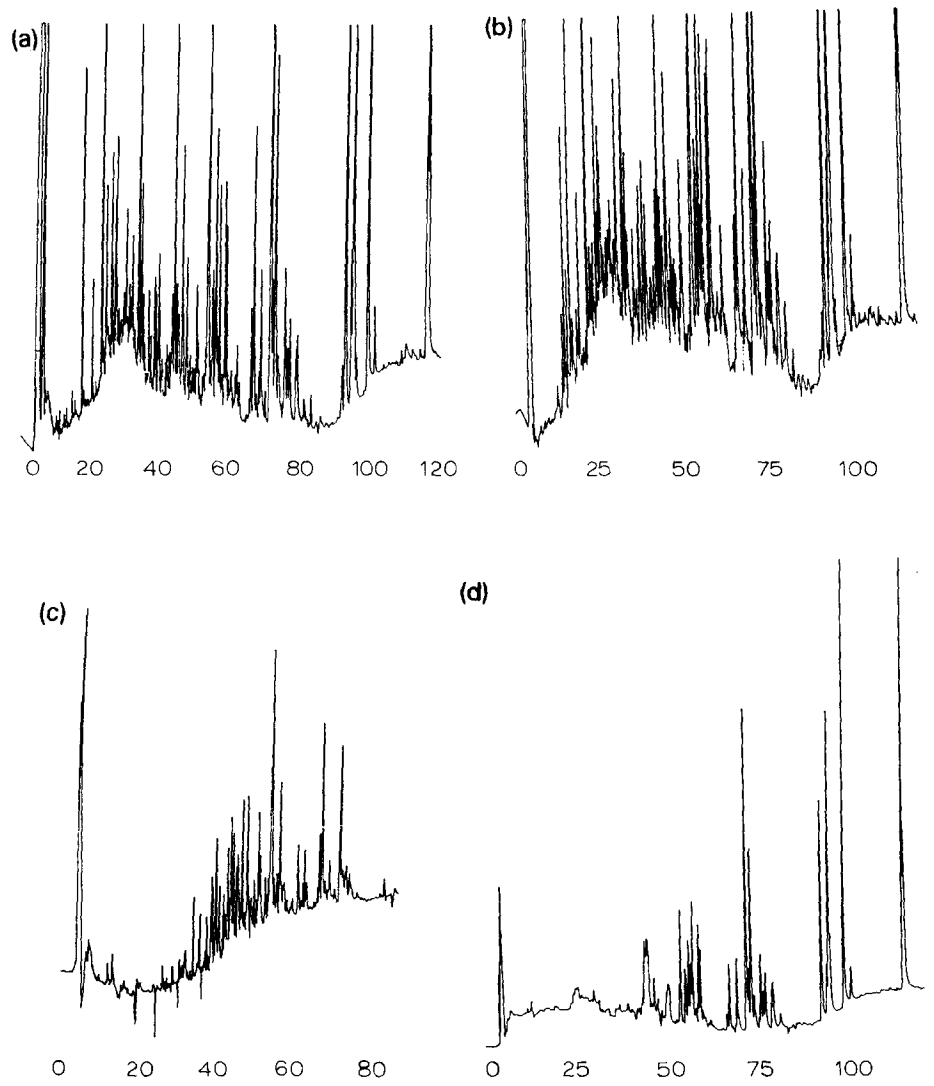

Fig. 5. Chromatograms corresponding to the different steps of the clean-up procedure. (b) Total organic extract from fly ash containing PCDDs, PCDFs and other extractable organic compounds. (a) Organic extract passed through the first column (A). (c) fraction of PCBs obtained from the alumina column (B). (d) Final fraction obtained from the alumina column, containing the PCDDs and PCDFs. Time scales in min.

PCBs, PCDDs and PCDFs was used. Fig. 3 shows that although the amount of solvent is not important, the polarity of the solvent is a key factor. Using the solvents in experiment 3 a good separation can be obtained, PCBs eluting in a fraction apart from PCDDs and PCDFs. The recommended procedure for extraction and clean-up based on this investigation is shown in Fig. 4.

The chromatograms in Fig. 5 show the different fractions obtained during the

TABLE I

RECOVERY OF PCDD AND PCDF ISOMERS

PeCDD = pentachloro dibenzo-*p*-dioxin; PeCDF = pentachloro dibenzo-*p*-furan; HxCDD = hexachloro dibenzo-*p*-dioxin; HxCDF = hexachloro dibenzo-*p*-furan; TCDD = tetrachloro dibenzo-*p*-dioxin; HpCDD = heptachloro dibenzo-*p*-dioxin; OCDD = octachloro dibenzo-*p*-dioxin.

Experiment No.	Isomers	Recovery (%)
1	1,2,3,7,8-PeCDD 1,2,3,7,8-PeCDF 2,3,4,7,8-PeCDF	109.11
	1,2,3,4,7,8-HxCDD 1,2,3,6,7,8-HxCDD 1,2,3,7,8,9-HxCDD 1,2,3,4,7,8-HxCDF 1,2,3,6,7,8-HxCDF 1,2,3,7,8,9-HxCDF 2,3,4,6,7,8-HxCDF	101.84
2	2,3,7,8-TCDD	87.1
3	1,2,3,4,6,7,8-HpCDD	95.16
4	OCDD	118

extraction and clean-up process. The benzene extract (Fig. 5b) from fly ash contains the PCDDs, PCDFs and all impurities. Fig. 5a corresponds to the benzene extract passed through the first silica column (A). The PCB fraction is in Fig. 5c and finally, the fraction containing the PCDDs and PCDFs exhaustively cleaned-up is in Fig. 5d. It can also be seen that PCDDs and PCDFs are separated according to their degree of chlorination.

DISCUSSION

An effective extraction and clean-up method for PCDDs and PCDFs has been devised. A multi-step clean-up is necessary to remove all interferents from these samples. Whereas the first step of the clean-up is commonly used with good results [7], the main problem is the separation of PCDDs and PCDFs from PCBs in the final step, and this separation has been achieved with the proposed method. There are two key conditions: the alumina activation and the polarity of the solvents.

The recovery for PCDDs and PCDFs isomers with different chlorine contents was checked with four experiments. Fly ash with all extractable organic compounds previously extracted was used. From Table I it can be seen that high recoveries were obtained for all isomers, ranging from 87.1 to 118%. Values higher than 100% have been explained elsewhere [17]. This effect is suspected to be related to the injection of samples into the gas chromatograph. Recoveries are probably influenced by errors associated with the measurement and handling of small injection volumes.

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