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Comparison of extraction methods for polychlorinated dibenzo-*p*-dioxins and dibenzofurans in fly ash using gas chromatography–mass spectrometry

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ABSTRACT

Four method for the extraction of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in municipal solid waste (MSW) incinerator fly ash samples were examined. A Soxhlet method was found to be the most efficient. However, the time required for extraction was more than 24 h. Ultrasonic extraction (UE) proved to be an inexpensive, efficient, reliable and rapid method. Studies of the effect of extraction time and temperature in UE showed that higher temperatures, longer times of extraction and increased number of repeated extractions with fresh solvent resulted in higher extraction efficiency.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) are the major toxic chlorinated organic contaminants of fly ash, and are produced by the incineration of any kind of waste that provides the necessary precursors [1–5]. The formation of PCDDs and PCDFs from combustion is a universal phenomenon. They have been detected in the emissions from automobiles, domestic stoves, furnaces and especially in minicipal solid waste (MSW) incineration, where they first were detected in fly ash by Olie *et al.* [1]. Because of their extremely high toxicity [6,7] and uncertain genotoxic potential [8], their determination in environmental samples is of great interest. In particular, the determination of PCDDs and PCDFs in MSW incinerator fly ash is important, because thousands of tons of such fly ash are produced every day.

MSW incinerator fly ash is usually extracted using a Soxhlet method for the isolation of organic pollutants. Soxhlet extraction (SE) is very time consuming and needs large amounts of organic solvents (350 ml) such as toluene or benzene. Ultrasonic extraction (UE) has been demonstrated to be a viable method for the extraction of other non-volatile organics, *e.g.*, polycyclic aromatic hydrocarbons in fly ash [9,10]. Previous studies of the UE of fly ash employed solvent and sample amounts comparable to those in the Soxhlet method, resulting in unsatisfactory extraction efficiencies for PCDDs and PCDFs [11].

This paper describes four methods for the extraction of PCDDs and PCDFs from MSW incinerator fly ash. A typical SE requires 350 ml of solvent, at least 5 g of fly ash and 24 h of extraction time. The UE method studied here required 60 ml of solvent, 1.0 g of fly ash and 4.5 h for effective extraction. Advantages of the UE method over other methods of extraction are discussed.

EXPERIMENTAL

Samples and materials

The fly ash was from an MSW incinerator in the USA. The same batch of fly ash was used in all experiments. Prior to extraction the fly ash was sieved and the fraction containing smaller particles

(< 150 μm) was used for extraction. Except for the SE, where 5.0 g were used, in all other methods 1.0 g of fly ash used.

Benzene and toluene were obtained from BDH (distilled-in-glass, suitable for chromatography and residue analysis). Quantification was done with a [^{13}C]PCDD standard mixture, which was synthesized in our laboratory [12] and contained the following concentrations (ng/μl) of each congener group: tetra(T)CDD (0.2), penta(P)CDD (1.0), hexa(H_6)CDD (3.0), hepta(H_7)CDD (4.0) and octa (O)CDD (1.8). The same standard was used for spiking the fly ash for recovery estimates. PCDFs were quantified externally using a standard containing a total of 9.7 ng/μl of PCDFs.

Procedures

Four methods of extraction were studied. Repeated extractions of fly ash samples from the same bulk of the stock fly ash were conducted separately for each method. All primary extracts obtained were concentrated to a volume of 1–2 ml using rotary evaporation and then further concentrated to *ca.* 50 μl in vials by a gentle stream of high-purity nitrogen. The exact volume of extract for each sample was determined using a high-performance liquid chromatographic syringe immediately after gas chromatographic–mass spectrometric (GC–MS) analysis. The general procedures used for all methods of extraction were as follows.

Soxhlet extraction (SE). Detailed procedures for Soxhlet extraction were reported previously [13]. Our extractions were conducted using 5 g o fly ash samples and different times and amounts of organic solvents (see Table II).

Acid digestion and Soxhlet extraction (ADSE). A 5-g amount of fly ash and 60 ml of 1 *M* hydrochloric acid were sonicated for 1.5 h at 45°C. The fly ash was filtered using a Buchner funnel and washed with 3 × 50 ml of deionized water (until the filtrate was neutral). The aqueous filtrate was extracted with 100, 50 and 50 ml of toluene in a separating funnel. The filter with the fly ash residue was placed in a glass thimble and extracted in a Soxhlet apparatus using 300 ml of toluene for a specific time. Both extracts (filtrate and Soxhlet) were combined before the concentration step.

Extraction by column elution (ECE). A 1.0-g amount of fly ash was packed into a glass column (20 cm × 0.8 cm I.D.) containing a glass-wool plug at the bottom. The column was eluted using 240 ml of benzene in three fractions of 80 ml which were collected and analysed separately. As the flow was driven only by gravity, each fraction took *ca.* 75 min to elute. The column was kept at 25°C during the elution. It is possible to heat the column to 100°C to increase the extraction efficiency [14].

Ultrasonic extraction (UE). A Branson Model 5200 ultrasonic bath (9.4 l, ultrasonic unit 200 W) was used. A water-filled supporting beaker containing capped test-tubes with fly ash and solvent was suspended from the lid of the bath. A maximum of six test-tubes were sonicated at once. Although the bath has a thermostat to set and control the temperature, it varied over a range of 3–4°C during the experiment. The temperature values given are the averages of several measurements of the water temperature in the beaker. Several experiments were conducted to study the effect of variation of the conditions of ultrasonication for the extraction of PCDDs and PCDFs from the fly ash samples.

Treatment of extracts. All sample extracts were first screened by GC with electron-capture detection (ECD) to assess the amount of chlorinated compounds present and whether the sample was suitable for GC–MS analysis. The instruments and conditions used are summarized in Table I. The detection limit of the applied methods is about 2 ppb[a] per congener group totalling 10 ppb of PCDDs. Several extractions were conducted using the above four methods. Although the SE method is used traditionally for the extraction and isolation of environmental contaminants from solid samples, the method is time consuming, requiring more than 24 h for satisfactory extraction. In addition, it requires large amounts of solvent (350 ml) and sample (usually more than 5 g). Hence there is a need for a simple, less expensive and reliable method for the extraction of environmental contaminants from solid samples such as MSW incinerator fly ash.

RESULTS AND DISCUSSION

The amounts of dioxins extracted using the four methods of extraction under various conditions are given in Table II. All the experiments reported were

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[a] Throughout this article, the American billion (10^9) is meant.

TABLE I

INSTRUMENTS AND CONDITIONS FOR GC–MS

Gas chromatograph	Hewlett-Packard 5890
Mass-selective detector	Hewlett-Packard 5970
Workstation	Hewlett-Packard 59970
Column	DB-5, 30 m × 0.25 mm I.D.
Injection	On-column, volume 1 or 2 μl
Temperature programme	80°C for 1 min, 15°C/min to 230°C, then 3°C/min to 300°C, held for 10 min
Run time	45 min
Ionizing voltage	70 eV
Ions monitored	$[M-COCl]^+$, M^+, $[M+2]^+$, $[M+4]^+$, for each congener group of tetra- to octa-CDD and -CDF, and ^{13}C-labelled CDD.
Retention time windows	14.5, 18.5, 22.5, 26.5, 31.0, 35.0 min for tetra-, penta-, hexa-, hepta- and octa-CDD and -CDF, respectively.

repeated three times. The amounts of total PCDDs and PCDFs extracted varied within ±5% in the repeated experiments.

For the recovery study, fly ash was spiked with a ^{13}C-labelled dioxin mixture prior to extraction. The relative extraction efficiency of a particular method can be assessed based on the recovery of the added ^{13}C-labelled reference material. The amount of total dioxins extracted using the four different methods and the values corrected according to recoveries are shown in Fig. 1. In the SE method two solvents, benzene and toluene, were studied. Toluene was better than benzene with respect to efficiency of extraction of dioxins. Moreover, toluene is easier to handle than the highly carcinogenic benzene. From Fig. 1 it can be seen that the SE and the ADSE methods have similar extraction efficiencies for PCDDs. A minor difference in the efficiency for H_6CDD extraction was noticed, which was offset by smaller differences of opposite nature for other compounds. In the ADSE method acid digestion, filtration and extraction of the aqueous acidic layer are additional time-consuming steps compared to the straightforward SE of fly ash. The extraction efficiency does not differs significantly between the SE and ADSE methods. Hence Soxhlet extraction alone is satisfactory for the extraction of solid samples such as MSW incinerator fly ash.

The efficiency of the UE method for the extractionof PCDDs and PCDFs from fly ash was studied under different conditions with variations in extrac-

TABLE II

AMOUNTS OF DIOXINS EXTRACTED (CORRECTED FOR RECOVERIES USING INTERNAL STANDARD) FROM FLY ASH (ng/g) USING VARIOUS METHODS OF EXTRACTION UNDER VARIOUS CONDITIONS

Experiment No.	Method	Solvent	Time (h)	Temperature (°C)	TCDD	PCDD	H_6CDD	H_7CDD	OCDD	Sum
1	SE	Benzene	24	40–60	2	75	220	240	86	620
2	SE	Toluene	48	40–80	16	200	410	740	280	1650
3	ADSE	Toluene	48	40–80	9	210	550	640	300	1710
4	ECE	Toluene	3.75	25	7	42	150	180	85	460
5	UE	Benzene	1.5	30	7	57	150	160	62	440
6	UE	Toluene	1.5	42	7	120	300	350	180	960
7	UE	Toluene	1.5	68	6	52	370	470	260	1160
8	UE	Toluene	1	68	7	130	330	450	240	1160
9	UE	Toluene	3	68	7	130	360	450	250	1200
10	UE	Toluene	6	68	7	120	380	480	270	1260
11[a]	UE	Toluene	1.5	68	7	31	72	98	61	270
12[a]	UE	Toluene	1.5	68	2	8	22	28	20	80
13[b]	UE	Toluene	1.5	68	2	8	22	28	20	80
14[b]	UE	Toluene	1.5	68	2	10	21	28	22	83

[a] Second extraction of the fly ash from experiments 9 and 10; quantification based on external standard, amounts not corrected for recoveries.

[b] Third extraction of the fly ash from experiments 9 and 10; quantification based on external standard, amounts not corrected for recoveries.

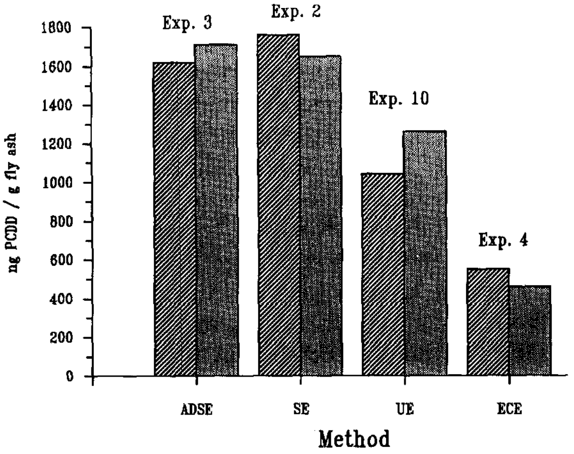

Fig. 1. Comparison of amounts of PCDDs extracted from MSW incinerator fly ash using different methods of extraction. See Table II for experiment numbers. Hatched boxes = quantified by external standard; dotted boxes = corrected for recovery of [^{13}C]PCDD.

tion time and temperature (Table II). It was observed that the extraction efficiency using the UE method was highest with higher temperatures and longer extraction times. Assigning the 24-h Soxhlet extraction a 100% extraction efficiency, about a 70% extraction efficiency was achieved within 1.5 h by UE at 68°C (experiment 7 in Table II). Re-extraction of the same fly ash twice and summation of the amounts of PCDDs and PCDFs, *i.e.*, the sum of experiments 9, 11 and 13 or of 10, 12 and 14, respectively, gave the amounts of total PCDDs and PCDFs extracted by UE, which were about the same as those of the SE method.

The temperature applied during extraction plays a very important role. The temperature during the SE method using benzene ranged from 40 to 55°C and using toluene from 45 to 80°C. In the UE method temperature can be controlled precisely. In this study the UE extraction was studied up to 68°C (which is the upper limit of the ultrasonicator) and the results are reported in Table II. Temperatures higher than 68°C in the UE method could have resulted in a higher extraction efficiency in a shorter time. The UE method also requires only 60 ml solvent and 1 g of fly ash sample compared with 350 ml of solvent and more than 5 g of fly ash needed in the SE method. The influence of temperature on extraction can also be seen from the amount of PCDDs extracted by SE at higher temperatures (45–80°C) and ECE at room temperature (25°C). Although the sample-to-solvent ratio (calculated) in the ECE is similar to that in the SE method, the extraction efficiency remains less than 50% for the ECE method. The efficiency of the ECE method can be improved by heating the column externally during the elution [14].

Fig. 2 shows the amounts of the individual tetra- to octachlorodioxins extracted from the fly ash. The pattern is a typical example of PCDDs detected in MSW incinerator fly ash, and was always the same, regardless of the total amount of dioxins extracted. The similarity of the pattern may be due to an even distribution of dioxins on and in the interior of the fly ash particles and specific solubilities of dioxin congeners in a particular solvent.

It was observed that in all the methods studied an increase in the temperature of the extraction resulted in a higher efficiency of the extraction of PCDDs from the fly ash. This might raise the question of whether PCDDs are formed from precursors by the catalytic activity of the fly ash at temperatures of about 50–80°C, which would lead to a seemingly enhanced extraction. To study this hypothesis, pre-extracted fly ash was spiked with pentachlorophenol (PCP). PCP has been shown to be an excellent and efficient precursor for the formation of PCDDs [15]. In order to distinguish between non-extracted native dioxins in the fly ash and those that were formed during the ultrasonic treatment at higher

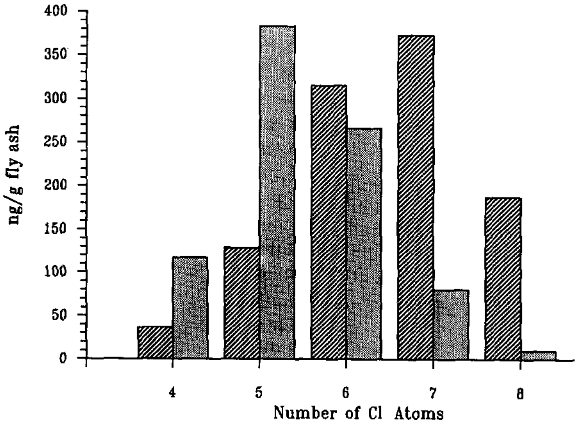

Fig. 2. Congener pattern for PCDDs and PCDFs extracted from MSW incinerator fly ash (experiment number 10 in Table II). Hatched boxes = dioxins; dotted boxes = furans.

temperatures, ^{13}C-labelled PCP used. ^{13}C-labelled dioxins were not detected in the extract of fly ash heated to 68°C during extraction. This leads to the conclusion that no dioxins are formed during ultrasonic treatment at a temperature of *ca.* 68°C for 3–6 h, at least not from chlorinated phenols, which are the most likely precursors for PCDDs at low temperatures. It has been reported that PCDD formation can occur above 150°C [15,16]. Hence it is less likely that the PCDDs and PCDFs are formed at 80°C during extraction, which was suggested recently [17].

Prolonging the ultrasonication time from 1.5 to 6 h, as shown in Fig. 3, had little effect on the amounts of PCDDs and PCDFs extracted. However, extracting the same sample (experiment 10) repeatedly with fresh solvent did yield larger amounts (Table II, experiments 11 and 12). From the overall comparison of the methods with respect to extraction efficiency, the methods ranked in the order acid digestion + Soxhlet = Soxhlet > sonication > column elution. Although acid digestion prior to Soxhlet extraction has been reported to be more effective [11], this was not found in our study. This shows that the efficiency of the method of extraction varies with different fly ash samples. The superiority of the Soxhlet extraction is due to the use of large amounts of solvent (*i.e.*, taking into account the total amount of solvent used and the cycle rate of "refreshing" the solvent). The temperature in the Soxhlet extractor reaches about 80°C if toluene is used, which seems to have a profound effect on the efficiency of extraction of PCDDs. The UE method can also recover a large portion of PCDDs and PCDFs from the fly ash. In the UE

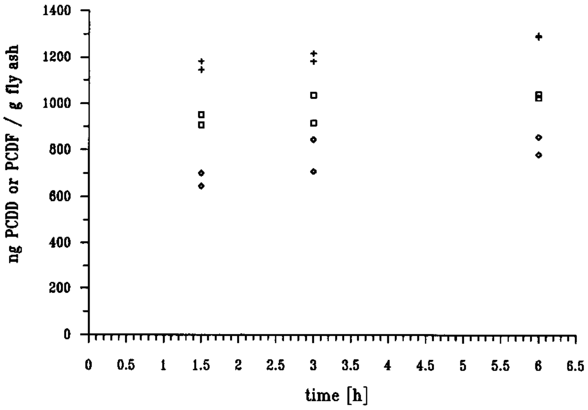

Fig. 3. Influence of sonication time on the amounts of PCDDs and PCDFs extracted. ☐ = PCDDs quantified by external standard; + = PCDDs corrected for recovery of [^{13}C]PCDD; ◇ = PCDF quantified by external standard.

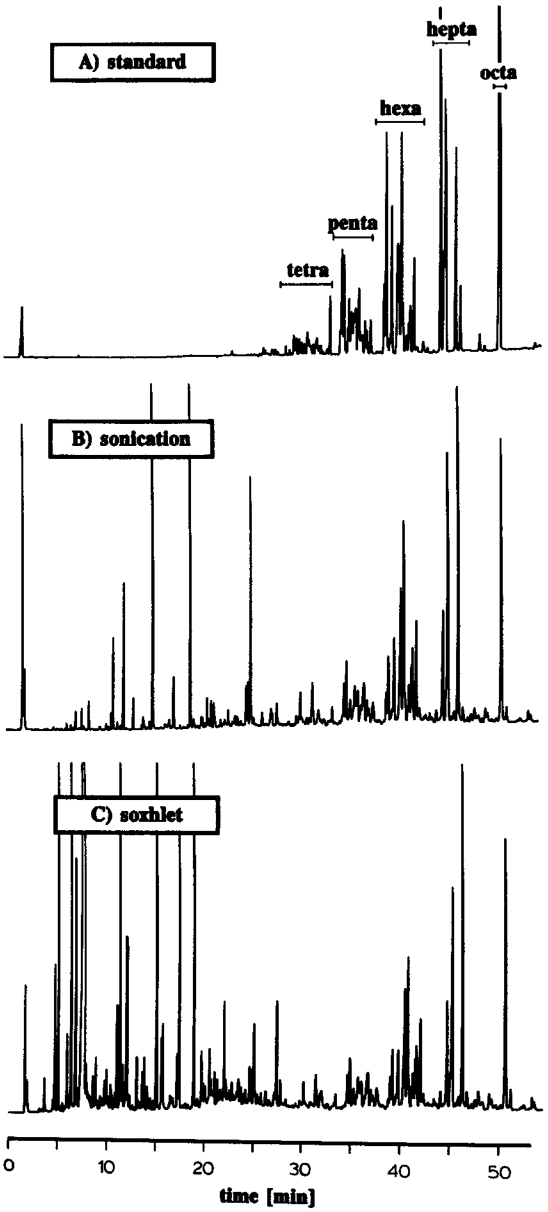

Fig. 4. GC–ECD showing PCDDs and PCDFs patterns in (A) standard containing labelled PCDDs (8.1 ng), native PCDDs (5.1 ng) and native PCDFs (14.2 ng); (B) sonication extract from experiment 10; and (C) Soxhlet extract from experiment 2.

method the solvent-to-sample ratio seems to be very important and renewal of the solvent once or twice during extraction increases the extraction efficiency considerably. In contrast to these methods, column elution only extracts the superficially adsorbed PCDDs and PCDFs on the fly ash, because even with large amounts of solvent, the amount extracted cannot be enhanced in experiment 6, where 98% of the PCDDs were extracted in the first 80 ml of benzene and the remaining 80-ml two fractions contained the rest. Temperature may have been a limiting factor because the elution was done at room temperature.

GC–ECD of fly ash extracts obtained by the SE and UE methods is shown in Fig. 4. In the retention time window of the PCDDs and PCDFs, there is no significant difference between two chromatograms resulting from sample extracts from the SE and UE methods. This shows that the UE method can be an excellent alternative to the time-consuming SE method. The peak patterns in the chromatograms are markedly different for the peaks eluting before a retention time of 20 min. Soxhlet extraction appears to be more efficient in extracting fast-eluting compounds, *i.e.*, compounds with higher volatility and lower molecular weight.

CONCLUSION

Ultrasonication is a fast, efficient and easy method for the extraction of PCDDs and PCDFs from MSW incinerator fly ash. It requires only 1 g of sample, 60 ml (3 × 20 ml) of toluene and an extraction time of 4.5 h (3 × 1.5 h), compared with more than 5 g of sample, 350 ml of toluene and more than 24 h in the Soxhlet extraction method. Hence the amounts of sample and solvent and the time required for the extraction of PCDDs and PCDFs by the SE method are about five times lower using the UE method. The UE method might also be applied to other matrices such as soil and sediments.

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