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Supercritical fluid extraction of polychlorinated dibenzo-*p*-dioxins from fly ash: the importance of fly ash origin and composition on extraction efficiency

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Abstract

Supercritical fluid extraction (SFE) of polychlorinated dibenzo-*p*-dioxins (dioxins) from fly ash samples, collected at different municipal waste incinerators, was investigated using supercritical CO_2 and compared to the classical Soxhlet extraction. Results were correlated to fly ash composition, which is strongly related to the fume purification system used in the incinerators. Fly ash collected at the bottom of the electrostatic precipitator is composed of dust coming from the combustion unit, but also of lime and eventually of activated charcoal injected in the fumes for acids and pollutants removal. When only lime is used for the fume purification, SFE of dioxins from fly ash leads to better results than Soxhlet extraction. The use of a binary cosolvent (trifluoroacetic acid in toluene) greatly increases the percentage recovery. When activated charcoal is used in conjunction with lime for the fume purification, SFE under classical extraction conditions is not powerful enough to extract dioxins, which are strongly adsorbed to the residual activated charcoal. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Extraction methods; Fly ash; Polychlorinated dibenzodioxins

1. Introduction

Supercritical fluid extraction (SFE) is usually proposed as an alternative to liquid–solid extraction such as Soxhlet or sonication for the analysis of organic pollutants in environmental matrices [1–8]. This method combines rapidity, selectivity and effectiveness and avoids the use of organic solvents, which will be, or are already, submitted to strict regulation.

Among non-polar organic pollutants analysed by SFE, polyaromatic hydrocarbons (PAHs) and polychlorobiphenyls (PCBs) have been extensively studied [1–8], but little has been published on the use of SFE in the analysis of polychlorinated dibenzo-*p*-dioxins (PCDDs[1] or dioxins) [9–19].

Analysis of dioxins has become an issue of major importance because of their carcinogenic nature [7,8]. The main source of dioxin emission is combustion processes such as waste incineration or steel industry. To allow a regular control of the emission, rapid and cheaper analyses are needed to replace the traditional extraction methods. The Soxhlet extraction method involves ultra pure, expensive and toxic solvents. During the extraction process, interfering compounds, that later affect the quantification, are

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[1]The polychlorinated dibenzo-*p*-dioxins, PCDDs, are abbreviated as follows: tetrachlorinated, TCDD; pentachlorinated, PeCDD; hexachlorinated, HxCDD; heptachlorinated, HpCDD; octochlorinated, OCDD. Numbers refer to the chloro-substituted positions.

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coextracted, and must be separated from dioxins using a number of chromatographic columns [20]. This paper studies the replacement of Soxhlet extraction by SFE for the analysis of dioxins in fly ash. The SFE extracts can be concentrated and analysed without any further clean-up.

Carbon dioxide is the most common fluid used for analytical purpose. Results published for dioxins analysis with this fluid are very variable: from 0 to 100% recovery. Use of N_2O is preferred and gives in general good results [9–19]. Unfortunately, this fluid can cause violent explosions, and needs special equipment. The experiments described in those papers were performed only for one kind of fly ash, and did not take into account the extreme variability of fly ash composition.

Fly ash composition varies greatly due to the diversity of garbage burned, but also to the fume purification system used. Indeed, lime, or a mixture of lime and activated charcoal, is injected in the fumes for acids and organic pollutants removal. The solid particles, composed of dust coming from the combustion unit and of lime+activated charcoal coming from the purification system, are removed by the way of an electrostatic precipitator before rejection of the fumes at the chimney (a more detailed description is given later). The fly ash samples studied here come from different municipal waste incinerators and are collected at the bottom of the electrostatic precipitator. They are representative of the particulate matter emitted at the chimney (which are submitted to control).

The present study correlates fly ash composition, which is strongly related to the fume purification system used in the incinerators, and SFE efficiency. Carbon dioxide was chosen as fluid due to its easiness of use. All 2,3,7,8-chloro-substituted isomers were followed. SFE results were compared to those obtained with 48 h Soxhlet extraction.

2. Experimental

2.1. Chemicals

Toluene and hexane are Baker Analysed Reagents, methanol is a Baker Analysed HPLC Reagent (J.T. Baker, Deventer, Netherlands). Dodecane was purchased from Merck–Schuchardt (Hohenbrunn, Germany), dichloromethane from VEL (Leuven, Belgium). HCl 92% was purchased from Merck (Darmstadt, Germany), H_2SO_4 95–97% is a Baker Analysed Reagent (J.T. Baker). The standard solution of 2,3,7,8-chloro-substituted $^{13}C_{12}$ labelled dioxins were purchased from Campro Scientific (Veenendaal, Netherlands). This solution of 2,3,7,8-chloro-substituted labelled dioxins, US Environmental Protection Aency (EPA) 1613 LCS, contains 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; 1,2,3,4,7,8-HxCDD; 1,2,3,6,7,8-HxCDD; 1,2,3,4,6,7,8-HpCDD at a concentration of 100 ng/ml and OCDD at a concentration of 200 ng/ml. The second standard used was the [^{13}C]1,2,3,4-TCDD at a concentration of 200 ng/ml (EPA-513ISS) (Campro Scientific). The alumina, activated, neutral, type 507c, Brockman I STD grade, ca. 1590 mesh (Sigma–Aldrich, Steinheim, Germany), was heated at 140°C overnight before use. Anhydrous Na_2SO_4 is a Baker Analysed Reagent (J.T. Baker) and was covered with toluene and left in an oven at 100°C overnight before use. NaCl and KOH are of analytical-reagent grade and were purchased from Merck.

2.2. Fly ash samples

Fly ash samples were very kindly collected by private industries at the bottom of electrostatic precipitators of different incinerators. Fly ash samples A, C, D, E and F come from municipal waste incinerators, but the exact origin of fly ash B is unknown.

Measures of specific surface of fly ash samples were performed using the BET (Brunauer, Emmet and Teller) method on a Sorptomatic 1900 instrument (Carlo Erba, Milan, Italy).

2.3. Pre-treatment

All fly ash samples were pre-treated during 2 h with 1 *M* HCl (z g of fly ash for $8\times z$ ml of HCl), under magnetic stirring. Fly ash was separated from HCl by centrifugation at 3000 rpm during 10 min, and rinsed three times with fresh water (separation also by centrifugation). Fly ash was dried overnight in an oven at 30°C, and kept in a closed vessel. To facilitate comparison, a sufficient quantity of fly ash

was prepared to allow Soxhlet extraction and SFE with the same stock. Fly ash B was sieved prior to HCl treatment to remove bigger particles.

2.4. Soxhlet extraction

The slightly modified EPA 8280 method was followed for classical dioxins analysis. 1.5 g of fly ash was spiked with 10 μl of the standard solution of 2,3,7,8-chloro-substituted labelled dioxins (EPA 1613 LCS). Soxhlet extraction was performed using 150 ml of toluene during 48 h. A Dean Stark was used to eliminate residual water, if present, at the beginning of the extraction. At the end of the extraction, the solvent was exchanged to 25 ml hexane. Hexane was successively washed with 5% NaCl solution, 20% solution KOH (maximum four washings), 5% NaCl solution again, concentrated sulphuric solution (maximum four washings), and with a last 5% NaCl solution. The organic layer was dried over Na_2S0_4 and concentrated to 2 ml. The extract was cleaned up on a 4 g neutral alumina column, with the first fraction of 10 ml hexane–dichloromethane (92:8) discarded and the second fraction of 15 ml dichloromethane–hexane (60:40) containing dioxins. One hundred μl of dodecane were added to this second fraction and the extract was concentrated by blowing it down to 100 μl under a gentle stream of nitrogen prior to GC–MS analysis.

2.5. SFE

SFE was carried out with an ISCO (Lincoln, NE, USA), Model 260-D (SFX 220) extractor. The flow-rate of the supercritical CO_2 (TP N25, Air Liquide, France) was adjusted to 1 ml/min with an ISCO restrictor temperature controller for coaxially heated capillary and adjustable restrictor. The restrictor temperature was similar to the extraction temperature with a maximum of 100°C. For SFE with a determined percentage of cosolvent, two pumps were connected with two backpressure control valves and a mixing tee. 1.5 g of fly ash was placed in a 2.5 ml extraction cell. The standard solution of 2,3,7,8-chloro-substituted labelled dioxins was diluted 25 times in toluene, and 250 μl of this solution (corresponding to the same quantity of labelled dioxins used in Soxhlet extraction) were added on the top of fly ash. The remaining void volume of the cell was filled with celite 545 (Baker Analysed Reagent, J.T. Baker). When trifluoroacetic acid (TFA 99%, Janssen Chimica, Geel, Belgium) is used, 1 ml of a 10% solution in toluene is deposited on fly ash 20 min before the addition of the standard solution and the celite. For the analytes trapping, a transfer tube (10 cm×1 cm I.D.) was packed with a plug of glass wool [dimethylchlorosilane (DMCS) treated, Alltech, Deerfield, IL, USA] and 500 mg of celite 545. The tube was sealed to the outlet end of the restrictor by a septum. A vial was placed under the transfer tube to recuperate the cosolvent eventually added. When the SFE was completed, the transfer tube was removed and compounds were eluted with 10 ml of dichloromethane in the vial placed under the transfer tube. Ten μl of the [$^{13}C_{12}$]1,2,3,4-TCDD solution and 100 μl of dodecane were added to the extract. The extract was then concentrated by blowing it down to 100 μl under a gentle stream of nitrogen prior to GC–MS analysis.

2.6. High-resolution GC–high-resolution MS (HRGC–HRMS)

All analysis were performed by HRGC–HRMS using a VG-AutoSpec-Q high-resolution mass spectrometer (Fisons Instruments, Manchester, UK) and a Hewlett-Packard (USA) 5890 Series II gas chromatograph.

The GC conditions were optimised to separate the various 2,3,7,8-chloro-substituted dioxins as followed: column: SP 2331 capillary column (Supelco, USA), 60 m×0.25 mm I.D., 0.2 μm film thickness; splitless injection of 1 μl of the extract at 275°C; initial oven temperature: 150°C; temperature programming: 150°C, held for 1 min, then increased at 40°C/min to 200°C, then increased to 273°C at 1.2°C/min, which was held for 16 min. He (N60 pure grade 99.9999%, Air Liquide) is used as carrier gas.

The mass spectrometer was operated in the electron impact ionisation mode using selected ion monitoring. The MS was tuned to a minimum resolution of 10 000 (10% valley), and was operated in a mass drift correction mode using PFK (perfluorokerosene) to provide lock masses. The two

most abundant ions in the chlorine clusters of the molecular ion were recorded for each isomer of native and labelled dioxins. The electron energy was set to 45 eV. The source temperature was 240°C.

A typical HRGC–HRMS run is illustrated in Fig. 1.

2.7. Identification and quantification

Only the 2,3,7,8-chloro-substituted isomers are followed. Peak identification criteria were as followed: signal/noise ≥5 for quantification; the isotope ratio of the two characteristic ions for each congener class within 20% of the theoretical value; the peak maxima for the molecular cluster ions coincide within 2 s; native dioxins elute within 3 s of their corresponding ^{13}C-labelled analogues. The selected ion profile areas for the characteristic ions for each native and labelled dioxins were measured. Native dioxins concentration was determined by isotope dilution as described in the EPA 8280 method. The concentrations were multiplied by the toxic equivalent factors of the Nato model, and results are expressed as pg TEQ (toxic equivalent)/g of fly ash. The percentage recovery of 2,3,7,8-chloro-substituted labelled dioxins (PRLDs) introduced before the SFE was estimated by the way of a second standard, the [^{13}C]1,2,3,4-TCDD, introduced after SFE. A reference solution containing the same quantities of both standards was analysed before each set of SFE extracts. The ratio between surface area of 2,3,7,8-chloro-substituted isomers and sur-

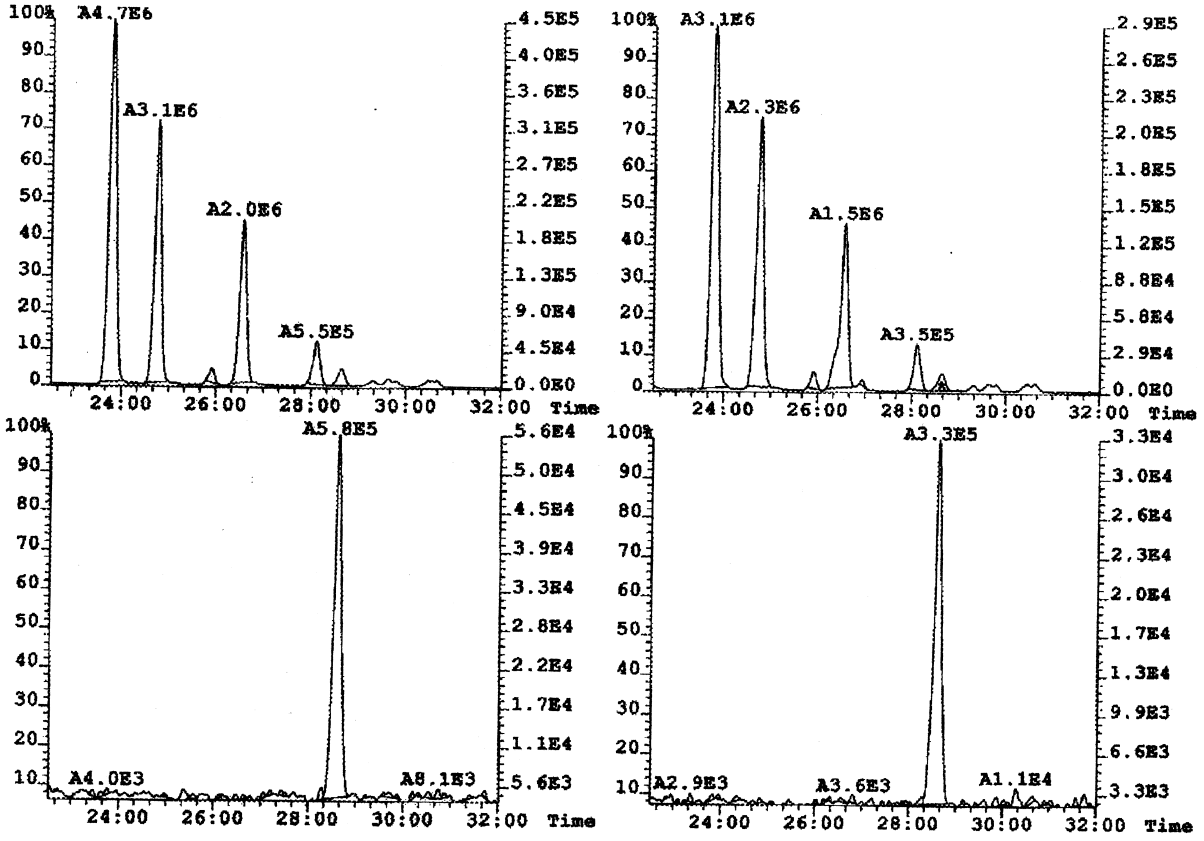

Fig. 1. Typical GC–MS run for PeCDD. The two top windows show the native isomers. The two most abundant ions in the chlorine clusters of the molecular ion were recorded (on the left: $^{12}C_{12}H_3O_2^{35}Cl_4^{37}Cl_1$, M_r: 355.8546; on the right: $^{12}C_{12}H_3O_2^{35}Cl_3^{37}Cl_2$, M_r: 357.8517). The two bottom windows show the ^{13}C-labeled 2,3,7,8-PeCDD (on the left: $^{13}C_{12}H_3O_2^{35}Cl_4^{37}Cl_1$, M_r: 367.8949; on the right: $^{13}C_{12}H_3O_2^{35}Cl_3^{37}Cl_2$, M_r: 369.8919). Time scales in min.

face area of [^{13}C]1,2,3,4-TCDD was determined for this reference solution and compared to the same ratio in SFE extracts. The estimation of the percentage recovery of native dioxins is based on the assumption that Soxhlet extractions give 100% recovery of both standard and native dioxins. The percentage recovery of native dioxins (PRNDs) can then be expressed as followed: PRND=PRLD· concentration measured in SFE/concentration measured by Soxhlet.

3. Results and discussion

3.1. Preliminary considerations

The pre-treatment of fly ash during 2 h with 1 *M* HCl greatly improved the efficiency of dioxins extraction and all fly ash used were systematically treated by this way (for Soxhlet extraction and SFE). Fly ash has spherical structure, even spheres within spheres. Compounds are adsorbed on the surface of these spheres on the outside as well as the inside. HCl may open some of these spheres thus making more material accessible to the extractant [21].

Forty-eight hour Soxhlet extraction with toluene is taken as reference, and considered as 100% extraction.

First SFE experiments were conducted with a fixed-flow restrictor, but no more than 20% of OCDD and 60% of HpCDD and HxCDD can be recovered in any experiments, and plugging of the restrictor can occur. The use of an adjustable flow, heated restrictor avoids the trapping of heaviest dioxins in the restrictor and allows a quantitative recovery of all isomers, when SFE conditions are sufficient.

Recuperation of compounds by decompression of supercritical CO_2 in an organic solvent leads to a loss of extracted compounds too. The decompression of supercritical CO_2 on an inert matrix, celite ($CaCO_3$), and the elution of celite with 10 ml of dichloromethane allows a quantitative recuperation.

Two hundred and fifty microlitres of a standard solution of labelled dioxins in toluene are introduced in the extraction cell before the extraction for the concentration measurements. The measured concentrations can be correct if the extraction of native and labelled dioxins is similar, even if the extraction is not quantitative. The use of a second standard, the [^{13}C]1,2,3,4-TCDD, introduced after the extraction allows to estimate the percentage recovery of native and standard dioxin by comparison with the Soxhlet results. This percentage recovery is sometimes more representative of the extraction efficiency than the concentration value.

3.2. Optimisation of SFE conditions for one kind of fly ash: fly ash A

SFE parameters such as temperature and pressure were optimised for the extraction of dioxins from one kind of fly ash, fly ash A.

The first SFE parameter tested is the temperature. At constant pressure, an increase in temperature diminishes the density and the solvating power of supercritical CO_2. However, the decrease of density can lead to an increase of analytes solubility due to the increase in vapour pressure of the solute. Increasing SFE temperature gives adsorbed molecules more thermal energy to overcome the desorption barrier and prevent native analytes from readsorbing once solvated in supercritical CO_2 [19,22–25].

The percentage recovery of native dioxins greatly increases with temperature at 400 bar, and more native dioxins can be extracted by SFE than by Soxhlet at 145°C, the maximum temperature available by our instrument (Fig. 2a). The extraction of standard is quantitative at this temperature. The extraction of dioxins, strongly adsorbed on fly ash, is mainly controlled by the matrix specific sorption behaviour and the effect of temperature is of prime importance.

At 145°C, the effect of pressure is not so important (Fig. 2b). The maximum pressure available by our extractor (500 bar) was preferred for the rest of the study because it allows reaching the maximum density at this temperature, and thus the maximum of supercritical CO_2 solvating power.

Experiments conducted at the same density 0.68 g/ml (47°C and 132 bar; 97°C and 306 bar; 147°C and 480 bar) show that temperature is the governing parameter rather than density: the extraction at 147°C is better than using a Soxhlet, but the percentage recovery does not exceed 40% at 47°C (Fig. 2c).

At 145°C, 500 bar, the extraction of dioxins is

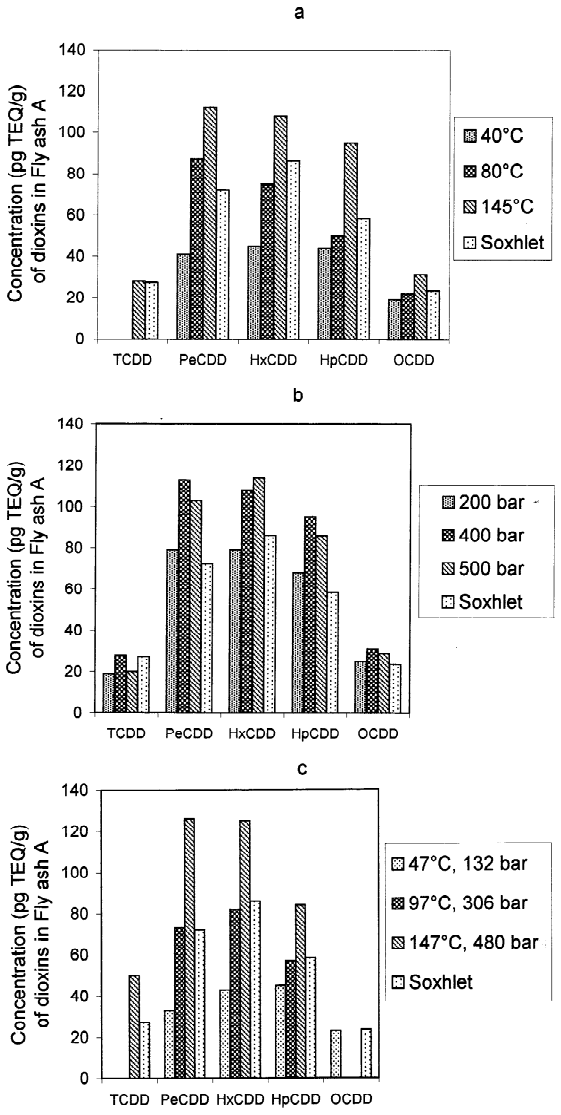

Fig. 2. (a) Effect of SFE temperature on the dioxins concentration measurements for fly ash A. Pressure: 400 bar, 1 h, 250 μl toluene as cosolvent. (b) Effect of SFE pressure on the dioxins concentration measurements for fly ash A. Temperature: 145°C, 1 h, 250 μl toluene as cosolvent. (c) Concentration measurements at constant density (0.68 g/ml), 1 h, 250 μl toluene as cosolvent.

almost quantitative in 10 min (80–100%). The toluene (250 μl) introduced with the standard solution of labelled dioxins acts as cosolvent. If the labelled dioxins are introduced as 10 μl of a concentrated solution, only 60% of native dioxins are extracted in 10 min. After 60 min, more dioxins are extracted when toluene is added as cosolvent, but in each cases, the percentage recoveries are superior to those obtained by Soxhlet.

3.3. Extension to other fly ash

The SFE conditions optimised for the extraction of dioxins from fly ash A (145°C, 500 bar, 1 h, 250 μl toluene introduced with the standard) were applied for the extraction of dioxins from other fly ash samples coming from different municipal waste incinerators: fly ash B to F. The recovery of native dioxins varies from 1 to 50%. Following these results, the study has been divided into two parts: first, try to improve the recovery by use of cosolvents and second, try to find the origin of the different behaviours.

3.4. Use of cosolvents

Dioxins are well soluble in supercritical CO_2, as demonstrated by the quantitative extraction from fly ash A. However, active sites of fly ash samples B to F strongly interact with dioxins, and the extraction of analytes is not easy. To overcome these interactions, cosolvent can be added to the supercritical CO_2. Little information is available to aid the choice of cosolvent because the actual action of these ones is not well understood. Among the different mechanisms proposed, cosolvents are supposed to (1) increase the solubility of the compounds in supercritical fluids, (2) displace compounds from active sites of the matrix and prevent their readsorption, (3) interact with the matrix- compounds to diminish activation energy of desorption, (4) make chemical association with the compounds by the way of low energy bounding and (5) alter the sample matrix (e.g., matrix swelling) [5,23,26].

Methanol, the most often used modifier, has been first tested as cosolvent with fly ash B. Five percent was added to supercritical CO_2 by the way of an auxiliary pump and the recovery of native dioxin was increased from 10 to 20% (Fig. 3).

Toluene is the best solvent for dioxins Soxhlet extraction, due to its aromatic, plane structure similar to that of dioxins. The π–π interactions can favour the displacement of dioxins from adsorption sites. Probably for the same reason, toluene gives better

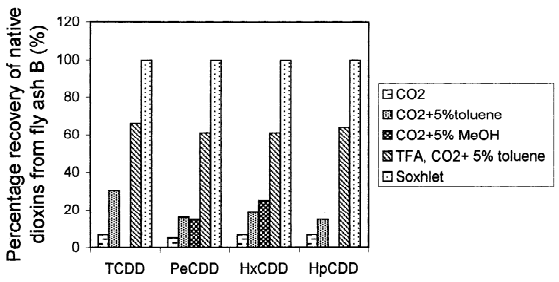

Fig. 3. Percentage recovery of native dioxins from fly ash B. SFE: 145°C, 500 bar, 1 h, different cosolvents.

results than methanol as cosolvent in SFE, but the difference is quite small.

Another approach is the addition of active components to the modifier in order to deactivate the adsorption sites, as proposed by Friedrich et al. [18,27]. A significant improvement of the extraction efficiency was observed when 1 ml of a 10% solution of TFA in toluene was deposited on fly ash, in the extraction cell, 20 min before the SFE. Besides the deactivation of active sites, TFA probably acts as HCl and destroys part of the matrix, making the dioxins more accessible for the extraction. The CO_2 was still modified with 5% of toluene. The percentage recovery reaches 60% for native and is quantitative for the standard.

The pre-treatment with TFA and extraction with CO_2 modified by 5% of toluene was repeated with fly ash E. In this case, the percentage recovery of native dioxins is not only greatly improved but is clearly better than the Soxhlet value, taken as 100%. Standard extraction is quantitative. Same experiments with fly ash F lead to similar results: quantitative extraction of the standard and better extraction of the native by SFE than by Soxhlet. These results put back into question the Soxhlet efficiency (Table 1).

Unfortunately, for Fly ash C and D, adding TFA and toluene did not improve the recovery to more than 10%, and none of the labelled dioxins, added on the top of fly ash before SFE, can be detected.

SFE were performed in triplicate and show a relative standard deviation (R.S.D.) of about 3 to 10%, which is significantly smaller than R.S.D. for triplicate Soxhlet extractions (12–25%). The high

Table 1
Comparison of dioxins SFE and Soxhlet extraction for the different kind of fly ash

	Concentrations (pg TEQ/g)					
	TCDD	PeCDD	HxCDD	HpCDD	OCDD	Total
Fly ash A						
Soxhlet (% R.S.D.)	27 (26)	72 (18)	86 (24)	59 (18)	24 (25)	63 (21)
SFE (% R.S.D.)	25 (24)	114 (1)	122 (7)	89 (4)	33 (3)	383 (4)
% SFE vs. Soxhlet	93	158	142	151	138	146
Fly ash B						
Soxhlet (% R.S.D.)	98 (15)	449 (14)	546 (12)	409 (16)	97 (12)	1599 (12)
SFE (% R.S.D.)	62 (12)	278 (5)	365 (5)	268 (8)	93 (11)	1067 (1)
% SFE vs. Soxhlet	63	62	67	66	96	67
Fly ash E						
Soxhlet (% R.S.D.)	44 (12)	92 (22)	176 (15)	156 (14)	26 (6)	494 (14)
SFE (% R.S.D.)	71 (20)	164 (4)	271 (11)	234 (8)	49 (15)	795 (4)
% SFE vs. Soxhlet	161	178	157	150	188	161
Fly ash F						
Soxhlet (% R.S.D.)	47 (21)	104 (28)	173 (16)	170 (14)	30 (22)	525 (25)
SFE (% R.S.D.)	66 (9)	156 (3)	230 (11)	227 (6)	46 (9)	725
% SFE vs. Soxhlet	140	150	133	134	153	138

SFE conditions: 145°C, 500 bar, 1 h, 1 ml of a 10% solution of TFA in toluene added in the extraction cell before SFE, except for fly ash A: addition of 250 μl of toluene as cosolvent.
Experiments performed in triplicate.

R.S.D. for TCDD is due to the small concentration of this compound.

In conclusion, the fly ash can be divided into three groups. The first group includes fly ash samples A, E and F, for which SFE gives better results than Soxhlet extraction. The second group includes fly ash B: the extraction of standard is quantitative, and the extraction of native reaches 60%. The last group includes fly ash samples C and D for which maximum 10% of dioxins can be extracted.

3.5. Origin of the different behaviours

To understand the different behaviours, some physico–chemical properties of the fly ash samples were investigated.

The structure of fly ash seen by electronic microscopy reveals a lot of differences, but these differences cannot be correlated to the SFE results.

The specific surfaces, determined by the BET method, were very small and similar for all kind of fly ash samples (8–14 m^2/g), except for fly ash B, which is lower than the others (2 m^2/g).

The chemical composition (Table 2) is strongly related to fly ash origin, and is the key of the explanation. The carbon content was determined by total combustion, and the other elements were determined by X fluorescence spectrometry (SRS 303 AS, Siemens, Germany). For a better understanding, a simplified scheme of an incinerator is given in Fig. 4. The fumes emitted by the waste combustion are directed to a contact reactor, where lime, or a mixture of lime and activated charcoal, is injected to neutralise acids and adsorb organic pollutants. The fumes pass then through an electrostatic precipitator to eliminate all particles and are rejected in the chimney. Each industry use its own fume purification system with one or two electrostatic precipitators, one or two contact reactors with injection of lime or lime plus activated charcoal.

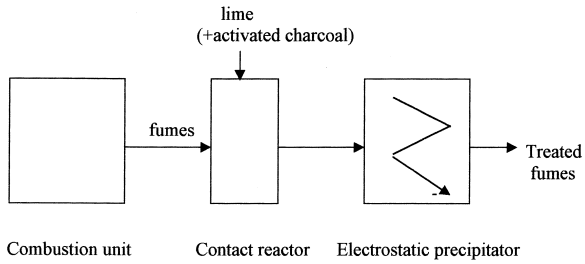

Fig. 4. Simplified scheme of an incinerator.

The aluminium and silicium content of fly ash is a good indicator of the dust coming from the combustion unit. Fly ash samples A, E and F are mainly composed of lime, as indicated by the high calcium content. This lime has diluted the dust coming from the combustion unit and the aluminium and silicium content is low. As only lime is used for the fume purification, the carbon level is very low. For these

Table 2
Chemical composition of fly ash

Chemical composition (%)	A	B	C	D	E	F
Na	1.5					
Mg			1.4			
Al	1.4	4	4.3	0.14	0.8	0.6
Si	2.6	7	8.3	0.27	1.46	1.3
P		1.25	1.2			
S	3.3	4.3	2.6	4.7	2	1.5
Cl	1.7	10	1.2	1.5	1.3	
K		6.8	1.4			
Ca	55	19	31	63	64	62
Ti		1.5	2			
Fe	1.1	2.4	1.9			
Zn	2.8	1.7	1.1		1.3	1.4
Pb		1.7				
C total	2.7	0.91	8.4	12.7	2.1	1.6

fly ash samples, SFE gives high extraction percentage.

Fly ash B contains a high percentage of dust coming from the combustion unit. The percentage of lime content is low. The dust seems to be a very good adsorbent and SFE is not quantitative. Only 60% of native dioxins can be extracted. The exact origin of fly ash B is unknown, the only knowledge is that the incinerator where fly ash was collected is of special design. The aspect of fly ash is very different than the other ones, and the specific surface is much smaller. It seems to be a very particular case.

The activated carbon is a very good adsorbent and is added to lime in order to catch organic pollutant emitted during the combustion process. Owing to this very good adsorbent property, the pollutants adsorbed on activated charcoal are very difficult to extract. When activated charcoal is used, SFE is not powerful enough as for fly ash C and D.

4. Conclusions

Mild SFE conditions may be sufficient for a quantitative extraction of dioxins from fly ash when no activated charcoal is added to lime in the fume purification system in the incinerator. The use of binary cosolvent (TFA in toluene) during SFE can significantly improve the dioxins recovery and leads, in some cases, to a better extraction than the classical Soxhlet method. When residual activated charcoal is present in fly ash, only 10% of native dioxins can be extracted, even under the strongest conditions tested.

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