Fast extraction of dioxins from fly ash: comparison of Soxhlet, supercritical fluid and microwaves-assisted Soxhlet extraction.

I.Windal*, G. Eppe*, A-C Gridelet*, L. E. Garcia-Ayuso+,
M. D. Luque de Castro+, E. De Pauw*

*University of Liege, Mass Spectrometry Laboratory, B6c Sart-Tilman, B-4000 Liege, Belgium. I.Windal@ulg.ac.be

+Department of Analytical Chemistry, Faculty of Sciences, University of Cordoba, E-14004 Cordoba, Spain

Introduction.

This paper investigates the replacement of Soxhlet by SFE or by microwave-assisted Soxhlet extraction for the extraction of dioxins from fly ash.
SFE combines rapidity, selectivity and effectiveness and avoids the use of organic solvents, which will be, or are already, submitted to strict regulation (1-4).
More recently, microwave-assisted extraction has received increasing attention by greatly reducing the extraction time with similar and even higher efficiency than the conventional Soxhlet extraction. A new type of microwave-assisted Soxhlet extraction, designed at the University of Cordoba, was used in this study (5). The device uses the conventional Soxhlet glassware and a focused-microwave digestor for irradiation of the sample cartridge at the required intervals while the fresh solvent drops on and passes through the solid sample. On one hand, the application of microwave energy facilitates the breaking of analyte-matrix bond and reduces the extraction time. On the other hand, the sample is repeatedly brought in contact with fresh portions of the solvent, thereby aiding displacement of the separation equilibrium.
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 fumes at the chimney. To take into account the extreme variability of fly ash composition, the fly ash samples studied here come from different municipal waste incinerators and are collected at the bottom of the electrostatic precipitator.
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. The microwave-assisted Soxhlet extraction was tested for one kind of fly ash, for which SFE is not powerful enough. All 2,3,7,8 chlorosubstituted isomers were followed. SFE and microwave-assisted Soxhlet extraction results were compared to 48h Soxhlet extraction.

Materials and methods.

1. Fly ash samples were kindly collected by private industries at the bottom of electrostatic precipitators of different incinerators. They were pre-treated during 2 h with HCl 1M.
2. The slightly modified EPA-8280 method was followed for conventional Soxhlet extraction, using 150 ml of toluene during 48 h.
3. SFE were carried out with an ISCO model 260-D (SFX 220) extractor. The restrictor temperature was similar to the extraction temperature with a maximum of 100°C. A standard solution of 2,3,7,8 Cl-substituted labelled dioxins was added on the top of fly ash before SFE. Analytes were trapped on celite ($CaCO_3$) and eluted with 10 ml of CH_2Cl_2. 10 µl of 1,2,3,4 $^{13}C_{12}$ TCDD solution were added to the extract before concentration. The recovery of 2,3,7,8 Cl-substituted $^{13}C_{12}$ dioxins introduced before the SFE and the recovery of native dioxins was estimated by the way the 1,2,3,4 ^{13}C TCDD, introduced after SFE.
4. The standard solution of 2,3,7,8 Cl-substituted labelled dioxins was added after the microwave-assisted Soxhlet extraction, due to difficulty to add it before. The extract was submitted to the same clean-up as for conventional Soxhlet extraction. The Prolabo Microdigest 301 (200 watts of maximum power) was used for the microwave irradiation.
5. All analysis were performed by HRGC-HRMS using VG-Autospec-Q high-resolution mass spectrometer and Hewlett Packard 5890 Series II gas chromatograph. Only the 2,3,7,8 Cl-substituted isomers are followed. Native dioxins concentrations were determined by isotope dilution as described in the EPA 8280 method.

Results and discussion.

1. SFE

a) Optimisation of SFE conditions for 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. In addition, increasing SFE temperature gives adsorbed molecules more thermal energy to overcome the desorption barrier and prevents native analytes from readsorbing once solvated in SC CO_2 (4, 6).

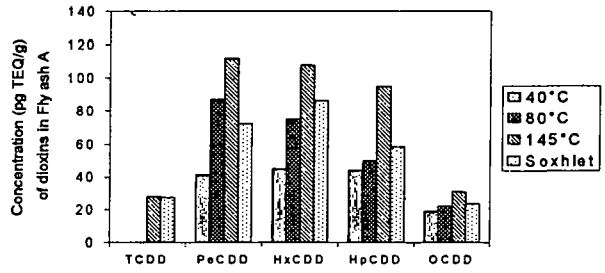

Fig. 1: Effect of temperature on the extraction of dioxins from fly ash A, at P=400 bars, 1h

The recovery of native dioxins greatly increases with temperature at 400 bars, and more native dioxins can be extracted by SFE than by Soxhlet at 145°C, the maximum operating temperature of our instrument (Fig. 1). The extraction of standard is quantitative at this temperature.
At 145°C, the effect of pressure is not so important. The maximum pressure available by our extractor (500 bars) was preferred for the rest of the study because it allows reaching the maximum density at this temperature, and thus the maximum of CO_2 solvating power.
At 145°C, 500 bars, the extraction of dioxins is almost quantitative in 10 minutes (80-100%). The toluene (250µl) introduced with the standard solution of labelled dioxins acts as cosolvent.

b) Extension to other fly ash.

The SFE conditions optimised for the extraction of dioxins from fly ash A (145°C, 500 bars, 1h, 250µl 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 out the origin of the different behaviours.

c) Use of cosolvents.

Methanol and toluene have been first tested as cosolvent with fly ash B. 5% of methanol or toluene was added to SC CO_2 by the way of an auxiliary pump and the recovery of native dioxin was increased from 10 to 20 %.
A significant improvement of the extraction efficiency is observed when 1 ml of a 10 % solution of trifluoroacetic acid (TFA) in toluene is deposited on fly ash in the extraction cell, 20 minutes 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 recovery reaches 60% for native and is quantitative for the standard. The pre-treatment with Trifluoroacetic acid and extraction with CO_2 modified by 5 % of toluene was repeated with fly ash E and F. In these cases, the recovery of native dioxins is not only greatly improved but is clearly better than the Soxhlet value, taken as 100%. Standard extraction is quantitative (Fig. 2).

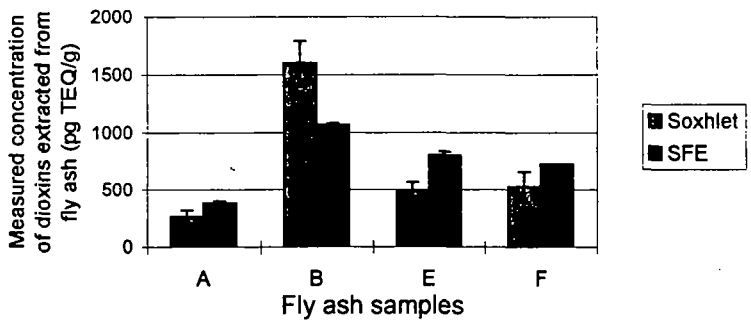

Fig. 2: Comparison of SFE and Soxhlet extraction for some kind of fly ash.
SFE: 1h, 145°C, 500 bars, addition of 1ml of TFA 10% in toluene for fly ash B, E and F

Unfortunately, for Fly ash C and D, adding TFA and toluene do 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.

e) Origin of the different behaviours.

The chemical composition is strongly related to fly ash origin, and is the key of the explanation. 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 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. The exact origin of fly ash B is unknown; the only information about the sample is that it was collected at an incinerator of special design. It seems to be a very particular case.

The activated charcoal 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 (Table 1).

Fly ash	Ca	Al-Si	C	SFE
A, E, F	++	-	-	OK
B	-	+	-	±
C	+	+	++	-
D	++	-	++	-

Table 1: Correlation between SFE results and fly ash composition.

2. Microwave-assisted Soxhlet extraction.

The SFE of dioxins from fly ash is very matrix dependent, at least in the tested conditions. To test the efficiency of microwave-assisted Soxhlet extraction, one of the most difficult matrix was chosen: fly ash C. The irradiation power was set to the maximum available for every experiments. The effect of time extraction (5, 10 or 15 cycles of the microwave-assisted Soxhlet) was investigated as well as the microwave irradiation time (IT=2 or 5 minutes).

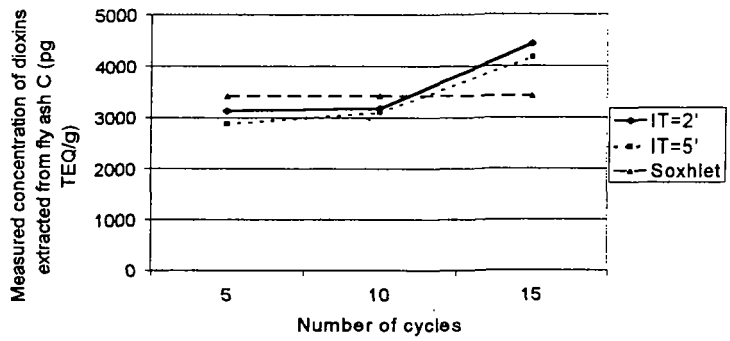

Fig.3: Measured concentration of dioxins extracted from fly ash C as a function of time (number of cycles).

More than 90 % of dioxins can be extracted in 5 cycles. More dioxins can be extracted than in 48h conventional Soxhlet if a longer extraction time (15 cycles, approximately 1h30-2h) is chosen (fig. 3). As for SFE, 1 ml of a 10 % solution of TFA in toluene was added on the sample before the extraction to improve the recovery. The experimental conditions were 15 cycles, and the irradiation time 2 or 5 minutes. In both cases, the recovery is very similar to the other experiments (table 1). The relative standard deviation for the 4 experiments, even performed in different conditions is very small (6 to 14%). When the same experiment is performed without irradiation, the recovery is about 50-60% (Table 2).

Concentration of dioxins in fly ash C (pg TEQ/g)							
Microwave-assisted Soxhlet extraction, 15 cycles						Conv. Soxhlet, 15 cycles	Conv. Soxhlet, 48 h
	TFA/tol IT = 2'	TFA/tol IT = 5'	IT =2'	IT=5'	*RSD*		
PeCDD	1342	1414	1564	1274	*9*	665	1130
HxCDD	1830	2033	1607	1480	*14*	991	1301,5
HpCDD	1101	1212	1112	1260	*7*	462	873,5
OCDD	138	166	142	157	*9*	46	114
Total	4410	4825	4425	4171	*6*	2257	3876

Table 2 : Concentration of dioxins in fly ash C.

Conclusions.

SFE can be considered as an alternative to conventional Soxhlet extraction method for low carbon level fly ash. When the percentage of carbon is high (15% for fly ash C), microwave-assisted Soxhlet extraction can be envisaged. Work is under progress using high temperature SFE.

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