

MICROWAVE EXTRACTION OF DIOXINS AND FURANS FROM FLY ASH

W. Tirlir, M. Donegà, G. Voto.

Eco Center – via Lungo Isarco Sinistro, 57 – 39100 Bolzano (BZ) – ITALY

Introduction

Microwave-assisted extraction (MAE) of organic pollutants from solid samples matrices is nowadays used by several laboratories (1,2,3). The advantages of this technique are basically saving extraction time and less consumption of solvent.

Microwave extraction seems to be a very attractive alternative to conventional methods like soxhlet extraction (4,5,6). But still some kind of samples are not easy to extract. For example fly ash needs to be pre-treated. Acid washing with Hydrochloric acid (HCl) gives good results (7). In our work we tried to combine sample pre-treatment, extraction and partially clean up procedures with a microwave-assisted extraction.

Materials and Methods

For the testing the certified fly ash sample CRM 490 from BCR (8) was used. Closed vessel MAE was performed with an Ethos E apparatus (Milestone, Sorisole, Italy). Samples can be extracted in up to twelve 100 ml closed TFE vessels in parallel.

The sample amount of 0.5 g for each testing was mixed and milled (Mixer Mill, Retsch) with Silica gel/H₂SO₄ mixture (44 %), placed with 50 ml of solvent in the vessels and sealed after applying magnetic stirring. MAE was performed with Heptane and with Toluene as a solvent.

With Toluene a higher extraction temperature of 140 °C was used (with Heptane 110 °C) and in this case to the Silica gel/H₂SO₄ mixture 0.5 ml of pure water was added. More water (0.5 ml) was added to the toluene before extraction.

Three extraction cycle of 15 min. each were performed.

Traditional soxhlet extraction with toluene was used to compare the extraction efficiency.

Soxhlet extracts were cleaned by multi-layer Silica column and afterwards with basic Alumina. MAE extracts were cleaned only with multi-layer Silica. Analysis of dioxins/furans was done according US-EPA 1613. A 60 m DB 5ms column (J&W) was coupled to a high resolution mass spectrometer (ThermoFinnigan MAT 95 XL).

Results and discussion

In table 1 are reported the results of the different extraction approaches. The sample with HCl pre-treated, classical soxhlet extraction with toluene gave the closest results to the certified values. Without HCl pre-treatment the soxhlet extracts presented considerable lower amounts of dioxins/furans. Replacing the HCl leaching with mixing and milling the sample with KHSO₄, extraction yields improved but were still not comparable.

For the MAE with a non polar solvent (Heptane) we did not use a microwave transformer like Weflon but by mixing the sample with 3 g of Silica gel/H₂SO₄ (44 %) a sufficient heating of the solvent was achieved (110 °C). But still the efficiency was not high enough. So when water was added to the

ANALYSIS I

sample/acidic Silica gel and Toluene was used as extracting solvent the efficiency improved and the extracted amounts were close to the certified values.

Using the DB 5ms column allows not to separate all interfering non toxic from the toxic (2,3,7,8-substitute) dioxin/furan congeners. So especially for the toxic penta dioxin/furans it does not necessarily mean that the extraction efficiency was higher than expected. But it is more likely that the contribute form a non chromatographically resolved congener increases the determined amount. This effect is also clearly visible when you compare the certified amount with the amount found after HCl pre-treatment and Toluene-Soxhlet extraction.

Table 1. Results of the extraction of fly ash CRM 490: all values in ng/g

Extraction	-	Soxhlet	MAE	MAE	MAE	Soxhlet	Soxhlet
Pre-treatment	-	HCl 1M	Silica/ H ₂ SO ₄ 4 g	Silica/ H ₂ SO ₄ 4 g	Silica/ H ₂ SO ₄ 3 g	-	KHSO ₄
Solvent	-	Toluene	Toluene	Heptane	Heptane	Toluene	Toluene
	Certified values						
2378 TCDD	0,169	0,180	0,170	0,151	0,132	0,067	0,104
12378 PCDD	0,67	0,769	0,715	0,555	0,529	0,304	0,557
123478 HxCDD	0,95	0,814	0,767	0,628	0,616	0,282	0,495
123678 HxCDD	4,8	4,628	4,010	2,575	2,699	1,381	2,304
123789 HxCDD	2,84	2,742	2,357	1,494	1,587	0,849	1,452
2378 TCDF	0,9	0,879	0,919	0,569	0,635	0,551	0,854
12378 PCDF	1,71	1,716	1,788	1,234	1,286	0,732	0,928
23478 PCDF	1,85	2,608	2,461	1,767	1,760	0,822	1,211
123478 HxCDF	2,37	2,279	2,363	1,777	1,750	0,947	1,281
123678 HxCDF	2,64	2,633	2,668	2,123	2,023	1,047	1,666
234678 HxCDF	2,47	2,924	2,992	2,484	2,427	1,235	1,995

References:

1. Chiu C, Poole G, Shu Y, Thomas R and Turle R; Organohalogen Compounds. 1996, 27, 333-338.
2. Vetter W, Weichbrodt M, Batista A, Lukas B; Organohalogen Compounds. 1999, 40, 305 - 312.
3. Noboru Imano and Kenji Nakaaki; Organohalogen Compounds 2000, 45, 90-93.
4. In Choul Ryu, Jung hoon Uopm, Youn Goog Lee, Seok Won Eom, Jae young Shin; Organohalogen Compounds 2000, 45, 78 - 81.
5. Satoshi Kawaiji, Motonobu Goto and Tsutomu Hirose, Organohalogen Compounds 2000, 45, 101-105.
6. Henkelmann B, Wottgen T, K.W.Schramm, A. Kettrup; ; Organohalogen Compounds. 1999, 40, 133 - 136
7. Kooke RMM, Lustenhouwer JWA, Olie K, Hutzinger O.; Anal. Chem. 1981, 53, 461-463.
8. Van Cleuvenbergen R, Kramer G. N, and Maier E. A; BCR information series. 1996, ISBN 92-827-7410-4