

ANALYSIS OF PCDD/PCDFs BY ION-TRAP DETECTOR. APPLICATION TO WASTE SAMPLES

Begoña Fabrellas, Paloma Sanz, David Larrazabal and Esteban Abad¹

POP's Study and Characterisation Project, Environmental and Technological Research Center. Ministry of Industry (CIEMAT). Avda. Complutense, 22. 28040-Madrid. Spain. Fax: 34-91-3466269, e-mail begona.fabrellas@ciemat.es

¹Mass Spectrometry Lab. Dept.of Ecotechnologies. CID-CSIC. Jordi Girona 18-26, 08034 Barcelona, Spain

Introduction

The initiation of the national inventory of industrial sources of PCDD/Fs in Spain (1) means, also, the evaluation of alternative analytical techniques to be applied by industrial laboratories to implement their quality controls in production processes. HRGC/HRMS instrumentation is too expensive to be carried out in routine controls and Tandem Mass Spectrometry with an Ion Trap Detector appears as an interesting device to be evaluated. Their applications and limitations with samples of different origin and level of contamination (municipal waste incineration fly- ashes, urban solid wastes) are being studied using HRMS and GC/MS/MS systems.

Materials and Methods

Optimisation of GC/MS/MS System

Tandem mass spectrometry by ion trap detector has been introduced as an interesting device in analytical laboratories and research groups. The utility of the MS/MS technique derives basically of their spatial-design and from the use of alternating voltages applied to the end-caps electrodes. These voltages are referred to as waveforms that are employed for the principal steps: *ion isolation, ion excitation and axial modulation*. Its mechanism of action has been evaluated and presented in several reports (2-11). Briefly, it can be resumed by this way: Ion-trap confines the ions within a single region where they experience time-depending electromagnetic fields. The isolation of ion species M^{+} (parent ions), formed from M which elutes within a specified retention-time window, is followed by the observation of specific fragment ion signals, such as $M-COCl^{+}$ in the case of chloro congeners.

GC/MS/MS analysis were obtained with a VARIAN SATURN 2000, equipped with a 3800 GC and 1079 programmable injector. Splitless injection in a CP-SIL 8 Low Bleed /Ms Chrompak capillary column (30m, 0.25 mm, 0.25 μ m film thickness) was used. The GC conditions were: Injector: 100°C for 0,2 min, then, 200°C/min to 300 °C, hold 20 min. Splitter initial open, closed during 0,2 min, and then open again. Splitter Flow: 60 ml/min. Column Oven: Initial 60°C for 3 min, 25°C/min to 235°C, hold 10 min, 10°C/min to 275°C, hold 3 min, and finally 10°C/min to 310°C and hold 3 min. The MS/MS parameters are represented in Table 1.

The key step is the optimisation of Collision Induced Dissociation Waveform (CID) for each of the native and labelled isomers. It has been achieved varying the following instrumental parameters in a resonant excitation mode ($q=0.4$): *Excitation amplitude* or amount of energy used to break the molecule and *excitation time* or duration of the excitation process. The method is defined in time by segments and channels. The segments are consecutive in time and include the range of masses to isolate. In each segment, the channels work separately in each isolated parent mass by the application of the Excitation storage level, the ejection of non selected ions and the application of CID to obtain the specific daughter ions. In our method we have worked with seven segments.

The compound specific MS/MS parameters in order of elution is represented in Table 2. Having optimised the method, a five point calibration curve was prepared over a concentration range of 2 pg-200 pg of TCDD/F, 10 pg-1000 pg of P₃CDD/F to P₇CDD/F and 20-2000 pg of OCDD/F. The identification of PCDD/F was made in accordance with basic criteria as : Product ions coming from losses of CO ³⁵ Cl and CO ³⁷ Cl with (S/N) >3, isotopic ratio between product ions within acceptable range of +/- 20% and labeled/native retention time of 2 s.

Table 1: Optimised GC/MS/MS conditions for the PCDD/Fs analysis

IONIZATION PARAMETERS		ION PREPARATION PARAMETERS	
Ion Trap Temp:	250°C	Mass Isolation Window:	1
Manifold Temp:	50°C	CID Waveform:	
Resonant			
Transferline Temp:	300°C	Excitation Time:	5 msec
Multiplier Offset:	10 ⁵ gain ± 200 V	Isolation Time:	5 msec
Axial Mod. Voltage:	4.0 V	Modulation Rate:	30 µsec/step
Emission Current:	95 µA	Ejection Amplitude:	20 V
Fil/Mul Delay:	15 min	Broadband Amplitude:	30 V
Scan Rate:	0,38 sec/scan		
Target TIC:	2000 counts		
Prescan Ion. Time:	1500 µsec		
Count Treshold:	1 count		
Mass Defect:	100 u		
RF Dump Value:	650 m/z		

Samples Extraction and Clean-up

Initial samples were provided by industrial and waste management sectors. Fly-ash from incinerators, sewage sludges and urban solid wastes have being analysed simultaneously by GC/MS/MS and HRGC/HRMS. Samples were fortified with 15 ¹³C ₁₂ -labelled PCDD/Fs congeners. Sample sizes were: 4 g of fly-ash, 20 g of USW and 10 g of Sludges. Acid pre-treatment of fly-ashes followed by a 48-h toluene extraction stage and the clean-up of extract using a multilayer silica, base alumina and PX-21 carbon adsorbents were carried out. Special treatment is applied in USW samples as detailed in reference (12). Sludge samples need a double treatment of silica previous to the alumina stage.

HRGC/HRMS conditions

HRGC/HRMS analysis of samples were performed using a Fisons 8000 Series gas chromatograph coupled to an Autospec Ultima (Fisons Instruments) mass spectrometer, SIM mode at 10000 of resolving power. A DB-5 fused silica capillary columns (60 m, 025 mm ID, 0,25 µm film thickness) was used for the HRGC.

Results and discussion

- Very good product ions spectrum were obtained for the calibration ranges. All masses showed good linearity with RSD for product ions across the five concentrations below 20%.

Table 2: Compound specific MS/MS parameters

PCDDs/PCDFs (Native and Labelled)	RETENTION TIME	SEGM.- CHAN.	PARENT ION	EXCIT. STORG. LEVEL	DAUGHT ER IONS	RATIO	CID AMPL (V)
¹³ C-2,3,7,8-TCDF	16.114	2-2	317.94	154	252/254	0.33	1.5
2,3,7,8-TCDF	16.145	2-1	307.9	145	243/245	1.00	1.8
¹³ C-1,2,3,4-TCDD	16.233	2-3	333.93	175	268/270	0.33	0.7
¹³ C-2,3,7,8-TCDD	16.584	3-3	333.93	175	268/270	0.33	0.7
2,3,7,8-TCDD	16.590	3-1	323.89	161	259/261	1.00	0.7
C ¹⁷ -2,3,7,8-TCDD	16.597	3-2	328	162	291/263	1.00	0.7
¹³ C-1,2,3,7,8-PeCDF	19.622	4-2	351.90	188	286/288	0.25	1.1
1,2,3,7,8-PeCDF	19.641	4-1	341.86	179	277/279	0.67	1.4
¹³ C-2,3,4,7,8-PeCDF	20.686	4-2	351.90	188	286/288	0.25	1.1
2,3,4,7,8-PeCDF	20.707	4-1	341.86	179	277/279	0.67	1.4
¹³ C-1,2,3,7,8-PeCDD	21.011	4-4	367.89	210	302/304	0.25	0.5
1,2,3,7,8-PeCDD	21.031	4-3	357.85	195	293/295	0.67	0.7
¹³ C-1,2,3,4,7,8-HxCDF	23.400	5-2	385.86	222	320/322	0.2	1.7
1,2,3,4,7,8-HxCDF	23.419	5-1	375.82	213	311/313	0.5	1.7
¹³ C-1,2,3,6,7,8-HxCDF	23.504	5-2	385.86	220	320/322	0.2	1.7
1,2,3,6,7,8-HxCDF	23.523	5-1	375.82	213	311/313	0.5	1.7
¹³ C-2,3,4,6,7,8-HxCDF	23.992	5-2	385.86	222	320/322	0.2	1.7
2,3,4,6,7,8-HxCDF	24.012	5-1	375.82	213	311/313	0.5	1.7
¹³ C-1,2,3,4,7,8-HxCDD	24.133	5-4	401.86	220	336/338	0.2	1
1,2,3,4,7,8-HxCDD	24.153	5-3	391.81	229	327/329	0.5	0.8
¹³ C-1,2,3,6,7,8-HxCDD	24.211	5-4	401.86	220	336/338	0.2	1
1,2,3,6,7,8-HxCDD	24.230	5-3	391.81	229	327/329	0.5	0.8
¹³ C-1,2,3,7,8,9-HxCDD	24.442	5-4	401.86	220	336/338	0.2	1
1,2,3,7,8,9-HxCDD	24.462	5-3	391.81	229	327/329	0.5	0.8
¹³ C-1,2,3,7,8,9-HxCDF	24.738	5-2	385.86	222	320/322	0.2	1.7
1,2,3,7,8,9-HxCDF	24.758	5-1	375.82	213	311/313	0.5	1.7
¹³ C-1,2,3,4,6,7,8-HpCDF	26.245	6-2	419.82	240	354/356	0.4	1.7
1,2,3,4,6,7,8-HpCDF	26.264	6-1	409.78	235	345/347	0.4	1.9
¹³ C-1,2,3,4,6,7,8-HpCDD	27.495	6-4	435.82	250	370/372	0.4	1
1,2,3,4,6,7,8-HpCDD	27.515	6-3	425.77	250	361/363	0.4	1
¹³ C-1,2,3,4,7,8,9-HpCDF	27.998	6-2	419.82	240	354/356	0.4	1.7
1,2,3,4,7,8,9-HpCDF	28.017	6-1	409.78	235	345/347	0.4	1.9
¹³ C-OCDD	30.136	7-3	471.78	275	406/408	0.33	0.8
OCDD	30.150	7-2	459.73	275	395/397	0.33	1.1
OCDF	30.278	7-1	445.74	280	381/383	0.6	1.7

- No more than four daughter ions should be monitored in each channel to assure the adequate sensibility.

- GC/MS/MS quantitative results obtained in fly-ash samples were similar than HRGC/HRMS data (around 15% of deviation) and also the PCDD/Fs congeners patterns (Fig 1 and Fig 2) had a good correlation. No problems in detection levels and quantitative parameters were found in these types of samples.

- In USW samples the LOQs have been affected by the presence of some interferences,. Due to the extremely low level of PCDD/Fs in these samples, an optimising of clean-up stages must be realised to implement the obtained results. Also, the interaction of this sample matrix with the columns stationary phase is responsible for the mobilisation of some retention times. Nowadays, the MS/MS congener pattern profile confirm the correlation with HRMS (Fig 3 and Fig 4)

- Preliminary analysis obtained by Ion-trap detector confirm this technique as alternative to use with waste samples as fly-ashes, with well-defined extracted and clean-up methods and with medium-high PCDD/Fs levels. In low level contaminated matrices, final results depend on the

nature of the sample. We are currently evaluating this matter in sewage sludges. Future research actions will be aim to improve this application.

Figure 1 :
Congener-specific distribution in MWI fly-ash

HRGC/MS/MS

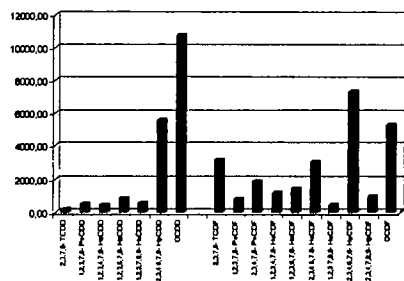


Figure 2
Congener-specific distribution in MWI fly-ash

HRGC/HRMS

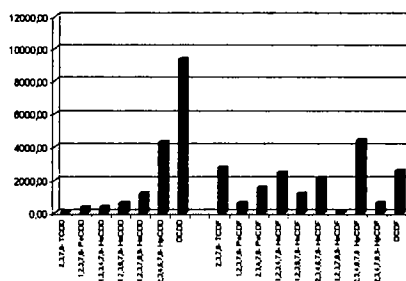


Figure 3
Congener-specific distribution in USW
HRGC/MS/MS

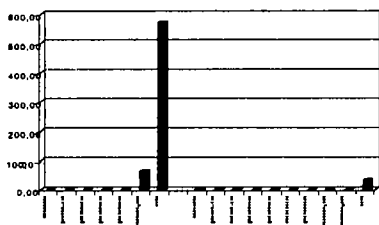
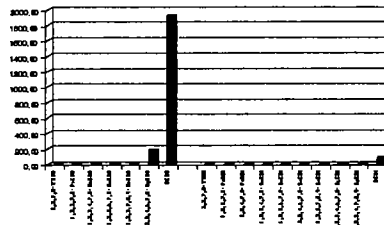


Figure 4
Congener-specific distribution in USW
HRGC/HRMS



Acknowledgements

We wish to thank especially Dr. Miguel Angel Perez from Varian for the software development and the implementation of the method and to Ana Maria Suarez, Pilar Miño and Juan Recuero for their contribution to this work.

References

1. Fabrellas, B., Sanz, P, Abad, E. Rivera, J. *Organohalogen Compounds*, 1999, 41, 491-494
2. Plomley J.B., Koester C.J, March R.E.; *Organic Mass Spectrometry*, 1994, 29, 372-281
3. Hamelin G., Brochu C., Moore S.; *Organohalogen Compounds*, 1995, 23, 125-129
4. Hayward D.G.; *Organohalogen Compounds*, 1995, 23, 119-124
5. Plomley J.B., March R.E.; *Analytical Chemistry*, 1996, 68, 2345-2352.
6. March R.E., *Journal of Mass Spectrometry*, 1997, 32, 351-369
7. Focant J.F., Eppe G., De Pauw E.; *Organohalogen Compounds*, 1999, 40, 101-104
8. Guarini A., Fiorani T., Busetto C.; *Organohalogen Compounds*, 1999, 40, 119-120
10. Skopp S., Oehme M., Brand H.; *Organohalogen Compounds* 1999, 40,261.
11. Hayward D.G., Hooper K., Andrzejewski D.; *Analytical Chemistry*, 1999, 71, 212-220
12. Abad, E. M.A. Adrados, J. Caixach, B. Fabrellas, J, Rivera. *Chemosphere* 40, 2000, 1143-1147