COMPARISON OF HRGC-MS/MS AND HRGC-HRMS RESULTS ON ENVIRONMENTAL AND FOOD SAMPLES IN SOME EUROPEAN LABORATORIES

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Introduction

At very low concentration, polychlorodibenzo-p-dioxins (PCDD) and polychlorodibenzofurans (PCDF) are currently determined by high-resolution gas chromatography/ high resolution mass spectrometry (HRGC-HRMS) as prescribed in US EPA Method 1613 and European Standard method EN 1948-1/2/3.

Initially, in order to differentiate between PCCD/Fs and interferents, such as polychlorobiphenyls, and $^{13}C_{12}$-PCDF and native PCDD whose isotopic clusters overlap, HRMS was necessary because only HRMS had the sensitivity and specificity required[1]. But these instruments are very expensive to purchase and to maintain. For that reason, laboratories have researched some more economic alternatives such as ion trap mass spectrometers using the tandem mass spectrometry technology (MS/MS or MS^3).

With this technology, high specificity is obtained by the isolation of the parent ion and subsequent selective collision induced dissociation before the analysis of the daughter ions.

This is especially sought after in the analysis of complex samples such as municipal incinerator (fly ash, slag and stack gas) samples and food samples, where interferences are widely present.

In term of interferences, HRMS would not be able to differentiate compounds of the same elemental composition. In contrast, QIT-MS/MS can separate these compounds but not the compounds with the same fragmentation pattern.

The comparison of PCDD/Fs levels obtained in QIT-MS/MS and HRMS on different samples and in different laboratories is presented here.

The laboratory of Rennes is working on the determination of PCDD/F on environmental samples by QIT-MS/MS, in collaboration with the laboratory of Nantes, working on food samples with the HRMS technology.

The laboratory of Liège is equipped with both instruments and is able to work on a widely range of samples.

Methods and materials

The stack gas sample was collected using a filter/condenser method in accordance with EN-1948 :1996. Fly ash and slag samples were collected on two different MSWI.

Fly ash was treated with HCl 1N for 2 hours prior to extraction. All the pollutants were removed from fly ash, slag, XAD-2 and filter by soxhlet extraction using toluene for 8 hours. Liquid-liquid extraction with toluene was performed to remove dioxin compounds from condensed water.

ANALYSIS II

Samples were cleaned-up on the classic liquid-solid adsorption chromatography using silica (Merck, France), and florisil (Merck, France) in open glass columns at atmospheric pressure.

All incinerator samples were analysed by high resolution gas chromatography coupled to low resolution mass spectrometry (HRGC/LRMS) using MS/MS in the laboratory of Rennes. For HRGC, a TRACE GC 2000 (ThermoFinnigan, France) equipped with a DB-5ms (J&W Scientific) fused silica capillary column (60m, 0.25mm I.D., 0.25µm film thickness) was used. For LRMS, a quadrupole ion trap GCQ (ThermoFinnigan) mass spectrometer was used in MS/MS mode with Multiple Reaction Monitoring (MRM). The MS/MS method had already been reported in details[2].

A part of the extract was sent to Nantes to be analysed by high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS). For HRGC, a 6890 (Agilent, France) equipped with a DB-5ms of 30m was used. For HRMS, a JMS 700D (Jeol, Japan) was used.

For food and feed samples, fortified beef fat, yolk and serum quality controls (QC) as well as naturally contaminated animal feed QC and a certified reference material BCR-607 milk powder were used. Animal feed and milk powder were Soxhlet extracted for 16 hours using respectively toluene and pentane-dichloromethane (1:1) as solvents; yolks extraction were performed on an ASE 200 extractor (Dionex, Sunnivale, CA, USA) using hexane as solvent. Serum samples were extracted by Solid Phase Extraction (SPE) cartridge using hexane as eluting solvent. Beef fat samples were already stored on fat extracted.

All samples were then loaded on an automated multi-column Power-Prep system (FMS, Waltham, MA, USA), excepted for animal feed samples where a preliminary sulphuric acid clean-up was needed before the Power-Prep clean-up. A complete description of both extraction and clean-up procedure can be found in previous papers [3,4].

The HRMS experiments were performed on an Autospec Ultima (Micromass, Manchester, United Kingdom). The HRMS was connected by a heated transfer line (275°C) to a Agilent 6890 Series (Palo Alto, CA, USA) gas chromatograph equipped with a A200SE autosampler (CTC Analytics AG, Zwingen, Zwitzerland).

The PTV-LVI-GC/MS/MS experiments were performed on a Finnigan PolarisQ ion trap held at 250°C (Austin, Tx, USA). The ion trap was connected by a heated transfer line (300°C) to a Thermoquest Trace GC 2000 (Milan, Italy) gas chromatograph equipped with a Combi Pal autosampler (CTC Analytics AG, Zwingen, Zwitzerland). The column was directly connected to a Programmed Temperature Vaporiser (PTV) injector. 10 µl of the final extract in toluene was introduced in solvent split mode into a 2 mm ID liner filled with silica wool.

The columns used were a Rtx-5MS 40 m with an internal diameter 0.18 mm and a stationary phase thickness of 0.18 µm (Restek corporation, Every, France) for both MS/MS and HRMS.

Table 1. Description of the different instruments used for the comparison between LRMS and HRMS

	France (Rennes/Nantes)		Belgique (Liège)	
	LRMS	HRMS	LRMS	HRMS
Mass	QIT GCQ	JMS 700D	QIT PolarisQ	Autospec
Ionisation	EI at 70 eV	EI at 38eV	EI at 70 eV	EI at 35 eV
Mode	MS/MS with MRM	SIM	MS/MS with MRM	SIM
Resolution	/	at least 10 000	/	10 000

Results and Discussion

The results obtained with QIT-MS/MS and HRMS on municipal incinerator samples are presented in table 2. The results, expressed on total concentration of PCDD/Fs are similar since the differences are between 3 and 20 %. In contrast, the differences in the TEQ results are more important and varied from 21 to 49 % since the quantification of some most toxic compounds give different results as shown in Figure 1. The higher differences (40 and 49 %) are obtained for samples that contain PCDD/F at very low concentrations which correspond to the limits of detection of the QIT-MS/MS used in Rennes.

Table 2. Comparison of MS/MS and HRMS on municipal incinerator samples

	Stack gas (pg/extract)	Fly ash A (pg/g)	Fly ash B (pg/g)	Slag A (pg/g)	Slag B (pg/g)
ΣPCDD/Fs	n=3	n=3	n=3	n=3	n=3
MS/MS	28 297	23 576	661 123	102,9	358,8
HRMS	23 990	22 910	691 950	95,0	448,9
Error (%)	15	3	4	8	20
TEQ Results					
MS/MS	3 070	1 230	10 700	5,46	43,02
HRMS	2 400	970	8 200	3,27	22,00
Error (%)	22	21	23	40	49

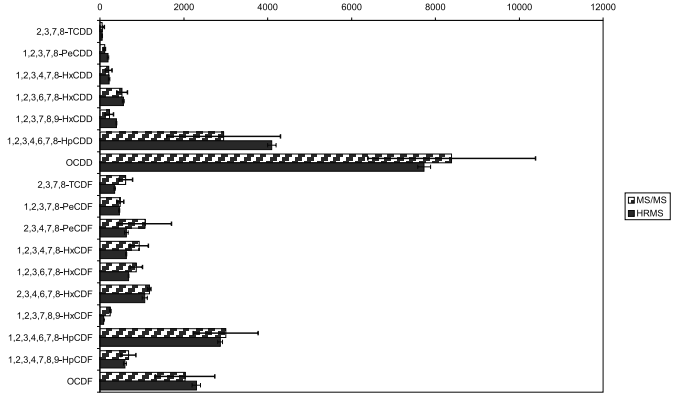

Figure 1. MS/MS and HRMS results for fly ash A

PTV-LVI-GC/MS/MS and Splitless-GC/HRMS were compared by performing analysis on five different matrices covering a concentration range of two orders of magnitude. The results are presented in table 3. The results, expressed on total concentration and on WHO-TEQ basis, show that the maximum difference is 12%. Moreover, Fisher tests pointed out that methods, interaction effects between methods and matrices effects are not significant for most of the 2,3,7,8 congeners excepted for 2,3,7,8 TCDF ; 1,2,3,4,7,8 HxCDD and 1,2,3,4,6,7,8 HpCDD.

ANALYSIS II

Table 3. Comparison of PTV-LVI-GC/MS/MS and splitless/HRMS analysis on food samples.

	Beef fat (pg/g fat)	yolk (pg/g fat)	Milk powder (pg/g powder)	Animal feed (pg/g dry matter)	Serum (pg/g serum)
ΣPCDD/Fs	n=5	n=5	n=5	n=5	n=5
MS/MS	38.0	174.6	7.7	1124	1.7
HRMS	34.6	177.9	7.9	1113	1.6
Error (%)	9	2	3	1	6
WHO-TEQ Results					
MS/MS	5.1	25.4	2.2	2.15	0.26
HRMS	4.9	25.6	2.5	2.2	0.23
Error (%)	4	1	12	2	12

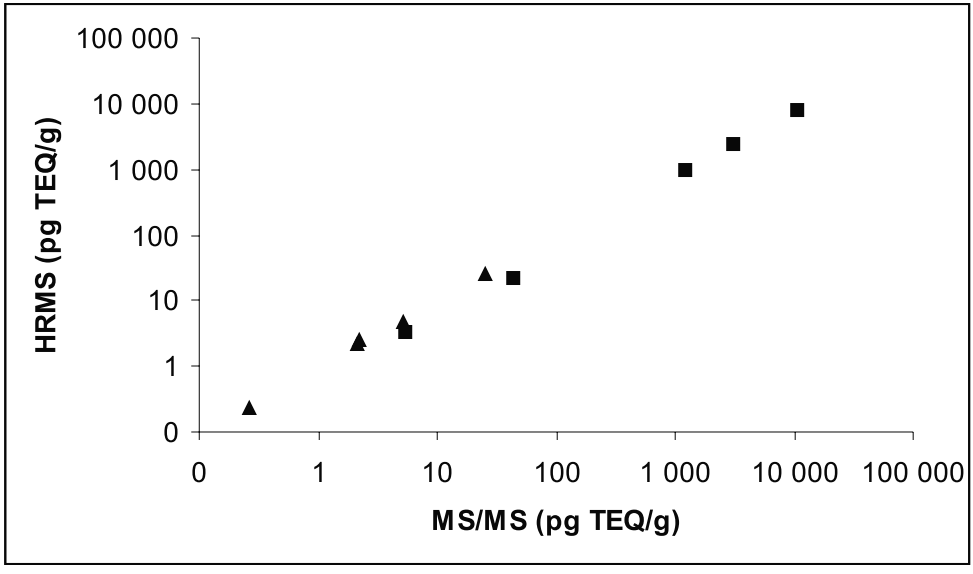

Figure 2. Correlation curve between HRMS and MS/MS results for incinerator samples (n) and food samples (5)

References

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