

DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND FURANS (PCDD/FS) IN ENVIRONMENTAL SAMPLES AND INCINERATOR ASH USING HIGH SENSITIVITY GC-MS/MS

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Introduction

The measurement of background levels of PCDD/Fs in the environment is a widespread activity carried out by many regulatory agencies globally. The chronic toxicity of these compounds to humans and wildlife at extremely low concentrations requires that the techniques used in determination must be both sensitive and selective enough to allow high confidence results. This is especially true when measuring background levels in environmental matrices, such as soil and sediment or by products from waste incineration processes.

Traditionally high resolution magnetic sector GC-MS (GC-HRMS) instrumentation has delivered the required analytical performance and has become the gold standard technique. In recent years there has been more interest in GC triple quadrupole instrumentation for this purpose, especially in the area of food safety control^{1,2}. For this and environmental analysis, it is necessary to deliver data that performs in the range of HRMS systems which means especially sensitive triple quadrupole systems are required.

Presented is the determination of PCDD/Fs in sediments, soils, bottom and fly ash (as incineration by-products) using GC-MS/MS. During this study, instrumental LOQs using GC-MS/MS were calculated in the low fg/ul concentration ranges. This and further analytical performance is discussed alongside GC-HRMS; especially degree of agreement between the techniques in some routine sample batches.

Materials and methods

Extracts from sediments, soils, incinerator fly ash and bottom ash were prepared using an in-house variation on EPA1613B method.

2µL of sample were injected in splitless mode onto a 60m x 0.25mm x 0.25µm DB5 MS GC column for PCDD/Fs separations. were performed GC-HRMS (MAT 95) and GC-MS/MS (Thermo Scientific TSQ Quantum XLS Ultra) were used to determine PCDD/Fs using isotope dilution quantitation. Detailed conditions for the SRM transitions during GC-MS/MS analysis are described elsewhere³

Results and discussion:

In order to deploy the GC-MS/MS approach to PCDD/F analysis in routine it was important to evaluate the performance limitations with respect to the required level. The approach chosen here was to perform a statistical analysis on limits of detections using increasingly diluted calibration solutions of PCDD/Fs analyzed on the triple quadrupole. Table 1 shows the calculated limits of detection of the triple quadrupole instrument as a result of diluting a EPA 1613 CS1 calibration solutions and running repeated injections (n=10).

The data suggested the GC-MS/MS sensitivity was not a limitation and was well within the range to be applicable for routine analysis of samples to the required levels; when compared to currently used methodologies.

Table 1 LOD of GC-MS/MS technique calculated at 99% confidence limits (n=10, except ^a were n =21) at differing dilution levels of CS1 (EPA1613). Also a comparison with HRMS data based on a CS1 precision test (n=5).

GC-HRMS	TSQ Quantum XLS Ultra GC-MS/MS						
LOD pg/μL	LOD pg/μL						
CS1	CS1 ^a	CS1 x 2	CS1 x 4	CS1 x 5	CS1 x 6	CS1 x 8	CS1 x 10
0.19	0.06	0.07	0.02	0.02	0.02	0.01	0.01
0.07	0.06	0.05	0.03	0.01	0.01	0.01	0.01
0.25	0.13	0.13	0.11	0.09	0.06	0.05	0.03
0.19	0.15	0.23	0.14	0.06	0.04	0.04	0.03
0.63	0.17	0.19	0.15	0.06	0.07	0.06	0.05
0.29	0.10	0.28	0.14	0.09	0.06	0.03	0.04
0.36	0.13	0.17	0.10	0.08	0.05	0.03	0.03
0.29	0.18	0.18	0.10	0.07	0.06	0.04	0.02
0.43	0.12	0.10	0.15	0.06	0.06	0.06	0.04
0.28	0.15	0.15	0.12	0.08	0.06	0.05	0.03
0.38	0.25	0.20	0.13	0.10	0.08	0.03	0.03
0.42	0.13	0.16	0.12	0.07	0.04	0.04	0.03
0.47	0.15	0.16	0.13	0.08	0.02	0.04	0.03
0.45	0.20	0.19	0.09	0.10	0.04	0.05	0.04
0.29	0.15	0.23	0.11	0.08	0.05	0.04	0.03
0.94	0.24	0.47	0.21	0.09	0.12	0.08	0.09
0.89	0.42	0.38	0.20	0.14	0.11	0.10	0.05

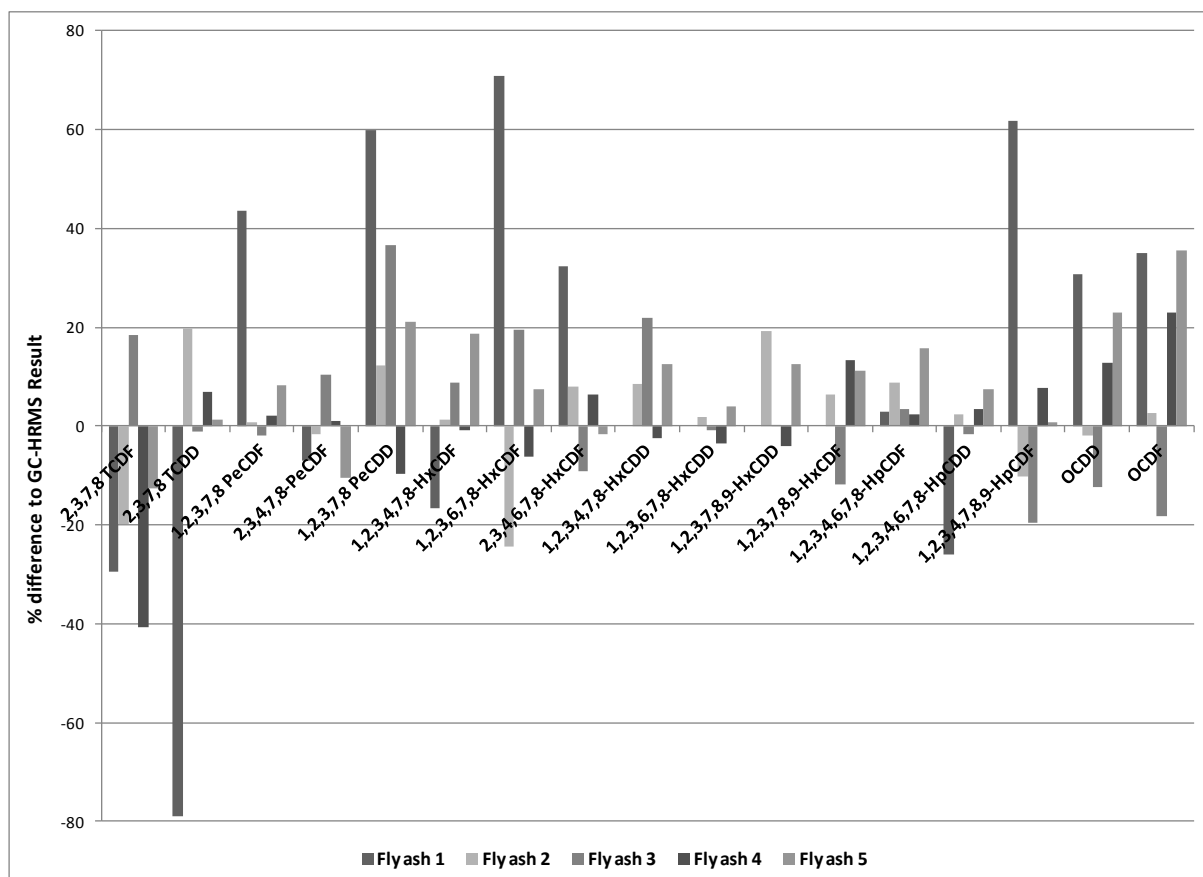
During this study, two routine batches of samples containing sediments, soils and fly ash samples were ran on a routinely used GC-HRMS system and repeated on the GC-MS/MS system to observe any differences in the calculated amounts that could appear due to differences in selectivity between the two techniques. Figure 1 shows the % difference in calculated GC-MS/MS result compared with the GC-HRMS result on a congener basis for five different fly ash samples.

The data obtained was only compared on single analysis of each batch and gives a first look to the selectivity differences between to the two methods of analysis; a more complete statistically vigorous follow up is necessary to understand the influence of measurement variation . The elevated concentrations typical with this sample type suggest that precision upon GC-MS measurement should not be a large source of error in the comparison. Although incinerator ash samples provides large opportunity for widespread interference the level of agreement (within 20%) between the calculated results on a congener by congener basis was generally good with >75% of results reported.

A number of negative deviations in calculated amount on the GC triple quadrupole were observed for 2,3,7,8-TCDF for most of the samples tested. The concentration of 2,3,7,8-TCDF recorded in these samples ranged from 6-237 ng/kg. This deviation could be due to interferences still remaining when using a high mass resolution separation rather than a structurally based MS/MS separation of co-eluting components. In contrast,

for some PCDD/Fs there is an elevated concentration reported using the MS/MS approach suggesting that a higher mass resolution separation may be necessary in this case.

Figure 1 The % difference of GC-MS/MS in calculated results compared to GC-HRMS for dioxin congeners in five different routine fly ash samples.



Another comparison was made on a routine soil and sediment sample as part of a regular batch in the laboratory. Presented in Table 2 in the actual values calculated on a congener basis using both the GC-HRMS and GC-MS/MS approach. The values obtained for GC-MS/MS showed a good level of agreement in the lower range of concentrations required for routine analysis of background environmental levels. This was confirmed with the level of compliance with the routine CRM QC sample ran with the batch. In the soil sample tested, the GC-MS/MS technique enabled ion ratio confirmed detection when the GC-HRMS system report a non-detect (ND). This is likely due to the relative sensitivities of the instrumentation (in this study) as selectivity problems were not suspected.

Table 2 The difference of GC-MS/MS in calculated results compared to GC-HRMS for dioxin congeners in a soil, and multiple sediment samples including a certified reference sediment sample.

Soil		Sediment 1		Sediment 2		SETOC 738 (CRM)	
GC-MS/MS	GC-HRMS	GC-MS/MS	GC-HRMS	GC-MS/MS	GC-HRMS	GC-MS/MS	GC-HRMS
ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg	ng/kg
0.992	1.23	16.0	10.4	2.15	1.51	17.9	17.1
ND	ND	1.85	2.29	2.03	5.10	23.1	23.9
1.26	<1.79	25.4	25.4	4.90	4.52	7.36	6.76
1.57	1.96	41.5	44.2	10.7	9.29	47.8	45.4
0.436	ND	5.49	5.71	9.14	7.95	7.26	6.91
1.89	1.89	56.1	57.3	64.8	71.9	43.8	45.1
1.81	2.14	64.8	55.0	223	197	15.1	14.7
2.53	2.83	86.9	91.5	9.47	11.5	20.2	18.4
0.271	ND	5.38	6.34	15.0	10.9	10.4	8.62
0.382	0.905	8.33	8.58	17.6	16.7	28.1	20.1
0.469	ND	6.62	6.97	17.5	14.0	21.4	22.4
0.932	ND	25.8	31.4	15.2	13.4	4.65	5.40
12.9	14.2	464	473	5.05	4.58	214	202
4.80	5.78	63.4	62.2	18.3	16.6	416	433
1.90	3.07	48.8	48.8	68.3	54.4	15.1	15.4
24.7	23.8	153	191	6.38	5.38	3020	3030
258	291	475	554	47.7	39.5	290	316

Further work will focus on rationalizing the selectivity differences of the two techniques with a statistical approach and method validation in a wide range of matrices. In addition, the alternative selectivity mechanism offered with the MS/MS approach will be explored with respect to looking to bring method efficiencies into the routine PCDD/Fs methods.

References:

1. Ingelido AM, Brambilla G, Abballe A, di Domenico, Fulgenzi AR, Iacovela N, Lamiceli L, Valentini S, De Felip (2012); Rapid Communications in Mass Spectrometry Vol 26, Issue 3, pg 236-242
2. Kotz A1, Malisch R, Wahl K, Bitomsky N, Adamovic K, Gerteisen I, Leswal S, Schächtele J, Tritschler R, Winterhalter H (2011); Organohalogen Compounds Vol. 73, 688-691
3. Silcock P, Krumwiede D, de Dobbeleer I, Huebschmann HJ, Kotz A (2011); Thermo Scientific Application Note 52266