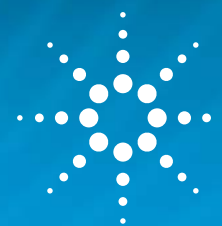# ENVIRONMENTAL ANALYSIS

A COMPARISON OF GC/MS-MS USING THE AGILENT 7000 GC-QQQ AND GC/HRMS FOR THE TRACE LEVEL ANALYSIS OF DIOXINS IN ENVIRONMENTAL SAMPLES

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SOLUTION NOTE

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ABSTRACT

A method for the determination of polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF) congeners at trace levels in environmental air and soil samples has been developed on the Agilent 7000 Triple Quadrupole GC/MS. Results indicate good agreement with the conventional GC/HRMS technique for the analysis of soil and waste incinerator stack emission samples. Based on the data obtained, there is evidence that GC/MS-MS methods can be used as screening techniques for the analysis of PCDDs and PCDFs in environmental samples.

INTRODUCTION

The determination of PCDD/Fs in environmental samples is complex and requires highly sensitive and selective instrumentation. Currently gas-chromatography coupled to high resolution mass spectrometry (GC/HRMS) is prescribed by conventional standard methods and is the reference technique for accurate and specific PCDD/F determination as described in US EPA Method 1613 (1). The current low resolution MS method, EPA 8280, allows for the analysis of PCDD/Fs in soil, sludge etc. at part-per-billion concentrations, levels that are not in the range of environmental samples. Regulations for soil, for example, are in the part-per-trillion concentrations levels. Recent studies have reported the achievement of comparable results by GC/MS-MS and GC/HRMS in food and feed samples, suggesting a potential for their application in this analysis (2, 3). The aim of this work is to provide a critical comparison between GC/MS-MS and the official GC/HRMS approach in the determination of PCDD/Fs in low-level environmental samples. For this purpose, the PCDD/F content of 22 soil samples and 5 waste incinerator stack emission samples were determined by both GC/MS-MS and GC/HRMS and the results were assessed.

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ANALYTICAL TECHNIQUE

SAMPLE PREPARATION

Approximately 10-30 g of soil samples were dried and spiked with $^{13}C_{12}$-labelled surrogate 2,3,7,8 PCDD/F congener standards, extracted with organic solvents, and purified following EPA Method 1613. Stack emission samples were sampled and purified following the EN 1948 method. Purified samples were analysed by GC/MS-MS and GC/HRMS. Quantification of each analyte was carried out using the isotopic dilution method. The limit of detection (LOD) was calculated individually for each sample on the basis of a signal-to-noise ratio of 3:1. Concentrations were expressed as toxicity equivalents (TEQs) in terms of pg TEQ/g, calculated by multiplying the detected concentration by the corresponding toxic equivalent factors (TEFs) (4). For the TEQ calculations, concentrations below the LOD were considered as half the LOD (middle bound method).

INSTRUMENTATION

GC/MS-MS: Agilent 7000 Triple Quadrupole Mass Spectrometer interfaced to an Agilent 7890 GC in EI+ mode using MRM acquisition method. Source and transfer line temperatures were set at 280°C. GC/HRMS: Measurements were performed using a high resolution method, according to US EPA Method 1613 and EN 1948, operating in EI+ mode, at a resolving power > 10,000. The analysis was performed in SIM mode and the monitored ions were M+ and M+2 for tetra-CDD/Fs and M+2 and M+4 for penta-, hexa-, hepta- and octa-CDDs/Fs. Chromatographic separation was performed using a 60 m x 0.25 mm x 0.25 μm 5 % phenyl polysilphenylene-siloxane capillary column, with splitless injection. The oven temperature program was: 160°C (1 min), 2.5°C/min to 300°C (6 min).

RESULTS AND DISCUSSION

Instrumental sensitivity was checked with an original standard, injecting 2 uL of a solution containing 50 fg of tetra-, 250 fg of penta-, hexa- hepta- and 5000 fg of octa-CDD/Fs. Results, as shown in the chromatogram in Figure 1, show a >>3:1 S/N for all congener peaks at these concentrations levels.
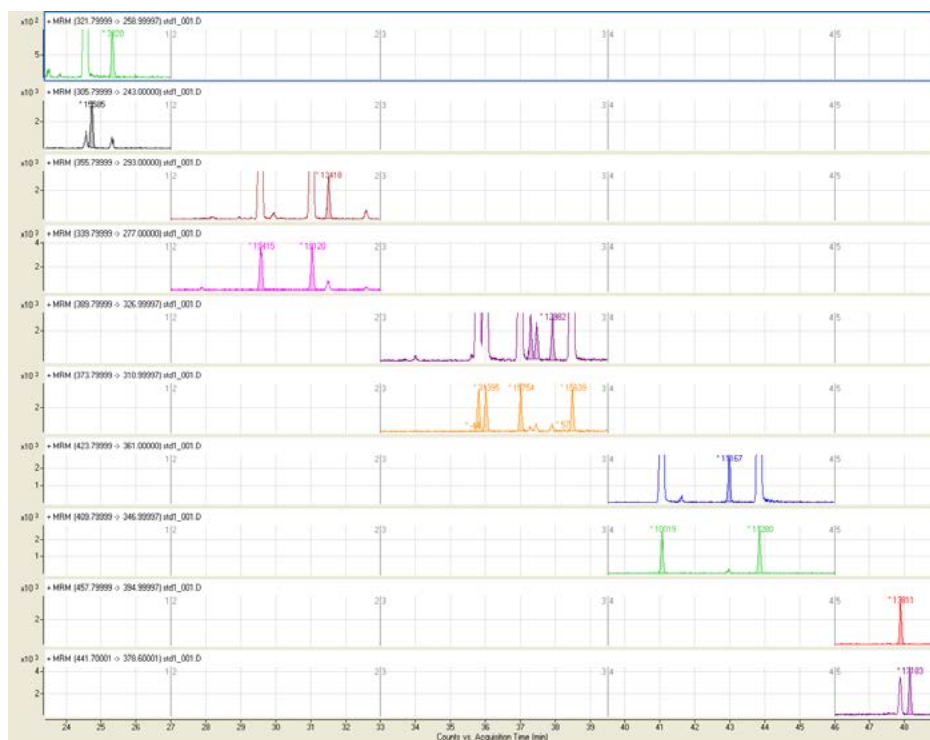

Figure 1: PCDD/F Standard Chromatogram. Standard concentrations range from 50 fg/uL to 5000 fg/uL, 2 uL injection.

The selectivity provided by the GC/MS-MS technique was comparable to that provided by the high resolution instrument. For example, the mass chromatograms of hexachlorodibenzodioxin congeners in an urban air sample, analysed by both GC/MS-MS and GC/HRMS, are shown in Figure 2. This sample has a 46 fg/m^3 TEQ concentration and represents a middle to low level urban environmental sample (5). The same congener peaks are clearly detectable by both approaches, with similar relative intensity, indicating similar specificity for environmental air sample analysis.
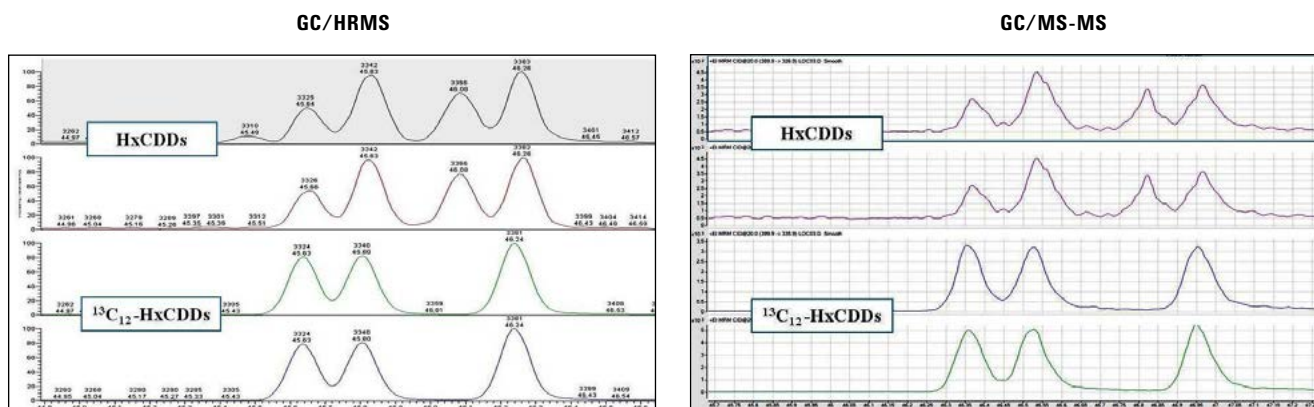
GC/HRMS   GC/MS-MS

Figure 2: Analysis of a low-level urban air sample (46 fg/m^3 TEQ concentration) by GC/HRMS and GC/MS-MS.

In Table 1, the PCDD/F TEQ values for the 22 soil samples, obtained by both GC/MS-MS and GC/HRMS, are reported. The PCDD/F soil concentrations range from 0.33 to 14.11 pg WHO-TEQ/g. Only one sample exceeds the limit of 10 pg WHO-TEQ/g (adopted in Italy for soils that have green and residential uses), while none exceed the threshold for commercial and industrial soils (100 pg WHO-TEQ g^{-1}) (6), indicating low contamination levels. It should be noted that most of the GC/MS-MS TEQ values are slightly higher than those produced by GC/HRMS. This is in part due to the higher GC/MS-MS LODs, resulting in higher middle bound TEQs.

PCDD/F TEQ values			
Sample	GC/HRMS - pgWHO-TEQ/g	GC/MS-MS - pgWHO-TEQ/g	|±Δ%|
1	0.33	0.56	69.70
2	0.51	0.53	3.92
3	0.52	0.93	78.85
4	0.54	1.13	109.26
5	0.58	0.74	27.59
6	0.60	0.61	1.67
7	0.62	0.78	25.81
8	0.65	1.29	98.46
9	0.67	1.48	120.90
10	0.70	0.89	27.14
11	0.91	2.12	132.97
12	0.99	1.35	36.36
13	1.24	0.85	31.45
14	1.29	1.54	19.38
15	1.75	1.98	13.14
16	1.96	1.48	24.49
17	2.17	2.34	7.83
18	2.43	1.48	39.09
19	2.77	2.77	0.00
20	2.85	2.94	3.16
21	5.76	5.37	6.77
22	14.10	14.11	0.07

Table 1. PCDD/F TEQ values obtained by GC/HRMS and GC/MS-MS methods and relative differences |±Δ%|.

Figure 3 reports the correlation between PCDD/F soil concentrations (expressed as WHO-TEQ) obtained by GC/MS-MS and GC/HRMS. Despite the low PCDD/F concentrations, the results obtained are in a good agreement, showing an overall correlation (expressed as R squared coefficient of correlation, R^2) of around 0.97.
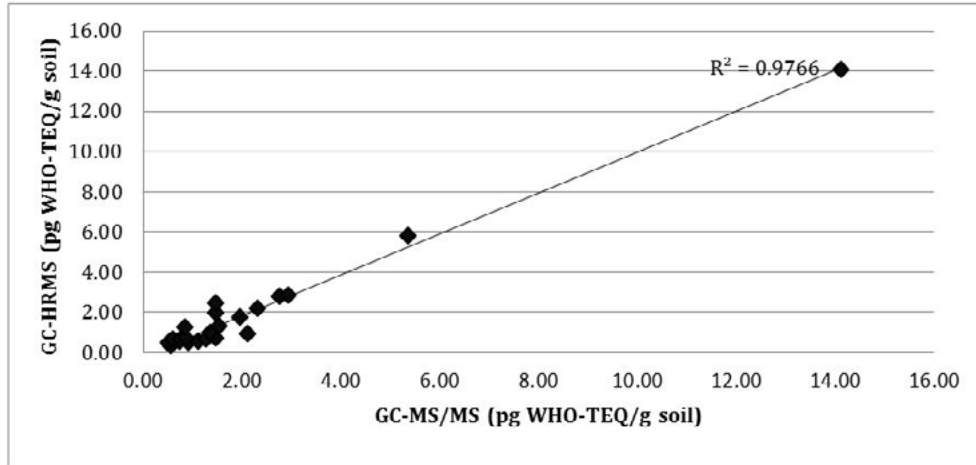

Figure 3. Correlation between PCDD/F soil concentrations (expressed as WHO-TEQ), obtained by GC/MS-MS and GC/HRMS

The same findings were also achieved when the correlation between GC/MS-MS and GC/HRMS PCDD/F individual congener concentrations were assessed. Figure 4 shows a good correlation coefficient, R^2 of 0.99, with the linear correlation being maintained over 6 orders of magnitude. The residential soil total TEQ limit in Italy is 10 pg/g. The level of uncertainty increases below this value, to approximately one order of magnitude (maximum).
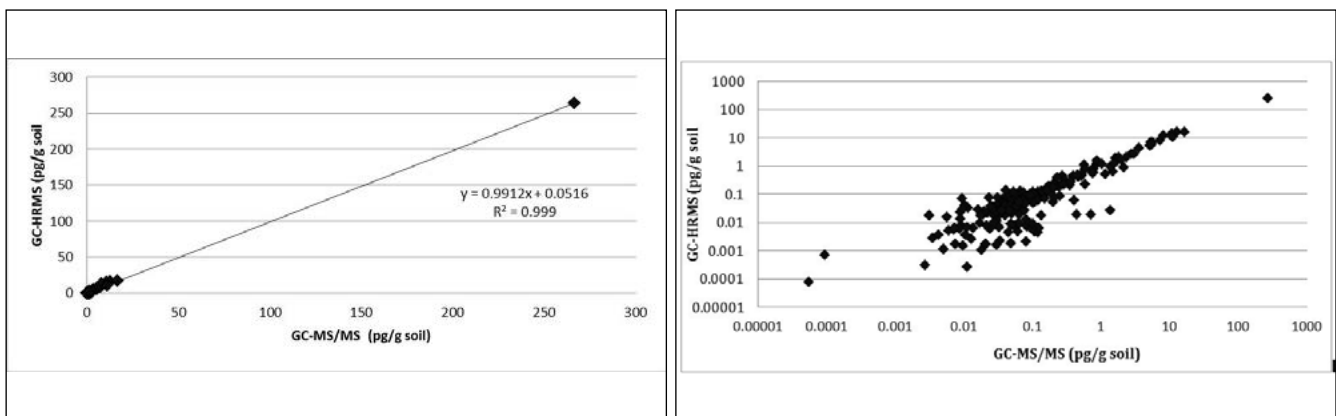

Figure 4. Correlation between PCDD/F individual congener soil concentrations, expressed as WHO-TEQ, obtained by GC/MS-MS and GC/HRMS on a linear scale (upper) and logarithmic scale (lower).

This agreement, as shown in Figure 5, is concentration dependent. The relative difference, expressed as $|\pm\Delta\%|$, between the two measurements in soil samples with lower PCDD/F concentrations (<1 pg WHO-TEQ/g) was 61%. At PCDD/F concentrations higher than 1 pg WHO-TEQ/g, the average relative difference is as low as 4 %, suggesting that in this range the Agilent 7000 Triple Quadrupole GC/MS is capable of quantitatively determining PCDD/Fs in environmental soil samples. This offers a realistic alternative approach to the classical GC/HRMS method, at least as a screening method, like the mentioned EC Regulations 1883/2006, 152/2009 and 252/2012 for the determination of PCDD/Fs in certain foodstuffs and feed samples.
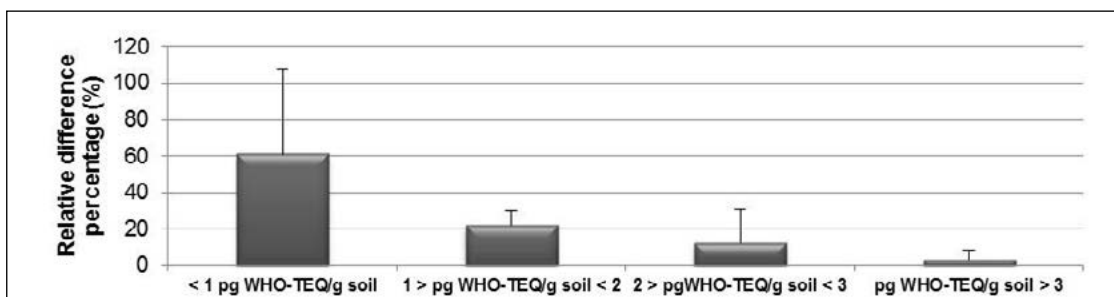

Figure 5. Relative difference percentage (%) between the GC/MS-MS and GC/HRMS methods, at different PCDD/Fs concentration ranges.

In Figure 6, the correlation between the PCDD/F ambient air and air emissions from a municipal solid waste incinerator (MSW) plant, obtained by GC/MS-MS and GC/HRMS, are reported. These results are for the individual congeners and are expressed as WHO-TEQ. The maximum TEQ limits set in Italy for these plants are 0.1 ng/m^3. Few outliers are observed and those that do exceed reflect an overestimation by the GC/MS-MS approach.
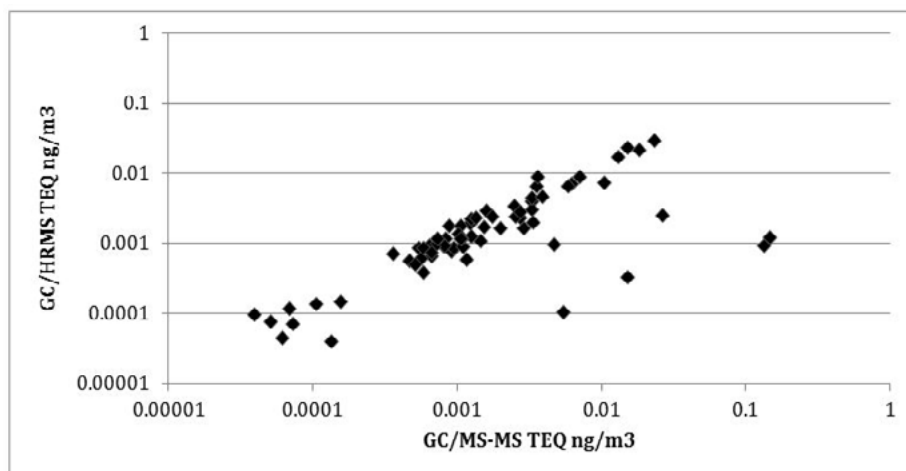

Fig. 6 Correlation between PCDD/F individual congener ambient air samples and air emission concentrations from a MSW plant, expressed as WHO-TEQ, obtained by GC/MS-MS and GC/HRMS (logarithmic scale).

CONCLUSION

The results of this study show good agreement between GC/MS-MS and GC/HRMS data for the analysis of soil samples containing at least 1 pg WHO-TEQ/g (10 times lower that residential soil levels) and MSW plant air emissions. Outliers have been observed for a limited number of congeners in the air emission samples but these results were never underestimated. Based on the data obtained, there is evidence to suggest that GC/MS-MS methods can be used as screening techniques for PCDDs and PCDFs in environmental samples. As is the case with food and feed dioxin analysis, this could enable a larger number of analytical laboratories the ability to screen air emissions and environmental samples for PCDDs and PCDFs.

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