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A single injection screening method for tetra-octa chlorinated PCDD/Fs in fish and flyash matrices using GC-Triple Quadrupole MS/MS

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Introduction

Confirmatory dioxin/furan analysis using high resolution gas chromatography – high resolution mass spectrometry (HRGC-HRMS) is an expensive and time consuming analysis, requiring highly trained instrument operators. The use of a screening method prior to confirmatory analysis can greatly reduce the workload of a HRGC-HRMS laboratory by highlighting samples that are either non-detect, or have concentrations at extremely high levels that may full outside the quantifiable range of the HRGC-HRMS method.

There are many PCDD/F screening methods currently available, using technologies such as bioassays or GC-MS/MS. Bio assays have the possibility of giving false positives and do not give a full idea of the profiles of PCDD/Fs that are present in a sample. Some GC-MS/MS methods require multiple injections to acquire toxic and non-toxic PCDD/Fs, or use function switching[1, 2,3,4], that ensures that all of the toxic 2,3,7,8-chlorinated PCDD/Fs are detected, but at the expense of some of the non-toxic PCDD/Fs (non-2,3,7,8-chlorinated PCDD/Fs).

The aim of this paper was to develop a rapid screening method, allowing the acquisition of all non-toxic and toxic PCDD/Fs in a single injection. The use of GC triple Quadrupole MS produces a method that is much easier to utilize when compared with standard HRGC-HRMS methods, with instrumental set up being much easier, and not requiring such highly trained instrument operators.

Methods and Materials

All GC-MS/MS analysis was performed using a Waters Quattro Micro GC triple Quadrupole mass spectrometer, directly interfaced to an Agilent 6890N GC oven, incorporating a CTC-PAL autosampler. Confirmatory comparison analysis was performed using a Waters AutoSpec Ultima double focussing magnetic sector mass spectrometer, directly interfaced to an Agilent 6890N GC oven, incorporating a CTC-PAL autosampler. All data acquisition and processing was performed using MassLynx version 4.0 and QuanLynx software.

The laboratory acquired two certified reference materials (CRMs), a flyash (Commission of the European Communities, Community Bureau of Reference – BCR, Reference material number 490) and Carp (National Research Council Canada, CARP-2). All standards were purchased from Cambridge Isotope Laboratories and Wellington Laboratories.

The two CRMs were extracted using methods based upon USEPA method 1613[5] to give a number of extracts in n-nonane. Two clean-up methods were employed, a standard method that is used routinely for the clean-up of samples to be analysed by HRGC-HRMS, and a reduced, single column clean-up, without $^{13}C_{12}$-labelled internal for assessment of samples by MS/MS.

A J&W DB5-ms 40m 180µm ID 0.18µm film GC column, using 1µL splitless injection was used for all analysis.

The GC temperature ramp 140°C for 3mins, 10.6°C/min to 220°C, 1.8°C/min to 260°C, 5.3°C/min to 310°C, hold 5mins was used for all injections with a He flow of 0.7ml/min.

For the GC-MS/MS analysis a five function multiple reaction monitoring (MRM) acquisition system was used monitor the two most abundant transitions from the molecular ion clusters for native and $^{13}C_{12}$-labelled dioxins and furans, with each function representing a single level of chlorination from tetra through to octa chlorinated. The setting of the time windows for this method would be performed in a similar manner to the HRGC-HRMS analysis.
For the HRGC-HRMS comparative analysis, a five function voltage selected ion recording (VSIR) experiment was acquired at a resolution of greater than 10,000 (5% height, 10% valley definition). The experiment was taken directly from USEPA method 1613[5].

Results and Discussion

All toxic and non-toxic PCDD/Fs, with the exception of 1,2,8,9-TCDF could be detected by the method. 1,2,8,9-TCDF is the last eluting tetra-furan using a DB5-ms column, and elutes just after 1,3,4,6,8-PeCDF, the first eluting penta-furan. The experiments were set up such that the acquisition switched from function 1 (tetra-chlorinated PCDD/Fs) to function 2 (penta-chlorinated PCDD/Fs) just before the elution of 1,3,4,6,8-PeCDF.
The labeled and fully cleaned up extracts were injected onto both the Quattro Micro GC and the AutoSpec Ultima and were processed using the QuanLynx quantification package.
The method can be utilized in either of two ways, firstly, samples can be processed through the single column reduced clean-up, and analysed as a semi-quantitative screen, to assess the possible levels of PCDD/Fs present in a sample of interest. This approach can be beneficial for the pre-screening of samples before they are prepared for HRGC-HRMS analysis, especially in the case of samples of industrial origin, that dependant upon the process of origin, may have extremely high levels of PCDD/F contamination present.
Secondly, if the samples are extracted and cleaned up using the full clean-up method, with labeled internal standards present, they can be screened using the GC-MS/MS method, with quantitative values determinable for the levels detected, with an absolute detection limit of <500fg. If samples prove positive from this analysis, the extract is then ready for immediate confirmatory analysis by an accredited HRGC-HRMS method with no extra treatment required.
For samples with PCDD/Fs present at below the detection limit of the method, it would be recommended that 10% of these samples are submitted for HRGC-HRMS analysis, to confirm the results of the screening, and provide further method validation information.

The results of the analysis of the two CRM extracts, following the full clean-up process using labeled internal standards were found to be within acceptable laboratory limits of the true values presented in table 1. These results were confirmed by HRGC-HRMS analysis, with no extra treatment of the sample required.

Table 1 gives the certified concentrations (with the producers uncertainties) for the two CRMs that were analysed.

Table 1

	CARP 2		CRM490 Flyash	
congener	ng/kg	+/-	ng/kg	+/-
2378-TCDF	18.2	1.6	900	50
12378-PeCDF	5.6	0.3	1710	120
23478-PeCDF			1850	110
123478-HxCDF			2370	120
123678-HxCDF			2640	140
234678-HxCDF			2470	170
123789-HxCDF			340	50
1234678-HpCDF				
1234789-HpCDF				
OCDF				
2378-TCDD	7.4	0.7	169	12
12378-PeCDD	5.3	1.3	670	40
123478-HxCDD	1.6	0.3	950	110
123678-HxCDD	5.8	0.8	4800	400
123789-HxCDD	0.78	0.12	2840	170
1234678-HpCDD	6.4	0.9		
OCDD	9.4	1.7		

Conclusions

GC Triple Quadrupole mass spectrometry offers a relatively cheap screening method for dioxins and furans that does not suffer from false positives as some other methods do. The ability to screen all toxic and non-toxic PCDD/Fs in a single injection allows the analyst to detect and view the profiles of PCDD/Fs in samples. A reduced clean-up, without labelled internal standard spiking could also increase the throughput of any screening method, specifically for a HRGC-HRMS laboratory performing pre-analysis screening to assess the levels present in industrial samples.

References

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