PCDD/Fs METHOD DETECTION LIMIT BY HRGC/LRMS/MS

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Abstract

Details of the analytical methodology to determine Method Detection Limit (MDL) for PCDD/F quantification from stack gas emissions is presented. Traditional methods of extraction, clean-up by liquid-solid adsorption chromatography at atmospheric pressure, and quantification by ion trap HRGC/LRMS/MS were used. Different concepts and terminologies for detection and quantification limits abound in the chemical literature, are clarified. The study shows that MDL values with 99 % confidence ranged from 0.0082 ng for TCDD to 0.1364 ng for OCDD.

Introduction

For ultra-trace analysis, method validation requires evaluating fundamental performance characteristics. Method Detection Limit (MDL) is considered a key issue for the determination of PCDD/Fs in different matrixes[1]. Method Detection Limit depends on the sample matrix but also on the instrument[1-3]. When analyzing these two requirements, we found out that it is difficult to obtain a standard material for dioxins and furans in emission samples. Also, there are few reports about MDL for PCDD/Fs determination by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry HRGC/LRMS/MS. Currently, MDL values are based on high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS). The Method Detection Limit is defined as the minimum concentration of an analyte that can be measured and reported with 99% confidence (giving a peak with a signal-to-noise ratio of 3)[4] though other works report MDL values with 95% confidence[3]. MDL takes into account the whole analytical process and it is determined from analysis of a sample in a given matrix containing all analytes. The samples must be prepared and processed as prescribed in the analytical method[4]. For PCDD/Fs analysis this includes labelled standard addition, extraction, clean-up and HRGC/MS analysis. The procedure requires a minimum of seven replicates of a sample spiked at the appropriate concentration for the analyte of interest. Here we report on the procedure followed and the results obtained to determine MDL for the analysis of PCDD/Fs in stack gas emissions by HRGC/LRMS/MS. The global uncertainty due to sampling on stack gas emissions is very difficult to evaluate. For this reason the measurement is focused on the analytical methodology. Therefore, limits of detection are just expressed in ng.

Materials and Methods

XAD-2 resin (Supelco) was selected as a matrix for MDL experiments. 30 g of XAD-2 resin was spiked with a native PCDD/Fs solution (EPA 1613 PAR) from Wellington. The material was prepared so that the levels of PCDD/F in the final material give clearly defined peaks with a S/N ratio between three and five. Noise was determined by Varian Saturn Workstation software using baseline peak-to-valley height ratio. Seven replicates of selected concentration values were prepared. All samples were extracted with toluene. Then, extracts were rotary concentrated and clean-up was performed by liquid-solid adsorption chromatography at atmospheric pressure using glass columns filled with silica, florisil and alumina as adsorbents. Standard solution mixtures of labelled PCDD/Fs EN-1948-SS and EN-1948-ES were added during extraction and EN-1948-IS during injection from Wellington. Purified extracts were analyzed by high resolution gas chromatography coupled to ion-trap low resolution mass spectrometry (HRGC/LRMS/MS) in a CP-3800 GC equipped with an 8400 autosampler coupled to a Saturn 2000 ion-trap spectrometer and a DB-5MS column (60 m x 0.25 mm I.D., 0.25 μm film thickness). The equipment was previously calibrated with EN-1948:1996 standard solutions in nonane (CS1 to CS6, Wellington Labs., Guelph, Ontario, Canada). Quantification of PCDDs/PCDFs was performed using the isotope dilution method. Relative Response Factors (RRFs) were determined using CS1 to CS6 injections and area comparison with ^{13}C labeled internal standards. Congener identification was carried out by comparison of retention times between labeled and native compounds based on co-elusion concept. MDL was calculated using

the Student *(t-value)* statistical factor (for 99% confidence and n – 1 degrees of freedom), *MDL = (t-value)*(s)* where *(s)* is sample standard deviation. MDL is evaluated using coefficients of variation (CV) for individual PCDD/Fs. This is a measure of data variability and is calculated as the estimated standard deviation divided by the arithmetic mean of the observed values, *CV (%) = (100) * s/$\overline{x}$* . Overall, the results are satisfactory as CVs are lower than 30%[1, 5].

Results and Discussion

Table 1 presents obtained results of Method Detection Limit for each PCDD/F congener and sample coefficient of variation. In general, parameter values are within acceptability criterion (CV < 30%). Values obtained by the MDL with 99 and 95 % of confidence are low. MDL values reported for PCDD/F analysis by HRGC/HRMS in food[1] ranged from 0.005 to 0.4 ng/kg and in soils[3] from 0.0074 to 0.0223 ng/kg with 95% confidence. On the other hand, limits of detection of 0.01-0.05 ng/l were obtained in the determination of PCDD/Fs in water samples by GC/MS/MS with an ion trap[6]. In this work we found values ranging from 0.0082 ng for TCDD to 0.1364 ng for OCDD, with 99 % confidence. Higher MDL were found for more chlorinated compounds, hexa to octa. MDL was calculated since standard deviation value represents not only a reliable estimation of the minimum amount that can be distinguished from the average amount of background present, but also the variability of the background throughout a study[2]. Additionally, it is crucial to consider that the sampling time is dependent on the expected concentration of the stack gas and the detection limit and range of the analytical procedure used by each laboratory. Thus, it is very important to determine the performance of the analytical end method and decide on a suitable sampling time to achieve an adequate limit of detection.

Table 1. MDL parameter values of PCDD/F analysis in stack gas emissions.

Compuesto	% CV	MDL (ng) 99% confidence	MDL (ng) 95% confidence
2378-TCDF	21	0.0193	0.0119
2378-TCDD	10	0.0082	0.0052
2378-PCDF	18	0.0647	0.0409
23478-PCDF	19	0.0840	0.0531
12378-PCDD	14	0.0453	0.0280
123478-HxCDF	19	0.0927	0.0555
123678-HxCDF	13	0.0517	0.0327
234678-HxCDF	21	0.0858	0.0530
123789-HxCDF	25	0.1177	0.0727
123478-HxCDD	24	0.1298	0.0777
123678-HxCDD	23	0.1016	0.0628
123789-HxCDD	8	0.0397	0.0245
1234678-HpCDF	16	0.0638	0.0394
1234789-HpCDF	20	0.0643	0.0398
1234678-HpCDD	32	0.1160	0.0695
OCDD	22	0.1364	0.0843
OCDF	12	0.0863	0.0517

Analytical considerations are of primary importance to establish the precision criteria, a pre-established CV of 20% to 30% is considered as an acceptable criterion for the ability to determine dioxin congeners in different matrixes[1-3]. In spite of a relative large variation it is noticed for the HpCDD (Figure 1) around 32%, it is near the acceptability criterion. In general, the values of CV were lower in most all the cases, showing a good correlation of the data.
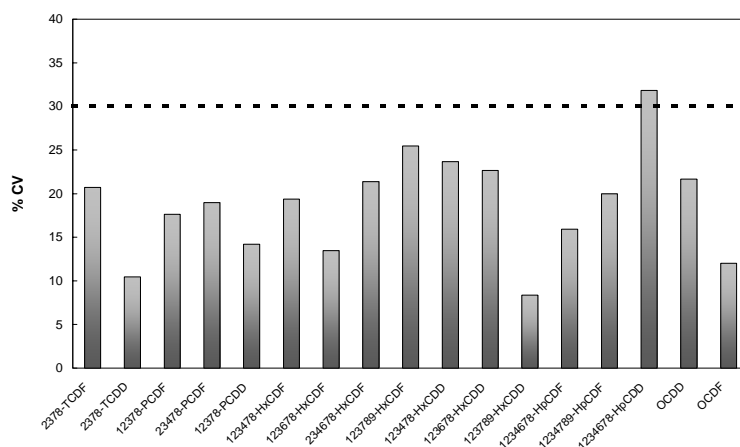
Figure 1. Coefficient of variation of PCDD/F congeners in the analyzed samples

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