Cod: 2.2008

EVALUATING A RAPID ATMOSPHERIC PRESSURE PHOTOIONIZATION - MASS SPECTROMETRY (APPI-MS) METHOD FOR THE DETECTION OF POLYCHLORINATED DIBENZODIOXINS (PCDD) AND FURANS (PCDF) IN REAL ENVIRONMENTAL SAMPLES COLLECTED WITHIN THE VICINITY OF INDUSTRIAL INCINE

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Introduction

The objective of the LIFE Dioxdetector Project is to develop new technologies enabling the continuous monitoring of polychlorinated dibenzodioxins (PCDDs) and furans (PCDFs) in the environment surrounding industrial incineration facilities. These methods may be used to evaluate pollutant dispersion and deposition, in order to assess environmental impact. PCDDs and PCDFs of course comprise a range of highly toxic compounds that may exist as particulates within the air or accumulate within water supplies, soil, or vegetation. They may be created either ubiquitously or naturally within the environment as a product of forest fires or volcanic eruptions. It is only since the industrial revolution, however, that it has become necessary to closely monitor their generation as a byproduct of manufacturing/combustion processes, in an effort to mitigate widespread contamination events. Of course, the environmental concentrations of these toxins are expected to be extremely low, therefore highly sensitive and accurate methods are required for their determination.

Here, we evaluate the performance of a novel low-flow Atmospheric Pressure Photoionization (APPI) source for the trace detection of various dioxins and furans using rapid Mass Spectrometry workflows.

Materials and method

Air, soil and biota (vegetable matter) samples were collected monthly from various locations within the vicinity of an industrial incinerator near Madrid, Spain. Soil and biota samples were prepared by soxhlet extraction in toluene and concentrated by rotavapor and nitrogen flow. Air samples were collected over a 24-hour period (700 m3 in total volume) upon both fiberglass filters and polyurethane foam (PUF). Analytes were extracted from both substrates and concentrated using the same methodology employed for the soil and biota samples.

Various ionization methods as electrospray (ES) and atmospheric pressure chemical ionization (APCI) were evaluated, however, only the low-flow APPI source was capable of providing the necessary performance, in terms of sensitivity, required for detecting all targeted analytes.

In total, 10 analytes (Table 1) including 2,3,7,8-tetrachlorodibenzodioxin (TCDD) were detected and characterized using the APPI-MS method.

Table 1. Dioxins and Furans detected and characterized in this work.

Both PCDDs and PCFDs were detected most efficiently in negative ionization mode. The most abundant ion always corresponded to the loss of a chlorine and addition of an oxygen, yielding [M-Cl+O]- ions. MRM methods were created in order to provide selectivity for each analyte. No chromatographic separation was employed; however, matrix effects were determined to have a negligible impact on analyte signals.

Triple Quadrupole Mass Spectrometry was chosen because of its unique potential for high sensitivity and selectivity. The mass spectrometer used was a Sciex´s Qtrap3200 working in negative Multi Reacting Monitoring Mode (MRM).

Figure 1 shows the schematic of the sample infusion, gasification, ionization and MS2 analysis.

Figure 1. Sample analysis diagram. Sample infusion, vaporization, ionization and MS2 analysis.

As shown the liquid sample is infused into the nebulizer using a silica capillary 50 µmOD at a 2µL/min rate. In the nebulizer the sample is vaporized at 400ºC using 99.999% N2 purity as nebulizer gas. The ceramic tube reduces substantially memory effects in the line due to surface adsorption mechanisms. In the ionization source sample vapors are ionized and effectively transmitted to the MS using electric fields. In the MS ions are declustered in the first MS vacuum stage, later the precursor ion is selected in

the first quadrupole and fragmented in the second one using N2 as collision gas. In the third quadrupole the product ion with the best signal to noise ratio is selected and transmitted to the MS ion detector.

Results and discussion
Typically mass detection limits were determined to be near the 1-pg level. As shown in Figure 2. Limit of detection in picograms for dioxins and furans with fast analysis APPI-M2 (blue, rhombuses) and with the method used for the National Dioxin Air Monitoring (red, squares), the limits of detection using the presented technology are generally lower (with one single exception) than ones obtained by NDDAMN according to EPA Method 1613 and CE N°1883/2006 .

Figure 2. Limit of detection in picograms for dioxins and furans with fast analysis APPI-M2 (blue, rhombuses) and with the method used for the National Dioxin Air Monitoring (red, squares)
The toxic equivalence (TEQ) was evaluated for each sample of PCDDs and PCDFs, over a period of three months, being analyzed at the moment the samples of the nine months remaining, of the twelve months sample period.
Therefore, we conclude that the APPI-MS2 technology applied to the detection of dioxins and furans allows fast and reliable atmospheric analysis, minimizing considerably operational times and costs, with respect other technologies available. In addition, the limit of detection can be easily improved using a more sensitive mass spectrometer since the background in the analysis cannel is very low. The APPI developed by SEADM allows polar and non polar compounds ionization with high efficiency and repeatability .
Furthermore, APPI-MS2 technology is easily transferable to any laboratory of atmospheric analysis, with the only requirement of having a triple quadrupole mass spectrometer or an IMS-TQMS for an improved signal to noise ratio.

Acknowledgements

References
1. The National Dioxin Air Monitoring Network (NDAMN) – Report of the Results of Atmospheric Measurements of Polychlorinated Dibenzo-p-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Dioxin-Like-Polychlorinated Biphenyls (PCBs) in Rural and Remote areas of the United States from June 1998 through November 2004.
2 US EPA Method 1613B – Tetra – through Octa-Chlorinated Dioxins and Furans by Isotope dilution HRGC/HRMS.
3 COMMISSION REGULATION (EC) No 1883/2006 of 19 December 2006 laying down methods of sampling and analysis for the official control of levels of dioxins and dioxin-like PCBs in certain foodstuffs

Table 1. Dioxins and Furans detected and characterized in this work.

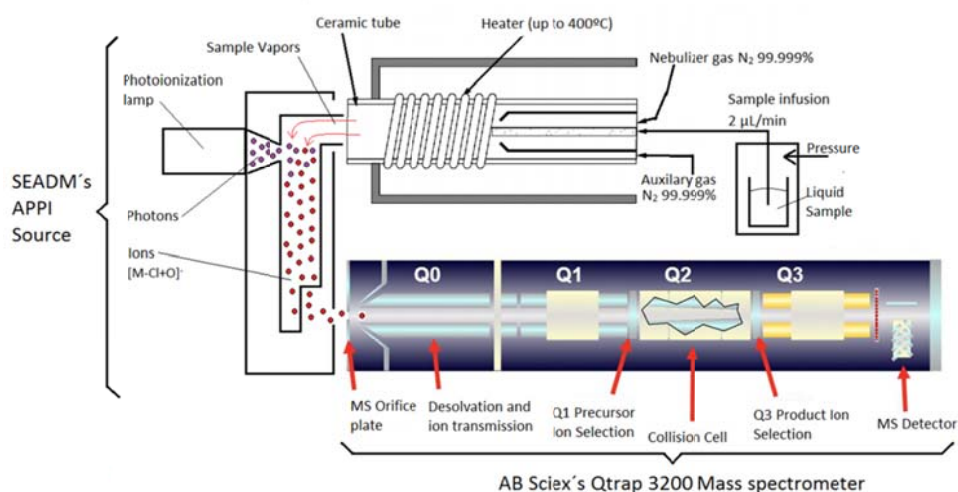|	
Tetrachorodibenzofuran	TCDF
Tetrachlorodibenzo-ρ-dioxin	TCDD
Pentachlorodibenzofuran	PeCDF
Pentachlorodibenzo-p-dioxin	PeCDD
Hexachlorodibenzofuran	HxCDF
Hexachlorodibenzo-p-dioxin	HxCDD
Heptachlorodibenzofuran	HpCDF
Heptacholorodibenzo-p-dioxin	HpCDD
Octachlorodibenzofuran	OcCDF
Octachlorodibenzo-p-dioxin	OcCDD

Figure 1. Sample analysis diagram. Sample infusion, vaporization, ionization and MS² analysis.
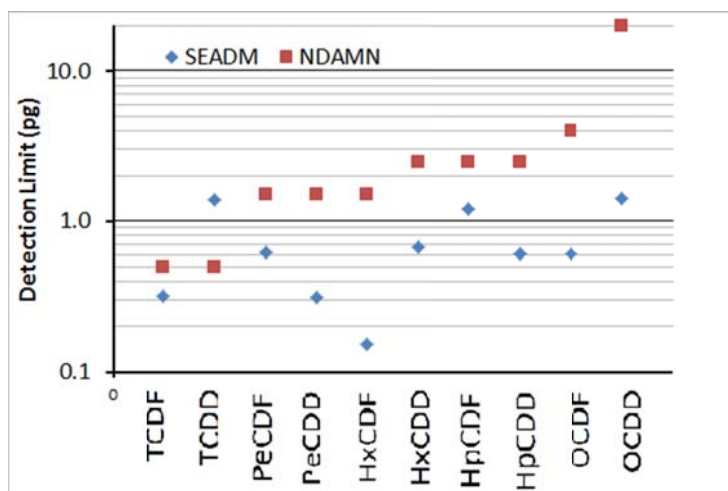
Figure 2. Limit of detection in picograms for dioxins and furans with fast analysis APPI-M^2 (blue, rhombuses) and with the method used for the National Dioxin Air Monitoring (red, squares)