

Rapid Atmospheric Pressure Photoionization-Mass Spectrometry (APPI-MS) Method for the Detection of Polychlorinated Dibenzo-P-Dioxins and Dibenzofurans in Real Environmental Samples Collected within the Vicinity of Industrial Incinerators

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Abstract : Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) 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. Since ionization of non-polar compounds through electrospray and APCI is difficult and inefficient, 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. Air, soil and biota (vegetable matter) samples were collected monthly during one year from various locations within the vicinity of an industrial incinerator in Spain. Analytes were extracted and concentrated using soxhlet extraction in toluene and concentrated by rotavapor and nitrogen flow. 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 including 2,3,7,8-tetrachlorodibenzodioxin (TCDD) were detected and characterized using the APPI-MS method. 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). Typically mass detection limits were determined to be near the 1-pg level. The APPI-MS2 technology applied to the detection of PCDD/Fs 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 channel is very low. The APPI developed by SEADM allows polar and non-polar compounds ionization with high efficiency and repeatability.

Keywords : atmospheric pressure photoionization-mass spectrometry (APPI-MS), dioxin, furan, incinerator

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