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Evaluation of the capabilities of atmospheric pressure chemical ionization source coupled to tandem mass spectrometry for the determination of dioxin-like polychlorobiphenyls in complex-matrix food samples

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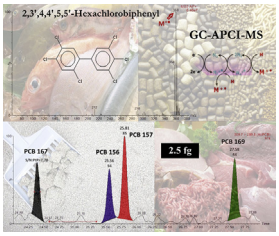
HIGHLIGHTS

- GC-(APCI)MS/MS with QqQ: a suitable alternative to GC-(EI)HRMS for DL-PCBs determination.
- LODs and LOQs as low as 0.0025 and 0.005 pg μL^{-1} respectively achieved for each DL-PCB congener.
- Enhanced sensitivity and specificity of APCI in comparison with EI source in QqQ instruments.

GRAPHICAL ABSTRACT



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ABSTRACT

The use of the novel atmospheric pressure chemical ionization (APCI) source for gas chromatography (GC) coupled to triple quadrupole using tandem mass spectrometry (MS/MS) and its potential for the simultaneous determination of the 12 dioxin-like polychlorobiphenyls (DL-PCBs) in complex food and feed matrices has been evaluated.

In first place, ionization and fragmentation behavior of DL-PCBs on the APCI source under charge transfer conditions has been studied followed by their fragmentation in the collision cell. Linearity, repeatability and sensitivity have been studied obtaining instrumental limits of detection and quantification of 0.0025 and 0.005 pg μL^{-1} (2.5 and 5 fg on column) respectively for every DL-PCB. Finally, application to real samples has been carried out and DL-PCB congeners (PCB 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189) have been detected in the different samples in the range of 0.40–10000 pg g^{-1}. GC-(APCI)MS/MS has been proved as a suitable alternative to the traditionally accepted confirmation method based on the use of high resolution mass spectrometry and other triple quadrupole tandem mass spectrometry techniques operating with electron ionization. The development of MS/MS methodologies for the analysis of dioxins and DL-PCBs is nowadays particularly important, since this technique was included as a confirmatory method in the present European Union regulations that establish the requirements for the determination of these compounds in food and feed matrices.

1. Introduction

Polychlorinated biphenyls (PCBs) belong to a broad family of anthropogenic organic chemicals known as chlorinated

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hydrocarbons. Due to their non-flammability, chemical stability and electrical insulating properties, PCBs were commonly used in the past in hundreds of industrial and commercial applications [1]. PCBs have been demonstrated to cause a variety of adverse effects on the immune, reproductive, nervous and endocrine systems of the living organisms, as well as other health effects [2]. As a result of their structure, PCBs are lipophilic and persistent, expected to be bioaccumulated (specially the coplanar ones) in the environment and biological matrices. Recently, a Working Group of the International Agency for Research on Cancer (IARC) has evaluated PCBs as carcinogenic for humans (Group 1) [3].

Among the total number of 209 PCB congeners, there are congeners that can take a planar conformation, which could confer on them toxicological properties, the same as those observed for dioxins (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs)) These PCBs congeners are called dioxin-like PCBs (DL-PCBs). Even though DL-PCBs are usually present at levels quite lower than other PCBs, they have demonstrated to be harmful to living organism at these very low levels like PCDD/Fs [4]). Consequently sensitive and selective analytical methodologies are needed, to demonstrate foods are safe. The analysis of DL-PCBs has been traditionally close related to that of dioxins. These PCBs have been assigned with toxicity equivalency factors (TEFs), taking the toxicity of the 2,3,7,8-tetraclorodibenzo-*p*-dioxin as a reference, similarly to what was previously done for all the toxic PCDD/Fs. Since 2006, maximum levels for the sum of PCDD/Fs and DL-PCBs in food and feedstuff products are listed, together with the maximum levels for PCDD/Fs in the same matrices, in the corresponding European Union (EU) regulations and directives. Furthermore, in 2002 the European Commission had already laid down methods of analysis for the official control of dioxins that also referred to the determination of DL-PCBs.

In these EU regulations and directives, confirmatory methods were based on high resolution gas chromatography coupled to high resolution mass spectrometry (GC-HRMS). The HRMS technique allowed to totally fulfill most of the basic requirements (i.e. high sensitivity and low detection limits, high selectivity and specificity and high accuracy). Alternatively, other techniques have been explored, in particular for the analysis of DL-PCBs: GCxGC-μECD [5], ECNI–LRMS (for non-ortho PCBs) [6,7] and ITMS/MS [8]. For real samples, accuracy, precision and LOQs obtained with these techniques in the analysis of food samples are in the same range (fish oil and fish), or slightly worse (milk and pork) compared to GC–HRMS results [8–10], confirming their potential for DL-PCB determination.

To complete the scenario, GC-MS/MS techniques have recently been approved as valid techniques for confirmatory methods for the determination of PCDD/Fs and DL-PCBs, according to EU Regulations No 589/2014 and 709/2014 of June 2014 [11,12]. However, specific criteria are applied to these techniques; in particular it is mandatory to monitor at least 2 specific precursor ions. Although from a theoretical point of view with ITMS/MS it is possible to monitor the product ions coming from a precursor cluster, from a practical perspective this would lead to an increment of the scan time and quite compromised sensitivity and peak shape. This would be even worse when monitoring the isotopically labelled internal standards. On the contrary, mass spectrometry instruments with a triple quadrupole configuration (QqQ) can perform multiple reaction monitoring, allowing to acquire various specific transitions (with different precursor ions) simultaneously. In addition, other criteria has to be fulfilled both for GC-HRMS and GC-MS/MS, such as those related to the sensitivity of the method. It is important to have appropriate LOQs since most food and feed samples showed low levels of PCDD/Fs and DL-PCBs, far below the maximum established. Quantitation at around one fifth of the level of interest has to be feasible.

Regarding available sources for GC-MS/MS, electron impact ionization (EI) have been the most widely used in this field. However, EI sources usually give a considerable fragmentation of the molecules, due to the high energy transferred to them during the ionization process which could affect selectivity in some samples as a consequence of a higher matrix effect. Considering these limitations related with EI sources, it is clear that MS/MS methods with QqQ could benefit from the use of soft and universal ionization techniques able to provide more abundant molecular ions and less in-source fragmentation, thus allowing to reach higher sensitivity. Atmospheric pressure chemical ionization (APCI) source has already demonstrated its efficacy in obtaining the molecular ion (or the protonated molecule) and enhancing sensitivity in many applications, mainly coupled to HPLC [13–15] or GC-(Q)TOF [16–18]. The GC-(APCI)MS/MS coupling with QqQ has not been fully tested, but it is showing promising results in terms of sensitivity when compared to GC-(EI)MS/MS methods [19,20].

This work follows up the pioneer contribution to the analysis of polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs/PCDFs) by GC-(APCI)MSMS which proved the capabilities of this technique as a real alternative to the HRMS instruments [21]. In the present work, a method for the determination of DL-PCBs in different food and feed complex matrices has been optimized and compared with the widely accepted GC-HRMS technique.

2. Materials and methods

2.1. Chemicals and reagents

Solvents for organic trace analysis (cyclohexane, dichloromethane, *n*-hexane and toluene) were from J.T. Baker (Deventer, The Netherlands), ethanol was from Merck (Darmstadt, Germany) and nonane was purchased from Fluka Chemie (St. Gallen, Switzerland). Silica and basic alumina for clean-up and fractionation were obtained from J.T. Baker and MP Biomedicals (Eschwege, Germany), respectively. Sulfuric acid (Merck) and sodium hydroxide (Carlo Erba, Milano, Italy) were also used to prepare modified silica.

Standard solutions of ^{13}C-labelled DL-PCBs for quantification (WP-LCS) and analytical recovery of the samples (WP-ISS), as well as calibration standards (WP-CS1 to WP-CS7), were from Wellington Laboratories Inc. (Guelph, Ontario, Canada).

2.2. Samples

Nine samples archived from Proficiency Test (PT) organized by the European Union Reference Laboratory (EU-RL) for Dioxins and PCBs in Feed and Food (2 pork meat, 2 lard, 1 whole egg and 1 egg yolk powder, 1 milk powder and 1 milk fat, and 1 mineral (sepiolite) together with 3 additional samples (1 fish, 1 spiked feed and 1 milk powder) were used for the evaluation of the applicability of the developed method.

2.3. Sample preparation

Matrices with high water content (pork meat, egg, fish) were freeze-dried as a pre-treatment step. Lyophilized samples and dry samples (milk powder, feed, egg yolk powder, mineral) were then spiked with a working standard solution, containing the 12 ^{13}C-labelled DL-PCBs in nonane, and extracted in a Soxhlet for aprox. 24 h with a mixture of cyclohexane:toluene (50:50) or ethanol:toluene (70:30) (in the case of milk powder and mineral matrices). Next, extracts were concentrated in a rotary evaporator