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Triple quadrupole tandem mass spectrometry: A real alternative to high resolution magnetic sector instrument for the analysis of polychlorinated dibenzo-*p*-dioxins, furans and dioxin-like polychlorinated biphenyls

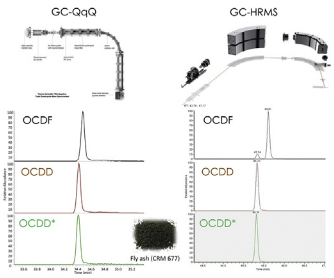
Ángel García-Bermejo [a], Manuela Ábalos [b], Jordi Sauló [b], Esteban Abad [b], María José González [a], Belén Gómara [a, *]

[a] *Department of Instrumental Analysis and Environmental Chemistry, IQOG (CSIC), Juan de la Cierva 3, 28006 Madrid, Spain*
[b] *Laboratory of Dioxins, Environmental Chemistry Department, IDÆA (CSIC), Jordi Girona 18-26, 08034 Barcelona, Spain*

HIGHLIGHTS

- GC-QqQ(MS/MS) has been validated to determine PCDD/Fs and DL-PCBs in foodstuff and environmental samples.
- GC-QqQ(MS/MS) is suitable to quantified low, medium and high concentrations of PCDD/Fs and DL-PCBs in real samples.
- GC-QqQ(MS/MS) is a real alternative to GC-HRMS for PCDD/Fs and DL-PCBs determinations.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper reports on the optimisation, characterisation, validation and applicability of gas chromatography coupled to triple quadrupole mass spectrometry in its tandem operation mode (GC-QqQ(MS/MS) for the quantification of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs, dioxins) and dioxin-like polychlorinated biphenyls (DL-PCBs) in environmental and food matrices. MS/MS parameters were selected to achieve the high sensitivity and selectivity required for the analysis of this type of compounds and samples. Good repeatability for areas (RSD = 1–10%, for PCDD/Fs and DL-PCBs) and for ion transition ratios (RSD = 0.3–10%, for PCDD/Fs, and 0.2–15%, for DL-PCBs) and low instrumental limits of detection, 0.07–0.75 pg μL^{-1} (for dioxins) and 0.05–0.63 pg μL^{-1} (for DL-PCBs), were obtained. A comparative study of the congener specific determination using both GC-QqQ(MS/MS) and gas chromatography-high resolution mass spectrometry (GC-HRMS) was also performed by analysing several fortified samples and certified reference materials (CRMs) with low (feed and foodstuffs), median (sewage sludge) and high (fly ash) toxic equivalency (TEQ) concentration levels, *i.e.* 0.60, 1.83, 72.9 and 3609 pg WHO-TEQ(PCDD/Fs) g^{-1}. The agreement between the results obtained for the total TEQs (dioxins) on GC-QqQ(MS/MS) and GC-HRMS in all the investigated samples were within the range of ±4%, and that of DL-PCBs at concentration levels of 0.84 pg WHO-TEQs (DL-PCBs) g^{-1}, in the case of feedstuffs, was 0.11%. Both

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* Corresponding author. Department of Instrumental Analysis and Environmental Chemistry, Institute of General Organic Chemistry, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain.
E-mail address: bgomara@iqog.csic.es (B. Gómara).

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instrumental methods have similar and comparable linearity, precision and accuracy. The GC-QqQ(MS/MS) sensitivity, lower than that of GC-HRMS, is good enough (iLODs in the down to low pg levels) to detect the normal concentrations of these compounds in food and environmental samples. These results make GC-QqQ(MS/MS) suitable for the quantitative analysis of dioxins and DL-PCBs and a real alternative tool to the reference sector HRMS instruments.

1. Introduction

Polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs, “dioxins”) and dioxin-like polychlorinated biphenyls (DL-PCBs, mono-*ortho* and non-*ortho* substituted congeners) are three well-known families of toxic and persistent organic pollutants (POPs) [1], which have been included in the Stockholm convention since it was adopted in 2001, and came into force in 2004 [2], in order to protect human health and the environment. These three families are usually measured in different types of matrices during food surveillance safety programs and environmental monitoring studies.

Due to their low concentration levels in food and feedstuff samples, usually at ultra-trace levels (pg g^{-1}) [3,4], and the complexity of environmental and food samples[5], their reliable determination requires complex multistep strategies including sample extraction, clean-up steps [6,7] and highly selective and sensitive instrumental techniques under strict quality assurance/quality control (QA/QC) criteria [8,9]. Regarding sample preparation, there are abundant bibliography about different methods of extraction and clean-up, in which, the latest trends are those that include on-line coupling of all extraction and clean-up steps with a final fractionation process to obtain dioxins and DL-PCBs in two different fractions which can be analysed separately. Details in sample preparation for PCDD/F and DL-PCB analysis are available in several review articles [5–7,10,11].

For instrumental determination, the use of selective and sensitive instrumental methods is required for the suitable determination of these compounds. Since 1994, gas chromatography (GC) coupled with high resolution mass spectrometry (HRMS), based on magnetic sector instruments, as described in the United States Environmental Protection Agency (US EPA) Methods 1613 and 1668B [12,13], has long been and, still is, the most often applied. Nowadays, this technique is considered a point of reference for the accurate and specific determination of these compounds in all type of samples, providing the required selectivity and detection limits. Nevertheless the use of GC-HRMS instrumentation requires a considerable investment, since this technique is relatively expensive and, consequently, the cost of the surveillance programs (thousands of samples per year) using HRMS is quite high. For these reasons, the HRMS magnetic sector is questioned, and alternative mass spectrometric instruments are continuously under development to be more economical than HRMS but with similar reliability.

Nowadays, the technical progress and developments in the GC–MS ion sources have increased the precision and sensitivity of this technology. In addition, the selectivity was also improved using triple quadrupole (QqQ) GC–MS systems, working in its tandem operation mode (MS/MS). These have led to GC-QqQ(MS/MS) technology being permitted for use in the European Union (EU) regulation to control the maximum levels for dioxins and DL-PCBs in food and feedstuffs as a full confirmatory method [8,9]. Until now, other techniques such as GC coupled to ion trap tandem mass spectrometry (GC-IT(MS/MS) [14–17] and comprehensive two-dimensional GC (GC × GC) coupled to micro electron capture detection (μ-ECD) [18] or time-of-flight MS (ToF-MS) [19,20] have shown their possibilities for being accepted as semi-quantitative, qualitative or screening methods in the PCDD/F and DL-PCB food analysis. In this sense, new regulations concerning methods of sampling and analysis for the control of levels of dioxins and DL-PCBs in certain foodstuffs and feedstuffs [8,9] were established in 2014. In these two new regulations, the GC-QqQ(MS/MS), has been considered, for the first time, as a confirmatory method for checking compliance with the maximum level, in addition to GC-HRMS. On the other hand, the dioxin and DL-PCB analyses in environmental samples are not regulated as they are in food and feedstuff analyses, but in most of the studies related with the analyses of those compounds in environmental samples, analytical methods based on US EPA Methods 1613, and 1668B using GC-HRMS are used [21–23] and only in a few of them other alternative techniques, such as GC–MS, are employed [24].

Since 2011, the results of some working groups (including ours), showing the capability of modern GC-QqQ(MS/MS) for dioxin and DL-PCB analysis, appeared in technical and scientific bibliography. These first investigations showed very promising and preliminary results of the enormous GC-QqQ(MS/MS) potential as an alternative technique to GC-HRMS for PCDD/F and DL-PCB analysis in real samples [25–28]. After the new regulation regarding food and feedstuff samples [8,9], appeared in June 2014, some other studies have been conducted [29–31] showing that GC-QqQ(MS/MS) meets the requirements set by the new EU regulation, discussing different analytical criteria in some food and feedstuffs samples such as vegetable oil samples [30] and dry fish and feed samples [29,31]. Despite the mentioned works, investigation on the GC-QqQ(MS/MS) performances involving other types of food matrices and, especially, environmental samples are currently very scarce but necessary.

Therefore, the aim of this research is to present a fully validated method for the analysis of PCDD/Fs and DL-PCBs in fortified samples and certified reference materials (CRMs) with low (food and feedstuffs), median (sewage sludge) and high (fly ash) concentration levels using GC-QqQ(MS/MS) technique. For this purpose, the ionisation MS parameters were optimised to achieve high sensitivity and several transitions, from different precursors to product ions, were evaluated at various collision energies in order to find the optimal conditions of sensitivity and selectivity. Quality parameters (*e.g.* linearity, accuracy, sensitivity, precision and selectivity) were also established before analysing different CRMs and spiked samples to validate the methodology. The GC-QqQ(MS/MS) method was evaluated by comparing the results with those obtained by GC-HRMS and those given by the CRMs and fortified samples in order to assess the applicability of the technique for this kind of analysis.

2. Materials and methods

2.1. Reagents and standards

Dichloromethane, toluene, cyclohexane and *n*-hexane for organic trace analysis were purchased from Merck (Darmstadt, Germany).