Journal of Chromatography A, 1513 (2017) 245–249

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Short communication

Analysis of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in stack gas emissions by gas chromatography-atmospheric pressure chemical ionization-triple-quadrupole mass spectrometry

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ARTICLE INFO

Article history:
Received 9 January 2017
Received in revised form 11 July 2017
Accepted 11 July 2017
Available online 12 July 2017

Keywords:
Dioxin analysis
Stack gas emissions
EN-1948
APGC
QqQ

ABSTRACT

A gas chromatography coupled to triple-quadrupole mass spectrometry (GC-(QqQ)MS/MS) including a soft-ionization through an atmospheric pressure chemical ionization (APCI) source based method was compared with the high resolution mass spectrometry (HRMS) standard reference method EN1948, for the analysis of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) in stack gas emissions. The stack emission samples were collected, both, by manual method sampling (from 6 to 8 h) and by long-term sampling systems (sampling time of several weeks). This work presents the first comparison of GC-(QqQ)MS/MS with APCI source with the European Standard EN1948 technique for stack gas emissions. Sample concentrations ranged from 0.5 to 596 pg I-TEQ/Nm^3. Comparative results in all investigated samples showed relative errors that were within ±15%. These results make GC-(QqQ)MS/MS with APCI suitable for the quantitative analysis of dioxins in the studied samples and create a real alternative tool to the reference sector GC-HRMS instruments.

1. Introduction

The standard reference method for determination of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs) in emission samples is based on the use of high resolution gas chromatography coupled to high resolution mass spectrometry (HRGC/HRMS) operated in Electron Impact (EI) mode and fitted with magnetic sector analyzers [1]. This methodology is highly selective and sensitive; however, highly qualified infrastructure and operators are required. In recent years there has been a search for an alternative to HRGC/HRMS and different methods and techniques have been considered such as ion trap based mass spectrometers working in MS/MS mode [2,3], and time of flight based mass spectrometers [4]. Although these techniques have provided promising results, they have not yet culminated in a consistent and robust routine analysis of these pollutants.

In the last years, a new generation of triple quadrupole MS instruments revealed itself as a significant promise, especially with respect to their sensitivity. The recently revived atmospheric pressure chemical ionization (APCI) source designed for GC has allowed the coupling of a GC with last generation QqQ instruments. Additionally, this soft-ionization technique for GC has been designed to overcome the extensive fragmentation that occurs in the EI sources, making possible to select the molecular ion as a precursor ion. This characteristic improves both sensitivity and selectivity of MS/MS methods [5–9] making this technique suitable for the analysis of ultratrace persistent organic pollutants (POPs) such as PCDD/Fs and PCBs [10,11].

Recently, GC-APCI-MS/MS with QqQ has also been used to determine dioxins in different complex samples such as environmental, air and food [5]. Discrepancies in sample concentration observed in a comparison of samples analyzed by GC-APCI-MS/MS with the HRMS methodology led to relative errors lower than 7%. A QA/QC control indicated a high performance in terms of chromatographic separation, linearity, S/N ratio, and a high ion abundance ratio of selected transitions. In terms of sensitivity, GC-APCI-MS/MS was better than the traditional GC-EI-MS/MS systems and compara-

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http://dx.doi.org/10.1016/j.chroma.2017.07.039
0021-9673/

Table 1
Information of the process and the emission sample collection.

Industrial Process		Sampling system	Sampling time (d)	Gas volume (Nm^3)
Municipal Solid Waste Incineration (MSWI)	MSWI1	Long term	28	675
	MSWI2		31	748
Hazardous Waste Incineration (HWI)	HWI1		21	499
	HWI2		23	548
Cement Kiln co-incineration	CP-Co		21	521
Steel Industry	MI1	Manual	0.4	~6
	MI2		0.4	~6
Municipal Solid Waste Incineration (MSWI)	MSWI3		0.4	~6

ble to GC-(EI) HRMS for dioxin determination. After many studies exploring tandem mass spectrometry as a valid methodology for the analysis of dioxins, GC–MS/MS was recently accepted as a confirmatory method for the analysis of dioxins in feed and food in the European regulation [10]. On the contrary, only HRMS approach is accepted in the EN-1948 European Standard for the determination of PCDD/FS and PCBs in stationary gas emissions. Considering the good results obtained by GC-(QqQ)MS/MS with APCI in feed and food, it is important to evaluate this technique in the environmental field. In this work GC-APCI-MS/MS with last generation QqQ is assessed for the analysis of emissions from stationary sources and compared with the data obtained by HRGC-HRMS.

2. Materials and methods

2.1. Reagents and standards

All solvents were of organic trace analysis and were readily available as commercial products. Amberlite XAD-2 was obtained from Supelco (Supelco, Bellefonte PA, USA). Polyurethane foams (PUFs) and filters were supplied by Monitoring Systems (Monitoring Systems, Wien, Austria). Multilayer silica, basic alumina and activated carbon were obtained from FMS Inc. (FMS Inc, Boston, USA). The PCDD/Fs selected for this study were the toxic compounds, 2,3,7,8 chlorosubstituted congeners, with the toxic equivalence factor (TEF) assigned by WHO [12]. Standard solutions of PCDD/Fs (EN-1948 CSL, CS1–CS4, ES and IS) were purchased from Wellington Laboratories Inc. (Guelph, Ontario, Canada) and were used for calibration, quantification and analytical recovery calculations, following the requirements described in EN1948:2006.

2.2. Sample collection

Stack gas emission samples were collected by both manual sampling method and long-term sampling method, following the main steps reported in previous papers [13,14]. The study included five samples obtained using long-term sampling system (Cement plant with co-incineration, Municipal Solid Waste Incineration, Hazardous Waste Incineration), and three samples taken by manual method system: Metal Industries and Municipal Solid Waste Incineration (Table 1).

2.3. Sample preparation

2.3.1. Extraction and clean-up

Samples from long-term sampling systems, consisting on polyurethane foams and filters were spiked before sampling with a mixture of thirteen ^{13}C PCDD/F mixture (EN-1948-ES, Wellington Laboratories, Canada) consisting on 4000 pg for tetra to hexa substituted compounds and 8000 pg for hepta to octa-ones. For the manual method, this amount was reduced by a factor of ten. The filter was pretreated according to a previously published protocol [14]. From this point, the analysis was followed with a 50% aliquot for short-term sample extract and with a 5% aliquot for the long-term ones, as previously suggested by Rivera-Austrui et al. [13]. Finally, the extract aliquots were concentrated and reconstituted with n-hexane prior to clean-up. The cleanup steps were conducted considering short and long term sampling time [13,14]. The following steps were based on the normal routine method according to the European Standard EN-1948:2006.

2.3.2. APCI-MS/MS analysis

The chromatographic analysis were performed using an Agilent 7890A gas chromatograph (Agilent Technologies Inc., Palo Alto, CA, USA), equipped with an Agilent 7693A autosampler, coupled to a triple quadrupole mass spectrometer, Xevo TQ-S (Waters Corporation, Manchester, UK), with an APCI source. The GC separation conditions are those reported by Portolés et al. [7,8]. Mass spectrometer was operated in SRM mode, acquiring one quantification transition and one confirmation transition for both, native and ^{13}C-labelled compounds, SRM transitions used can be found in van Bavel et al. [5]. In the SRM method, automatic dwell time (values ranging from 20 to 60 ms) was applied in order to obtain at least 15 points per peak. Targetlynx (a module of MassLynx) was used to handle and process the acquired data.

2.3.3. HRGC-HRMS analysis

The HRGC-HRMS analysis met the requirements described in the European Standard EN1948 [1]. These analysis were performed on a gas chromatograph (Agilent 6890N, USA) fitted with a DB-5MS (60 m × 0.25 mm i.d. × 0.25 μm film thickness) fused silica column (J&W Scientific, Folsom, CA, USA) coupled through a heated transfer line kept at 280 °C to a high resolution mass spectrometer (Waters, AutoSpec Ultima NT) controlled by Masslynx data system and operated in SIM mode at 10,000 resolving power (10% valley definition). Quantitation was performed using the isotopic dilution method. Relative response factors were calculated for each individual analyte from six different calibration solutions for PCDD/Fs. Details of the HRGC-HRMS analysis has been previously reported by our laboratory [13,14].

3. Results and discussion

3.1. Linearity, repeatability and LODs

In order to test the reliability/analytical characteristics of the instrumental method, parameters such as linearity, repeatability, and limits of detection (LODs) were evaluated.

The linearity of the method was studied by analyzing the standard solutions (in triplicate) at six concentrations (CSL, CS0.5, CS1–CS4) ranging from 0.1 ng/mL to 40 ng/mL for the Tetra PCDD/Fs, from 0.5 to 200 ng/mL for the Penta through Hepta PCDD/Fs, and from 1.0 to 400 ng/mL for the Octa PCDD/Fs. The linearity was satisfactory, with correlation coefficients (r) > 0.9990. The relative standard deviation (RSD) of the relative response factors (RRFs), as defined in standard methods EPA 1613 or EU 1948,