



Application of low-temperature CP-Sil 88 column for the isomeric analysis of toxic 2378-substituted PCDD/Fs in incinerator flyash and sewage sludge using a triple quadrupole GC–MS/MS

Jude A. Onwudili^{a,*}, Yaghoub Hajizadeh^a, Safari Zainal^a, John Upton^b, Paul T. Williams^a

^a Energy and Resources Research Institute, University of Leeds, LS2 9JT, UK

^b Agilent Technologies (Formerly Varian), Oxford OX5 1QU, UK

ARTICLE INFO

Article history:

Received 19 May 2011

Received in revised form

16 September 2011

Accepted 27 September 2011

Available online 1 October 2011

Keywords:

Dioxins

Furans

Analysis/mass spectrometry

Flyash

Sewage sludge

ABSTRACT

The seventeen 2378-substituted polychlorinated dibenzo-p-dioxins and dibenzo-p-furans (PCDD/Fs) congeners have been separated and analyzed in sewage sludge and incinerator flyash samples using a CP-Sil 88 column (50 m × 0.25 mm I.D., 0.25 μm film thickness) operating at a maximum oven temperature of 240 °C. The column was used on a Varian 450-GC with a Varian 320-MS Triple Quadrupole. Calibration standards were used to determine the transition chemistries of the 2378-substituted PCDD/F congeners in the gas chromatography/mass spectrometry (GC–MS/MS) system. The five-point calibration curve for each of the congeners showed very good linearity with R^2 values greater than 0.999. The recovery of labelled compounds ranged from 50% to 120%. Analytical results from a reference flyash (BCR-490) and a reference sewage sludge (BCR-677) compared very well with the certified values, giving percentage deviations in I-TEQ (international toxic equivalents) of 4.93% and 0.53%, respectively. Results from 'real' flyash samples underscored the level of progress made in the abatement of dioxin emissions from incinerators; the old incinerator flyash contained much higher PCDD/F concentrations than the modern one. In addition, the concentrations profiles of PCDD/Fs in the 'real' sewage sludge from two UK wastewater treatment plants (WWTPs) showed that one contained a total PCDD/Fs content of 314 ng I-TEQ kg⁻¹, while the other gave a total of 53 ng I-TEQ kg⁻¹. Over an 18-month period of operation, no significant loss of analytical performance was observed from the low-temperature column.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Incineration of the organic fraction of municipal and industrial solid wastes and other organic-rich wastes (e.g. sewage sludge) has the advantage of efficient energy recovery from these wastes, and also leads to dramatic mass and volume reductions. Incineration has therefore become the main alternative to the landfilling of these types of wastes. Incineration of organic wastes will continue to contribute to the achievements of the targets of the EU Landfill Directive, which requires member states to drastically reduce the amount of biodegradable wastes sent to landfills [1]. However, operation of incinerators can often generate significant negative public perception with respect to the possible release or emission of incomplete combustion products to the environment. Such emissions include the highly toxic polychlorinated dibenzo-p-dioxins

(PCDD) and polychlorinated dibenzofurans (PCDF). Other sources of PCDD/Fs in the environment include releases from automobile exhausts, pulp and paper mill effluents, household washing machine effluents and the production/use of organochlorine compounds [2–4].

PCDD/Fs are a chemical group of 210 chlorinated tricyclic aromatic hydrocarbons and environmentally stable micro-pollutants, known as one of the most hazardous compounds to human health and the environment [5–7]. There are serious concerns about the high toxicity of PCDD/Fs congeners with chlorination in the 2378 positions as confirmed by studies carried out by several multi-lateral bodies such as the United States Environmental Protection Agency (USEPA), Ontario Ministry of Environment and the European Commission [8,9]. Hence in recent years, stringent regulations have been enforced to reduce the release of these and many other hazardous pollutants into the environment [10].

The required analysis of PCDD/Fs within often complex matrices poses a significant problem to the analyst. Analysis of PCDD/Fs in environmental matrices requires several steps that include extraction/isolation, clean-up and/or pre-concentration before

* Corresponding author at: School of Process, Environmental and Materials Engineering, Faculty of Engineering, University of Leeds, LS2 9JT, UK.
Tel.: +44 113 343 2353; fax: +44 113 246 7310.

E-mail address: j.a.onwudili@leeds.ac.uk (J.A. Onwudili).

measurement by gas chromatography. The high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) is the instrumental benchmark for the analyses of PCDD/Fs. However, HRGC/HRMS is very expensive and requires very skilled analysts to deliver certifiable results. Other less-costly techniques that benefit from high signal to noise ratio, may provide a cost-effective and fit-for-purpose alternative to traditional HRGC/HRMS analyses of PCDD/Fs [11]. Although, GC–MS/MS systems would result in loss of high resolution during analysis of PCDD/F in complex matrices, they can be reliably used for screening of clean non-complex matrices without the high cost associated with HRGC/HRMS systems.

The Ministry of Environment, Ontario, Canada, was the first major research group to publish the successful determination of PCDD/Fs with a gas chromatography–mass spectrometry/mass spectrometry system (GC–MS/MS) [9,12]. The authors reported that in some matrices, fewer chemical interferences were observed with GC–MS/MS than with HRGC/HRMS. Since then, the improvement in both selectivity and sensitivity of GC–MS/MS to PCDD/Fs screening has become well accepted within the scientific community [11,13].

In mass analyzers such as the HRMS, triple quadrupole and ion trap, during PCDD/F analysis various isomers, congeners and dioxin-like compounds could fragment into ions of identical mass. These interfering species could give rise to significant errors during analyte measurements. The analytical principles of the various mass analyzers are well documented. For instance, the capability of GC–MS/MS systems for PCDD/F analyses could be explained using the triple quadrupole systems as example. In the triple quadrupole MS/MS system, several ions are formed from the specific analyte in the ion source but only those selected as precursor ions, based on the developed transition chemistries of the analyte, are allowed to travel through the first quadrupole, Q1. By this filtering exercise, the precursor ions travelling through Q1 are, for example, the m/z 322 ion from 2378-TCDD and any m/z 322 ions that are due to the matrix. On entering the second quadrupole, Q2, the precursor ions are subjected to a Collision Induced Dissociation (CID) process. This is achieved by having a collision gas, typically argon, at low pressure within Q2 and applying collision energies by means of ion acceleration between a potential difference. If the collision has sufficient energy, the precursor ion may dissociate to product ions. These can then be measured by means of the third quadrupole, Q3. If the CID energies cause both the dioxin m/z 322 and the matrix m/z 322 to dissociate, the selectivity is reliant on differences in the product ions produced and monitored. Hence, by careful selection of the precursor ion, the collision energy and the product ion or ions measured by Q3, the analysis becomes very selective towards the PCDD/F

Apart from the sample preparation procedure, the chromatographic step is a key factor in successful analysis of PCDD/Fs. Dioxin-specific columns have been developed over the years to reduce the problems of co-elution of congeners, isomers and other compounds with the PCDD/Fs of interest [14–16]. Recently, Reiner [17] produced a comprehensive review of the performances of various columns employed in PCDD/Fs analyses and found that at least one case of analyte co-elution was reported on each of the columns. This is due to the large number of PCDD/F congeners and similar compounds such as PCBs, PCDEs, PBDEs and halogenated dioxins and furans [17]. High peak resolutions, stability and low column bleed appear to be the main attributes of good quality dioxin analysis as a consequence of low concentrations of analytes of interest.

The generic 5% phenyl-based columns would continue to have a dominant presence in PCDD/F analysis due to its reliability, stability and good analytical separation capacity [17]. However, the development of alternative fit-for-purpose columns may provide

immense benefits in terms of shorter analysis times, excellent resolution of peaks of interest and cheaper running costs. The choice of GC column is a balance between the resolution of the PCDD/Fs congeners and the stability of the phase in relation to temperature. As an example of this, the CP-Sil 88 column from Varian is excellent for specific PCDD/Fs separations but the upper operating temperature is limited to 240 °C isothermal [18,19]. This may cause a build up of high boiling point contamination from dirty sample types as injections progress. The build-up of contaminants would affect the performance of the CP-Sil 88 column if means of back-flush or column clean-up is not incorporated. By contrast, the more generic VF-5MS column can be operated up to a temperature of 325 °C, indicating less build-up of contaminants on the column but may have lower chromatographic separation ability for PCDD/Fs than the CP-Sil 88 column.

The HRMS remains the reference method of choice for the analysis of PCDD/Fs for regulatory and litigation purposes. Relatively cheaper mass analyzers such as the ion trap and the triple quadrupole for PCDD/F screening are now acceptable since the data generated are deemed fit-for-purpose for the sake of the measurement required [20,21]. Currently, GC with MS/MS in the form of ion trap and triple quadrupole detectors have been applied for the analysis of persistent organic pollutants (POPs) in various matrices including fruits and vegetables, food, fats and oils, flyash and other environmental samples [22,23]. The underlying benefit of triple quadrupole GC–MS/MS is that it offers a high degree of selectivity, good sensitivity and a high, non-specialist, throughput capability.

The two stages of mass analysis in triple quadrupole GC–MS/MS offers a possibility of the application of selected reaction monitoring (SRM), which is arguably one of the most selective and most sensitive techniques for the confirmation and quantification of trace analytes in environmental samples, in spite of the normally high background chemical noise [20]. Hayward [11] reported that the triple quadrupole MS/MS technique was reproducible, with little reduction in sensitivity or spectral quality during the analysis of the seventeen 2378-substituted PCDD/Fs. GC–MS/MS is also thought to offer an overall gain on total analysis time by allowing simultaneous identification and quantification [20], a feature comparable to high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) technique. The initial applications involving new generation of triple quadrupole instruments dates from 2003, when the potential of the technique was investigated for the screening of dioxins and furans in fish and flyash samples [20,24,25]. The use of triple quadrupole GC–MS/MS for the screening of dioxins and furans has been approved by the United States Environmental Protection Agency (USEPA) for the Department of Water [21].

Our research group has published several papers [26,27] involving the analyses of PCDD/Fs in flyash using the classical VF-5MS (5% phenyl column; DB-5 equivalent) fitted to GC with tandem ion trap MS/MS. This paper details the application of a recently acquired triple quadrupole GC–MS/MS for the analysis of PCDD/Fs. More importantly, a low-temperature, low-bleed dioxin-specific CP-Sil 88 column has been used in this work. This column has the capacity to specifically separate the seventeen 2378-substituted PCDD/F congeners. The aim here is to benchmark the results from this equipment, based on the automated method development (AMD) protocol followed, against certified reference samples of flyash and sewage sludge. Real samples of flyash and sewage sludge were employed in an ongoing research into the development of PCDD/Fs abatement technologies. Furthermore, the concentration profiles of the seventeen 2378-substituted PCDD/Fs four 'real' solid samples were measured using the procedure developed. The performance of the CP-Sil 88 column, triple quadrupole GC–MS/MS and the entire analytical method over an 18-month period was also evaluated.

Download English Version:

<https://daneshyari.com/en/article/7687104>

Download Persian Version:

<https://daneshyari.com/article/7687104>

[Daneshyari.com](https://daneshyari.com)