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Comprehensive two-dimensional gas chromatography time of flight mass spectrometry (GC × GC-TOFMS) for environmental forensic investigations in developing countries

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ABSTRACT

The disposal and dumping of toxic waste is a matter of growing concern in developing countries, including South Africa. Frequently these countries do not possess access to gas chromatography-high resolution mass spectrometry (GC-HRMS) for the determination of persistent organic pollutants (POPs). This publication describes an alternative approach to the investigation of toxic waste using comprehensive gas chromatography coupled to time of flight mass spectrometry (GC × GC-TOFMS). The technology permits both comprehensive screening of toxic samples for numerous classes of organic pollutants and also quantitative analysis for the individual compounds. This paper describes the use of this technique by analysing samples obtained from a hazardous waste treatment facility in South Africa. After sampling and extraction the samples were analysed for polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and four dioxin-like non-*ortho* substituted polychlorinated biphenyls (PCBs). The quantitative values, as well as detection limits, obtained using the GC × GC-TOFMS methodology compares well with those obtained using GC-HRMS; the accepted benchmark technology for this analysis. Although GC × GC-TOFMS is not a target compound analytical technique (as is GC-HRMS), it is possible to obtain information on numerous other classes of organic pollutants present in the samples in one analytical run. This is not possible with GC-HRMS. Several different column combinations have been investigated for handling very complex waste samples and suggestions are presented for the most suitable combination.

1. Introduction

The disposal of toxic waste is of enormous concern to authorities in developing countries. Facilities are not as rigorous or as well maintained as those in more developed countries, and poorer countries are sometimes driven to import toxic waste for disposal as a means of raising revenue (Birnbaum and de Vito, 1995; Schecter et al., 2006). Monitoring procedures and methods are generally poor and legal controls are not in place to govern disposal and handling. This allows unscrupulous operators to profit by waste disposal that is criminally negligent. The Forensic Science Laboratory of the South African Police Services has investigated a number of cases involving hazardous and toxic waste dumping and disposal in South Africa.

This paper describes the use GC × GC-TOFMS (Commission Regulation 1881, 2006; Korytár, 2006; Semard et al., 2009) for the qualitative analysis of priority pollutants of environmental concern, and the specific quantitation of PCDDs, PCDFs and dioxin-like non-ortho substituted PCB compounds in hazardous waste. Selectivity, sensitivity and detection limits are addressed in a subsequent paper submitted for publication (de Vos et al., submitted for publication).

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In developing countries, methodology and equipment for GC-HRMS (EPA Method 1613, 1994; Eppe et al., 2004; Reiner et al., 2006) for the determination of POPs is frequently not in place (Focant et al., 2001a). In South Africa there is no established facility capable of routine GC-HRMS determinations of POPs and especially PCDD/F analysis (Batterman et al., 2009). An alternative approach using GC × GC-TOFMS, an emerging technology that can be used to analyse complex samples, has been implemented (Focant et al., 2004a,b,c,d,e; Reiner et al., 2006).

Comprehensive GC × GC is a technique in which two GC columns using different modes of separation are connected together in series. Between the two columns is a thermal modulator (Dimandja et al., 2003; Focant et al., 2003, 2004c; Semard et al., 2009) which traps portions of eluent from the first column and re-injects them onto the second column. This process occurs repeatedly, thus all the compounds from the sample are subjected to two distinct separations, resulting in a separation superior to that possible on a ^{1}D GC system (Schoenmakers et al., 2003), with many more compounds resolved as a result of the multiplicative increase in peak separation number. In addition, the sensitivity of the GC × GC system is also improved approximately 10-fold relative to ^{1}D GC by the focusing effect of the modulator (Korytár, 2006; Semard et al., 2009).

GC × GC-TOFMS is unique in being the only technique that has the ability to detect all the compounds of complex samples at the levels needed for priority pollutant determination in a single analysis. It can provide rapid and comprehensive determination of whether a sample contains compounds harmful to human and animal health. Positive samples can then be sent for quantitative analysis using the reference GC-HRMS technique (Eppe et al., 2004; Reiner et al., 2006). The costs associated in analysing negative samples would then not be incurred.

GC × GC-TOFMS can also be used to obtain quantitative data, and is capable of reaching the levels stipulated in Environmental Protection Agency (EPA) Method 1613 (1994) for the quantitation of the 17 PCDDs and PCDFs (Focant et al., 2004c; Hoh et al., 2007). The results obtained by GC × GC-TOFMS for the quantitation of these compounds in the samples (described in Section 3.3) were compared with results obtained for the same sample set using GC-HRMS to confirm the validity of the quantitation, as this is the first time such a comprehensive environmental screening and PCDD determination has been done in South Africa using GC × GC-TOFMS.

PCDDs and PCDFs are well-known anthropogenic compounds formed as by-products during combustion processes used in waste disposal. 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TeCDD: Te = tetra, Pe = penta, Hx = hexa, Hp = hepta) has been determined as the most toxic man-made chemical (Pereira, 2004) and methods for the determination of this compound, along with 16 other chlorinated PCDD/Fs, are described in EPA Method 1613 (1994) and in European Method EN-1948 (1996).

The toxicity of the compounds making up this set is defined in terms of the toxic equivalency factor (TEF) (van den Berg et al., 2006). The 2,3,7,8-TeCDD congener is assigned a value of one, and the other compounds are related to it by measuring their relative toxicity. The total toxic equivalency (TEQ) value is calculated from the sum of the individual toxic equivalency factors (TEFs) for all 17 PCDD/F congeners. The contribution of each congener to the total value has to be established and it is therefore essential to separate the 17 PCDD/F congeners from each other, especially the seven hexachlorodibenzo-*p*-dioxins and furans (HxCDD/Fs).

The cost and sophistication of GC-HRMS is of concern in developing countries, including South Africa. GC × GC-TOFMS was selected as an alternative quantitative technique having been used previously for PCDD/F analysis, though little attention has been focussed on combining the accurate quantitative capability of GC × GC-TOFMS with broad level priority pollutant screening.

2. Experimental

2.1. Chemicals

For the sample extraction and GC-HRMS analyses, all solvents used were *Pestanal* reagents (*Riedel-de Haën*, Seelze, Germany). Nonane, *Puriss* analytical-reagent grade standard for GC, was purchased from *Fluka* (Steinheim, Germany). Sodium sulfate anhydrous was *Baker*-analyzed (*J.T. Baker*, Deventer, Netherlands). Liquid nitrogen (LN_2) was purchased from *Air Liquide* (Liege, Belgium). Chromatographic pure grade helium gas (99.9999%) was purchased from *Air Products* (Vilvoorde, Belgium). The internal standard solution of the 17 2,3,7,8-chloro-subsituted $^{13}C_{12}$ labelled PCDD/Fs congeners (EDF-4144), the calibration standard solution (EDF-4143), and the syringe (recovery) standard (EDF-4145) were purchased from *Cambridge Isotope Laboratories* (*CIL*, Andover, MS, USA). The EDF-4143, EDF-4144, and EDF-4145 concentrations of the native and labelled congeners are summarized in a previous report (Focant et al., 2001b). The $^{13}C_{12}$-labelled PCB internal standard spiking solution (EC-5023), as well as the ten-point calibration solution (EC-5022), was obtained from *CIL*. For PCDD/Fs and non-ortho-PCBs, a mixture of $^{13}C_6$-3,3′,5,5′-tetrachoro biphenyl (TeCB-80) (Korytár, 2006), $^{13}C_6$-1,2,3,4-TeCDD, and $^{13}C_6$-1,2,3,4,7,8,9-HpCDF was used as the recovery standard. Non-ortho-PCB recovery rates were calculated against $^{13}C_6$-TeCB-80. Recovery rates for TeCDD/F and PeCDD/F were calculated against $^{13}C_6$-1,2,3,4-TeCDD. Recovery rates for HxCDD/F, HpCDD/F, OCDD/F were calculated against $^{13}C_6$-1,2,3,4,7,8,9-HpCDF. Details on MS standards are available elsewhere (Pirard et al., 2003).

Because calibration solutions are based mainly on concentration levels and availability, the European Method EN-1948 standards were chosen for GC × GC-TOFMS calibration purposes. These solutions were purchased from *Wellington Laboratories* (Guelph, Canada) and contained the 17 native compounds and the corresponding extraction standards ($^{13}C_{12}$-congeners), sampling standards and syringe standards. Additional PCDD/PCDF and PCB calibration standards were obtained from *Cambridge Isotope Laboratories* (CIL, Andover, MA) and included the internal standard and the recovery standard for these compounds (EDF-4143, EDF 4144 and EDF 4145). For quantitation purposes, only the PCDD/Fs and the non-ortho substituted dioxin-like PCBs were included.

2.2. Samples

A hazardous waste treatment facility was investigated under suspicion of having illegally disposed of toxic materials, in contravention of the South African Environment Conservation Act (Act 73 of 1989). These materials included toxic chemical residues generated in the course of manufacturing assorted chemicals and products, including pesticides and herbicides.

The facility made use of furnaces to incinerate the waste into an inert form for disposal. After the wastes had been treated to destroy the hazardous organic compounds, sludge from settling tanks was buried on the premises in contravention of a number of laws and regulations. Information received was that the incineration process involved two stages of combustion and incineration; one at 650 °C to burn the majority of the compounds and then a second at 900 °C in an attempt to destroy residual organic compounds. The material brought to the facility for disposal thus included chemical wastes and residues.