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Quadrupole mass spectrometer operating in the electron-capture negative ion mode as detector for comprehensive two-dimensional gas chromatography

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Abstract

A recently introduced rapid-scanning quadrupole mass spectrometer (qMS) with an electron-capture negative ion (ECNI) option, the Perkin-Elmer Clarus 500, was tested as a detector for comprehensive two-dimensional gas chromatography (GC × GC). The parameters influencing the data acquisition rate in the scan mode, such as scan time and inter-scan delay, and in the selected ion monitoring mode, such as dwell time and inter-channel delay, were evaluated. In the scan mode, good-quality mass spectra covering a range of 300 Da can be obtained at an acquisition rate of 23 Hz; in selected ion monitoring, an acquisition rate of 90 Hz can be achieved when monitoring a single ion. Compared with electron ionisation, the use of electron-capture negative ionisation causes no extra peak broadening. As applications, mixtures of polychlorinated *n*-alkanes (PCAs), polybrominated diphenyl ethers (PBDEs) and polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were analysed. The separation of PCAs based on their number of chlorine substituents was confirmed for the first time by using GC × GC–ECNI qMS in the scan mode and a significantly improved limit of detection was achieved for BDEs (10–150 fg injected) and CDD/Fs (10–700 fg injected) in the selected ion monitoring mode.

Keywords: Comprehensive two-dimensional gas chromatography; Quadrupole mass spectrometry; Electron-capture negative ion; Dioxin analysis; Polychlorinated alkanes; Polybrominated diphenyl ethers

1. Introduction

Comprehensive two-dimensional gas chromatography (GC × GC) is a powerful separation technique for the analysis of highly complex mixtures. Since its introduction in 1991 [1], it has become a research tool of growing interest: several instruments are commercially available today and over 150 papers have been published in this area. The principles and instrumental requirements of GC × GC have been extensively discussed, e.g. in [2,3]. For the present study, it is relevant to emphasize that the outcome of a GC × GC run is a series of high-speed second-column chromatograms with peaks having widths of 120–600 ms at the baseline [3]. In order to properly describe these very narrow peaks and avoid extra peak broadening caused by the detector, GC × GC has to be coupled to detectors with a high data acquisition rate and small internal volume. Therefore, it does not come as a surprise that virtually all early studies were done with flame ionisation detectors (FID), which have data acquisition rates up to 200 Hz and dead volumes which are effectively zero [4]. More recently, the combination of GC × GC with a micro electron-capture detector (μECD) has shown very good results, in particular for the analysis of polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) [5–7]. The μECD is fast enough (up to 100 Hz) but some peak broadening due to a still too large cell volume was observed even with this smallest commercially available model of ECDs [8]. However, whenever identification and/or confirmation of identity are required, the

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use of a mass spectrometric detector is mandatory. At present, time-of-flight mass spectrometers (ToF MS) with data acquisition rates of up to 200 Hz are available and – as has been demonstrated in numerous studies (e.g. [9–11]) – they are fully compatible with GC × GC. However, as yet there is no commercially available instrument with a chemical ionisation option (although there briefly was a prototype on the market a short while ago), which is a highly desirable option when organohalogenated compounds have to be analysed. In addition, ToF MS instruments are very expensive. Consequently, using a quadrupole MS, preferably with electron-capture negative ionisation, as a GC × GC detector instead, is of decided interest.

The main limitation of a quadrupole MS (qMS) is its relatively slow scan speed. To overcome the limiting value of 2.43 scan/s of the Hewlett-Packard, Model 5972 instrument, Frysinger and Gaines [12] proposed to broaden the chromatographic peaks (from 0.2 to 1 s in the second dimension) by increasing the run time, when marine fuel was analysed by thermally modulated GC × GC–qMS. Shellie et al. [13], for the analysis of essential oils, and Kallio et al. [14], for the analysis of polycyclic aromatic hydrocarbons in urban aerosols, using the up-graded Hewlett-Packard, Model 5973 instrument, preferred to limit the scan range to ca. 200 Da to achieve a rate of 20 scan/s, while Debonneville and Chaintreau [15] opted to monitor a single ion in a study of allergens in fragrances and achieved a frequency of 30.7 Hz. In the present study, a recently introduced fast-scanning quadrupole mass spectrometer, the Perkin-Elmer Clarus 500, has been evaluated as a detector for GC × GC. Our focus was on its use in the electron-capture negative ion (ECNI) mode, which has not been studied so far. Its applicability is demonstrated by means of analyses in which soft ionization is highly required, viz. those of polychlorinated *n*-alkanes (PCAs), polybrominated diphenylethers (PBDEs) and PCDD/Fs.

2. Experimental

2.1. Samples and chemicals

3,3′,4,4′,5-Pentachlorobiphenyl (CB 126; Promochem, Wesel, Germany) with concentrations of 540 and 54 pg/μl in isooctane, and 1,1,1,3,9,11,11,11-octachloroundecane (Chiron, Trondheim, Norway) with a concentration of 15 pg/μl in isooctane, were used to evaluate the qMS system. Three standard mixtures and an eel sample were used for the applications. A mixture of chlorinated decanes with 65% chlorination and a total concentration of 10 ng/μl was purchased from Dr. Ehrenstorfer (Augsburg, Germany). A standard solution containing 2,3,7,8-TCDD and 2,3,7,8-TCDF, both with a concentration of 100 fg/μl, 1,2,3,7,8-PeCDD, 1,2,3,7,8-PeCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, all with a concentration of 500 fg/μl, and OCDD and OCDF, both with a concentration of 1000 fg/μl, was prepared by diluting the commercial standard mixture EDF 7999 (CIL, Andover, MA, USA) in iso-octane. A 100-fold concentrated mixture was used to optimize the qMS conditions. A standard mixture containing BDE congeners 28, 75, 71, 47, 66, 77, 100, 119, 99, 116, 154, 153, 138 and 190 (numbering identical to PCBs [16,17]), all with concentrations of 150 fg/μl, and congeners 49, 85 and 183, each with a concentration of 50 fg/μl, was prepared by mixing standard solutions of each congener (AccuStandard, New Haven, CT, USA) in iso-octane.

An aliquot of an eel sample containing ca. 1 g of fat was mixed with sodium sulphate, allowed to dry for 3 h and Soxhlet-extracted for 12 h with hexane/acetone (3:1, v/v) at 70 °C [18]. The solvents used were of nanograde quality, and were obtained from Promochem. The extract was concentrated on a rotary evaporator, dissolved in 2 ml of dichloromethane, and cleaned by gel permeation chromatography over two Polymer Laboratories (Church Stretton, UK) gel columns (300 × 25 mm, pore size 10 μm), using dichloromethane at 10 ml/min. The 18–23 min fraction was collected, concentrated under nitrogen, dissolved in iso-octane and further purified by shaking with sulphuric acid. After separation of the iso-octane phase, the sulphuric acid phase was washed twice with pentane to extract all BDEs. Finally, the pentane/iso-octane mixture was concentrated under nitrogen to 2 ml (iso-octane) and eluted over a 1.6 g silica column (2% deactivated) with 11 ml iso-octane and 10 ml 20% diethyl ether in iso-octane. The fractions were combined and concentrated to 1 ml (iso-octane).

2.2. GC × GC–qMS

The GC × GC system was built from a Clarus 500 MS (Perkin-Elmer, Shelton, CT, USA) equipped with a dual-jet liquid CO_2 modulator system. The principles and operation of the dual-jet modulator are discussed in [19]. It is relevant to mention here that the oven of the instrument used is rather small (at least compared to Agilent or Thermo Electron GCs). Therefore, the position of the CO_2 jets plays an important role in the retention-time repeatability. The best repeatability was obtained when the jets were mounted just behind the door, i.e. as far as possible from the thermocouple. A DB-1 (100% methylpolysiloxane) and a DB-XLB (proprietary) fused-silica column, both with dimensions of 30 m × 0.25 mm × 0.25 μm and purchased from J&W Scientific (Folsom, CA, USA), were used as first-dimension columns. A 1 m × 0.10 mm × 0.10 μm 007-65HT (65% phenyl-methylpolysiloxane) from Quadrex (New Haven, CT, USA) and a 0.9 m × 0.10 mm × 0.10 μm LC-50 (50% liquid crystalline-methylpolysiloxane) from J&K Environmental (Milton, ONT, Canada) were used as second-dimension columns. In the DB-1 × 007-65HT set-up, which was used for system evaluation and the analysis of the PCAs and PBDEs, one end of the second-dimension col-