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Group separation of organohalogenated compounds by means of comprehensive two-dimensional gas chromatography

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Abstract

Separations of 12 compound classes, polychlorinated biphenyls (PCBs), diphenyl ethers (PCDEs), naphthalenes (PCNs), dibenzothiophenes (PCDTs), dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), terphenyls (PCTs) and alkanes (PCAs), toxaphene, organohalogenated pesticides (OCPs), and polybrominated biphenyls (PBBs) and diphenyl ethers (PBDEs) by comprehensive two-dimensional gas chromatography were evaluated. Five column combinations, DB-1 × 007-210, DB-1 × HT-8, DB-1 × LC-50, DB-1 × 007-65HT and DB-1 × VF-23ms were used to study, primarily, group-type separations, but attention was devoted also to within-class separation, especially for those classes which were not addressed in much detail before, the PCNs, OCPs, PBBs and PCTs. The DB-1 × 007-210 column set did not offer any extra separation compared to one-dimensional GC. For the DB-1 × HT-8 column combination, the useful principle of congener separation on the basis of number of halogen substituents in a molecule was confirmed (PCBs, toxaphene) and extended (PCTs, PBDEs). No practically useful group-type separation was observed for this column combination. The DB-1 × LC-50 set provides group separation based on planarity: planar compounds such as PCDDs, PCDFs, PCDTs and PCNs are much more retained than, and therefore separated from, non-planar analytes. Within the classes of PCBs, PBBs and PCTs highly useful separation of planar from non-planar compounds was also observed. The DB-1 × 007-65HT column set effectively separates PCAs and PBDEs from all other compound classes, and provides a good separation of brominated and chlorinated analogue classes from each other. This column set was the most efficient one for within-class separation of OCPs and PCNs. Finally, DB-1 × VF-23ms yields excellent within-class separations, especially of non-aromatic compounds, viz. OCPs, toxaphene and PCAs. No group separation was observed here. The applicability of the approach was demonstrated for a sediment extract and a dust extract. In the sediment extract, PCDDs, PCDFs, PCAs and PCNs were identified and their efficient separation was achieved. In the dust sample, separation of PCAs and PBDEs was achieved and several new PBDE congeners were identified.

Keywords: Comprehensive two-dimensional gas chromatography; Organochlorine compounds; Organobromine compounds; Polychlorinated biphenyls; Polychlorinated diphenyl ethers; Polychlorinated naphthalenes; Polychlorinated dibenzothiophenes; Polychlorinated dibenzo-*p*-dioxins; Polychlorinated dibenzofurans; Polychlorinated terphenyls; Polychlorinated alkanes; Toxaphene; Organohalogenated pesticides; Polybrominated biphenyls; Polybrominated diphenyl ethers

1. Introduction

The congener-specific analysis of most classes of organohalogenated compounds is a challenging task, because of (i) the closely similar characteristics of the congeners and isomers within a single class, (ii) mutual interferences by related classes of organohalogens, and (iii) in real-life analysis, interferences caused by matrix constituents. Therefore, analytical procedures usually have to include complicated and time-consuming multi-step sample pre-treatment, because even state-of-the-art (one-dimensional) gas chromatography (1D-GC), combined with selective mass spectrometric detection often cannot solve the problem. One way to improve the situation is to considerably increase the separation efficiency of the GC analysis by replacing 1D-GC by so-called comprehensive two-dimensional gas chromatography (GC × GC). In GC × GC, two independent separations are applied to an entire sample – within the run time of the first-dimension separation – which effects a much enhanced

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overall resolution [1,2]. Another aspect that makes GC × GC attractive is the ordered structure, which is observed in the 2D plane for structurally related compounds. Such ordering often allows the classification and preliminary identification of unknown peaks based on their position in the GC × GC chromatogram, and is an efficient tool for screening purposes. The best-known early example are the bands of, e.g. paraffins, naphthenes and mono- and di-aromatics in 2D chromatograms of petrochemical samples [3,4]. More recently, ordered structures have been reported for polychlorinated biphenyls (PCBs) [5,6], polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) [5,7] and toxaphene [8]. On-going work in the field of polychlorinated alkanes (PCAs) [9,10] also appears to be successful. However, despite the wide-ranging interest in the use of GC × GC for organohalogen analysis [5–13], only limited attention has been devoted to the separation of the various compound classes of interest from each other. In the present paper, this interesting problem will be studied for the five classes of organohalogens mentioned above, and also for polybrominated and polychlorinated diphenyl ethers (PBDEs and PCDEs, respectively), polychlorinated naphthalenes (PCNs), polychlorinated dibenzothiophenes (PCDTs), polychlorinated terphenyls (PCTs), organochlorine pesticides (OCPs) and polybrominated biphenyls (PBBs). For each class of interest, a representative set of individual congeners-plus-isomers and/or technical mixtures will be studied. While the main aim is the group-type separation, some attention will also be devoted to within-class separations, especially for those groups which were not addressed in much detail before (PCNs, OCPs, PBBs and PCTs). The applicability of the approach will be demonstrated for a sediment extract (PCDD/Fs) and a dust extract (PBDEs and PCAs).

2. Experimental

2.1. Samples and chemicals

A standard mixture of each compound class was prepared either from individual congeners or from technical mixtures. The list of the compound classes and their detailed composition is given in Table 1. The congener concentrations varied between 1 and 100 ng/ml. Each solution was spiked with CB 40 (Promochem, Wesel, Germany) as internal standard to a final concentration of 50 ng/ml in order to check the retention-time stability.

The sediment sample was prepared by the Institut Químic de Sarrià (Barcelona, Spain) according to a method validated for PCDD/F determination by GC–HRMS. A brief summary is as follows: 8 g of sediment of marine origin (Western Scheldt) collected in the Netherlands were Soxhlet-extracted with toluene during 12 h. The extract was purified on a multilayer silica column (containing from top to bottom layers of anhydrous sodium sulphate, sulphuric acid–silica, activated silica, sodium hydroxide–silica, activated silica, silver nitrate–silica, and glass wool). The purified extract was transferred with *n*-hexane to a SPE carbon tube (Supelclean ENVI-Carb, 3 ml, 0.25 g, Supelco, Bellefonte, PA, USA). The first fraction, which contained the PCBs, was eluted with *n*-hexane and *n*-hexane–toluene (72:25, v/v) and the second fraction, which contained the PCDD/Fs, in the back-flush mode with toluene. The PCDD/F fraction was purified on a Florisil column (Florisil PR, 60/100 mesh; Supelco) and finally on a column containing layers of anhydrous sodium sulphate, activated silica, sulphuric acid–silica and glass wool. The sample was finally concentrated to 25 μl.

The dust sample was prepared according to a method validated for PCA and PBDE determination by GC–ECNI-MS. A brief summary is as follows: 2 g of dust of indoor origin collected in a Spanish (Madrid) household were extracted with Soxhlet for 12 h with 160 ml *n*-hexane–acetone (3:1, v/v) at 70 °C. After the addition of CB 112 and [^{13}C]-BDE 209 as internal standards, the extract was concentrated on a rotary evaporator, and demineralized water (adjusted to pH 2) was added and the organic layer collected. The aqueous phase was extracted two more times with isooctane. The organic extracts were combined and concentrated in 2 ml of dichloromethane. The extract was cleaned by gel permeation chromatography over two Polymer Labs. (Church Stretton, UK) gel (polystyrene–divinylbenzene) columns (300 mm × 25 mm; pore size, 10 μm) connected in series, using dichloromethane at 10 ml/min. The collected fraction (18–23 min) was concentrated under nitrogen, dissolved in isooctane and further purified by shaking with conc. sulphuric acid. Finally, the pentane–isooctane mixture was concentrated under nitrogen to 2 ml (isooctane) and purified on a silica column (deactivated with 2% water) with 11 ml isooctane and, next, 10 ml diethylether–isooctane (15:85, v/v). The latter fraction contained the PBDEs and PCAs and was concentrated to 1 ml (isooctane).

2.2. GC × GC–μECD

The GC × GC system was built from an HP6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatograph equipped with a loop-type carbon dioxide jet modulator (KT2002 CO_2 system; Zoex, Lincoln, NE, USA). The principles and operation of the KT2002 modulator are described in [16]. The hot air pulse duration was 200 ms, the hot jet temperature was 400 °C, and the modulation period varied between 8 and 9 s, depending on the column combination used (see Table 2 below). At the start of each run, the CO_2 flow was adjusted by using a needle valve to keep the cold-jet temperature at 0–10 °C, at an initial oven temperature of 90 °C. Helium gas (Hoek Loos, Schiedam, The Netherlands) with a purity of 99.999% was used as carrier gas at a constant flow of 1.2 ml/min. A micro-ECD (Agilent) was operated at 280 °C, with 99.999% pure nitrogen (Hoek Loos) as make-up gas at a flow-rate of 150 ml/min. The data acquisition rate was 50 Hz. One microliter samples were