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Short communication

Selective extraction of halogenated compounds from data measured by comprehensive multidimensional gas chromatography/high resolution time-of-flight mass spectrometry for non-target analysis of environmental and biological samples

Shunji Hashimoto*, Yasuyuki Zushi, Akihiro Fushimi, Yoshikatsu Takazawa, Kiyoshi Tanabe, Yasuyuki Shibata

National Institute for Environmental Studies, Division of Environmental Chemistry, Onogawa 16-2, Tsukuba, Ibaraki 305-8506, Japan

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ABSTRACT

We developed a method that selectively extracts a subset from comprehensive 2D gas chromatography (GC × GC) and high-resolution time-of-flight mass spectrometry (HRTOFMS) data to detect and identify trace levels of organohalogens. The data were obtained by measuring several environmental and biological samples, namely fly ash, soil, sediment, the atmosphere, and human urine. For global analysis, some samples were measured without purification. By using our novel software, the mass spectra of organochlorines or organobromines were then extracted into a data subset under high mass accuracy conditions that were approximately equivalent to a mass resolution of 6000 for some samples. Mass defect filtering as pre-screening for the data extraction was very effective in removing the mass spectra of hydrocarbons. Those results showed that data obtained with HRTOFMS are valuable for global analysis of organohalogens, and probably of other compounds if specific data extraction methods can be devised.

1. Introduction

Global analysis, which can be used to search for a large number of compounds simultaneously, is one approach for addressing the increasingly diverse range of contaminants. Direct measurement of samples without any compound loss is ideal for complete, global detection of contaminants. We have been developing a new apparatus consisting of comprehensive 2D gas chromatography (GC × GC) directly coupled with quadrupole-type tandem mass spectrometry (qMS/qMS) or high-resolution time-of-flight mass spectrometry (HRTOFMS) to achieve global analysis and exact quantification at the same time [1–4]. We have shown that halogenated compounds can be detected comprehensively and selectively in environmental samples by employing a neutral loss scan (NLS) on GC × GC–qMS/qMS [2]. However, the sensitivity of the NLS in this system is insufficient to detect trace levels of organohalogens and incapable of identifying compounds from their unit mass records. The ability of GC × GC–HRTOFMS to characterize compounds has also been reported by Ochiai et al. [5] and Ieda et al. [6] Mitrevski and Marriott [7], and Serrano et al. [8]. HRTOFMS is therefore expected to be a powerful tool for separation, identification, and quantification of each compound from its mixture, although it is not easy to extract any information on compounds from the GC × GC–HRTOFMS because of the massive amount of data.

Recently, automated screening and searching of GC × GC–TOFMS data has been studied intensively because of the impossibility of manually interpreting the complex data [9–13]. These studies are very interesting, but, as Haglund et al. [13] points out, screening may be inaccurate in the case of samples that include complex matrices, because of inadequate separation capability and the presence of a gap between the accurate mass and nominal mass owing to the use of unit mass data. We therefore developed a method that extracts precise mass spectra corresponding to Cl or Br isotopic patterns from the GC × GC–HRTOFMS data in order to find and identify trace levels of organochlorines or organobromines.

2. Experimental

2.1. Samples and sample preparation

Five types of sample were provided for this study. Indoor air sample was collected in our laboratory from 30 September to 5 October 2011. By using a mini-pump MP-Σ30 (Sibata Scientific

* Corresponding author. Tel.: +81 29 850 2531; fax: +81 29 850 2531.
E-mail address: shunji@nies.go.jp (S. Hashimoto).

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Technology Ltd., Tokyo, Japan), a total air sample of approximately 4 m^3 was collected at a rate of 0.5 L min^{-1} into a Tenax-TA tube (Gerstel GmbH & Co. KG, Mülheim an der Ruhr, Germany) for processing in a Thermal Desorption Unit (TDU, Gerstel). The samples were immediately sealed and stored at −80 °C until measurement.

Samples of fly ash extract, sediment and soil were provided according to our previous reports [1,2]. Sediment and soil samples were cleaned in only a chromatography column containing 5 g of sulfuric acid silica gel (44% sulfuric acid/silica gel (w/w) for dioxin analysis, Wako Pure Chemical Industries, Osaka, Japan).

Approximately 300 ml of urine was collected from each of two healthy adult males and combined. A portion (approximately 50 ml) of the sample was extracted with hexane, and another portion of the sample was extracted with hexane after deconjugation with β-glucuronidase. Each of the extracts was concentrated into 100 μl for measurement.

2.2. Chemicals

Thirty-five polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/Fs), 62 polychlorinated biphenyls (PCBs), 43 persistence organic pollutants (POPs), 39 polybrominated diphenyl ethers (PBDEs), and 21 chlorinated and 11 brominated polyaromatic hydrocarbons (PAHs) were used to check the retention times in 2D chromatograms and to identify halogenated compounds in accordance with the methods used in our previous report [2].

2.3. Measurement instruments and conditions

Samples were measured with a 6890GC (Agilent Technologies, Palo Alto, CA, USA) with a KT2004 GC × GC system (Zoex, Houston, TX, USA) coupled with a JMS-T100GC (JEOL, Tokyo, Japan) HRTOFMS. The conditions and parameters of the GC × GC–HRTOFMS are shown in Table 1. Air samples were injected into the GC × GC apparatus by thermal desorption with a TDU (Gerstel).

Table 1
GC × GC–MS/MS and HRTOFMS conditions for organohalogens.

TDU Instrument	Gerstel TDU and CIS4
TDU program	from 40 °C holding for 0.5 min to 180 °C at rate 720 °C min^{-1} holding for 0 min to 340 °C at rate 50 °C min^{-1} holding for 5 min
CIS4 program	from 0 °C holding for 0.1 min to 300 °C at rate 12 °C min^{-1} holding for 3 min
Desorption mode	Splitless
GC × GC Instrument	Agilent 6890 GC Zoex KT2004 (in 6890GC)
1st column	GL Science InertCap 5MS/Sil (60 m length, 0.25 mm i.d., 0.1 μm film thickness)
2nd column	SGE BPX-50 (1.5 m length, 0.1 mm i.d., 0.1 μm film thickness)
Oven program	from 70 °C holding for 1 min to 180 °C at rate 50 °C min^{-1} holding for 0 min to 230 °C at rate 3 °C min^{-1} holding for 0 min to 300 °C at rate 5 °C min^{-1} holding for 16.133 min
Injection	volume: 1 μl, temp: 280 °C, method: splitless
Carrier gas	type: He, mode: constant flow, initial head pressure: 488.8 kPa at 70 °C
Modulation	period: 4 s, releasing: 0.35 s
HRTOFMS Instrument	JEOL JMS-T100GC
Ion source	mode: EI+, temp: 250 °C, ionizing voltage: 35 V, ionizing current: 600 μA
Analyzer	resolution: 6000, recording range: 35–550 *m/z*, cycle: 25 Hz
Detector	MCP voltage: 2700 V

2.4. Data processing

2.4.1. Developing software to extract subsets from GC × GC–HRTOFMS data

We developed software that extracts only the mass spectra of organochlorines or organobromines from net-CDF converted data from the GC × GC–HRTOFMS system. The software was built by Microsoft Visual Studio C# 2010 (Redmond, WA, USA) and operates on Microsoft Windows (both 32-bit and 64-bit versions). The software reads a netCDF file as input data and extracts from the whole data set only those mass spectra that have chlorine or bromine isotopic patterns; no settings are used for target mass numbers. The software can vary the parameters—namely the mass accuracy (MA)

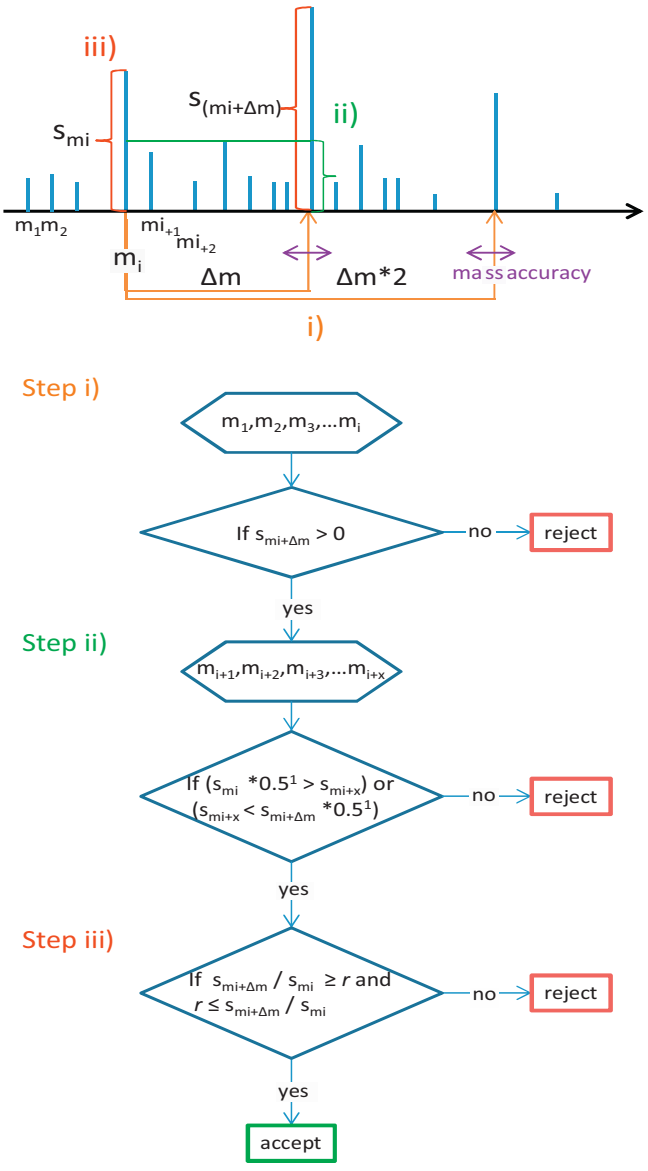

Fig. 1. Process of isotopic pattern detection using ClBr Extractor software. Mass spectra that are Δm, $(2 \times \Delta m)$, $(3 \times \Delta m)$ … $(n \times \Delta m)$ larger than m_i are searched for around a mass spectrum (m_i) to find isotopic patterns. If they are found, then the mass spectra between the masses m_i and $m_i + n \times \Delta m$ are checked to see if they are smaller than the mass spectra found in step *i*. (This step is optional.) If the spectra satisfy the conditions in *i* and *ii*, then finally the ratio of $(m_i + n \times \Delta m)$ to m_i spectrum intensities is compared with the theoretical isotopic ratio. Finally, when the calculated ratio satisfies the set margin of error of the theoretical isotopic ratio, the spectra are retained in the data. Where Δm is the mass difference of isomers, Δm for chlorine and bromine was calculated as 1.99705 = ^{37}Cl (36.965903)–^{35}Cl (34.968853) and 1.997953 = ^{81}Br (80.916291)–^{79}Br (78.918338), respectively.