

Recent Development of Two-Dimensional Gas Chromatography Mass Spectrometry and its Application

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ABSTRACT

The past decades have seen the fast development of multi-dimensional separation technologies, which are capable of separating increasingly complex mixtures. One good example is the comprehensive two-dimensional Gas Chromatography (GC × GC) that can achieve orthogonal separation by connecting two capillary columns with different stationary phases in series and obtain the total peak capacity. In this the new development of GC × GC and its application are discussed, including the upgrading of GC × GC and the modulators, the molecular identification of un-resolved complex compounds, and the significant environmental consequences, etc. The remarkable high peak capacity and the versatile features of GC × GC have attracted wide attention in environmental chemistry and the related disciplines and sub disciplines.

Keywords: Comprehensive two-dimensional gas chromatography; Molecular identification; Toxic equivalency factors

INTRODUCTION

Over the past decades of rapid development of instrumentation in the analytical chemistry field, the new generation of multi-dimensional separation technologies, for example comprehensive two-dimensional gas chromatography (GC × GC) has dramatically improved the separation ability of complex mixtures. In one-dimensional GC, mixtures are separated by their different affinity to the stationary phase, retained by the capillary column, and eluted at different times. They are sequentially identified by the Mass Spectrometry (MS) based on the mass spectrum patterns. GC × GC separates analysts by locating two capillary columns with complementary stationary phases in the oven, e.g., non-polar and polar stationary phases. A modulator is installed to cut the effluents from the 1st column into cryo-focused segments and inject them into the 2nd column. In the original design of the modulation, ambient temperature air was the trapper and resistively heated conductive paint was applied [1]. In the next generation, contemporary thermal modulator was invented using liquid CO₂ or N₂ as the cryogen, which was able to trap low boiling point compounds efficiently

[2-4]. However, the high consumption of cryogen largely elevates the operational cost of routine measurement, thereby impeding the popularization of GC × GC. Recently, great efforts have been made to develop cryogen-free thermal modulators, for e.g., vortex cooler and thermoelectric cooler. For example, Luong et al. introduced a compact Thermal Independent Modulator (TiM) with thermoelectric cooling and mica thermic heating device [5]. The new development of modulators provides portability and flexibility and fosters the wide application of GC × GC.

LITERATURE REVIEW

Multiple research areas benefit from the high peak capacity, selectivity, and sensitivity of the established separation technique, e.g., food chemistry, cigarette industry, petroleum industry, and atmospheric chemistry [6-9]. The related disciplines and the number of research articles published in the past five years using GC × GC are shown in Figure 1. However, GC × GC data treatment can be extremely complicated and demanding. New approaches must be carefully constructed to take the most advantage of multi-dimensional chromatographic information.

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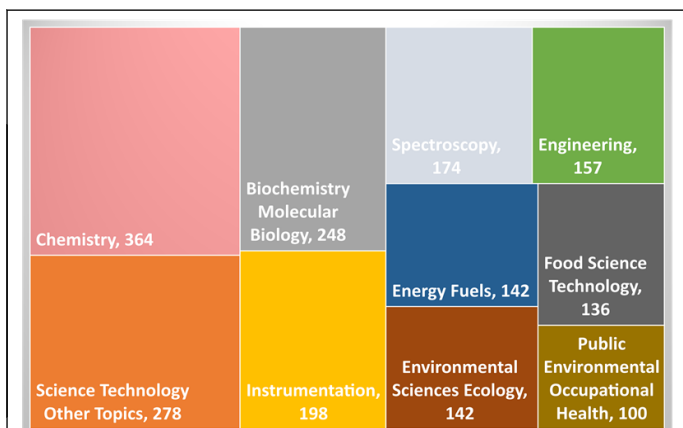


Figure 1: The research disciplines and the number of research articles published in the past five years using GC × GC.

Among the tens of thousands of organic species in the bulk organics, Polycyclic Aromatic Hydrocarbons (PAHs) are genotoxicants. Exposures to PAHs and the derivatives through inhalation, ingestion, and dermal contact are associated with an increased risk of cancer [10,11]. Nevertheless, due to the limitations of analytical instruments and the lack of authentic standards, the enormous airborne PAHs and the derivatives are far less identified, not to mention quantified. Priorities are given to 16 PAHs (i.e., naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzoanthracene, chrysene, benzofluoranthene, benzofluoranthene, benzopyrene, benzoperylene, indenopyrene, and dibenzoanthracene) that were highlighted by US Environmental Protection Agency (EPA) due to high human risks and persistence in the environment, leaving the majority PAHs unresolved.

DISCUSSION

Past studies have established incomplete combustion processes as the main sources of PAHs and the derivatives on global and regional scales. For example, vehicle exhaust was reported to be the largest contributor to PAHs in urban Xiamen [12]. Only reporting the concentration of the speciated PAHs, for e.g., 16 EPA PAHs, underestimates the levels of vehicular emission by a large scale. 141 possible monocyclic aromatic hydrocarbon or PAH formulas were detected in aerosol samples collected from roadside, urban, and suburban sites in Hong Kong using the ultrahigh-resolution mass spectrometry, confirming that the un-speciated PAHs dominate the total mass outside the 16 US EPA priority PAHs [13].

Ultrahigh-Resolution MS (UHRMS) provides remarkable mass resolving power and mass accuracy (usually mass accuracy < 1 ppm), enabling the determination of molecules without the use of authentic standards. One good example of UHRMS is the Fourier-Transform Ion Cyclotron Resonance MS (FTICR-MS). In principle, FTICR-MS relates the cyclotron frequency in a fixed magnetic field with the mass to charge ratio (m/z).

$$f = \frac{qB}{2\pi m}$$

Where f is the cyclotron frequency; B is the magnetic field strength; q is the ion charge; m is the molecular ion mass. Masses are resolved by the ion cyclotron resonance frequency as it rotates in the magnetic field, and all ions are detected simultaneously, which differs significantly from other MS techniques. MS resolution can be improved either by increasing the magnet strength or the detection duration time. FTICR-MS provides ultrahigh resolution and mass accuracy that are required to reliably assign the molecular formulas. Peaks were assigned mathematically calculated formulas due to the mass defect of the elements. For example, the nominal mass (International Union of Pure and Applied Chemistry (IUPAC) mass) of C, H, O, N, S, and electron are 12 (12), 1 (1.007825), 16 (15.9949146), 14 (14.003074), 32 (31.97207), and 0 (0.00054858), respectively. For a given ion $C_cH_hO_oN_nS_s$, the theoretical molecular mass is:

$$MW_{theoretical} = 12 \times c + 1.007825 \times h + 15.9949146 \times o + 14.003074 \times n + 31.97207 \times s \pm 0.00054858$$

Depending on the polarity of the ion source UHRMS iterates c , h , o , n , s values so that the deviation between $MW_{theoretical}$ and detected MW falls within the mass accuracy of the instrument.

It was found that compared with speciated PAHs, the un-speciated PAHs accounted for more than 97% of the total PAH mass emitted by Heavy-Duty Diesel Vehicles (HDDVs) [2]. In their study, chassis dynamometer tests were conducted and the gaseous and particulate emissions from one China IV and two China VI HDDVs were collected using Tenax TA sorbent tubes (C1-AXXX-500, Gerstel, Germany) and quartz filters (QM-A, Whatman, UK) separately. Samples were thermally desorbed by an automated thermal desorption system (TD100-xr, Markes, UK) and analyzed by a GC × GC interfaced with a Time-of-flight mass spectrometry (ToF-MS, LECO Pegasus4D, LECO Corporation). To deal with the complex GC × GC data, they established a novel “three-step” approach to speciate and quantify the PAHs by constructing class-screening programs based on their characteristic fragments and mass spectrum patterns [3]. Basically, unknown peaks were recognized as the PAH groups once the mass spectrum patterns matched the pre-defined criteria.

On one hand, speciated PAHs were found to be comparable with previous studies, confirming the robustness of the new method. On the other hand, benefiting from the powerful separation technology and new approach, the un-speciated PAHs were identified and quantified for the first time and the Emission Factors (EFs) were computed. Substantial higher EFs of un-speciated PAHs than speciated PAHs were observed. The un-speciated/speciated PAH ratios were in the range of 84-806 and 34-61 in the particle and gas phases, respectively. Individual PAHs are unequally toxic and the minimum Toxic Equivalency Factors (TEFs) were introduced to evaluate the overall toxicity level in a conservative way [14].

$$TEF_{PAH} = \sum (PAH_i \times TEF_i)$$

Where TEPAH is the Benzo(a)pyrene (BaP) equivalent TEF of total PAHs ($\mu\text{g km}^{-1}$); PAHi is the EF of PAH i ($\mu\text{g km}^{-1}$); TEFi is the minimum TEF of different PAH categories. As expected, Chen et al. reported two orders of magnitude higher BaP equivalent toxic EFs than previous studies, especially in the particle phase [2]. The BaP equivalent toxic EFs of particulate PAHs for China IV and China VI vehicles were 19.2 ± 21.1 and $2.6 \pm 1.3 \mu\text{g km}^{-1}$ in comparison with 0.06 and $0.02 \mu\text{g km}^{-1}$ for China IV and China V HDDVs reported by Zheng et al [2].

CONCLUSION

These results have important implications for emission inventory, PAH toxicity estimation, and pollution reduction policies. Un-specified PAHs call for careful re-evaluation in future work. We rely on solid and accurate measurement of emission data to inform the public and policy makers the real environmental consequences. The findings also motivate the modelers to re-assess the air-quality and toxicology models by incorporating the newly resolved PAH concentrations or TEF values. The complex mixtures are ubiquitous and originate from multiple sources, and this study opens paths for characterizing complex mixtures with the powerful GC \times GC plus ingenious data treatment approaches.

AUTHOR CONTRIBUTIONS

Xiao He (First Author and Corresponding Author): Writing-Original Draft, Validation, Visualization, Funding Acquisition.

Xuan Zheng (Corresponding Author): Project Management, Validation, Funding Acquisition.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

REFERENCES

- Liu Z, Phillips JB. Comprehensive two-dimensional gas chromatography using an on-column thermal modulator interface. *J Chromatogr Sci*. 1991;29(6):227-231.
- He X, Zheng X, Zhang S, Wang X, Chen T, Zhang X, et al. Comprehensive characterization of the particulate IVOCs and SVOCs from heavy-duty diesel vehicles using two-dimensional gas chromatography time-of-flight mass spectrometry. *Sci Total Environ*. 2022;1-20.
- He X, Zheng X, You Y, Zhang S, Zhao B, Wang X, et al. Comprehensive chemical characterization of gaseous I/SVOC emissions from heavy-duty diesel vehicles using two-dimensional gas chromatography time-of-flight mass spectrometry. *Environ Pollut*. 2022;119284.
- Vendeuvre C, Bertoncini F, Duval L, Duplan JL, Thiébaud D, Hennion MC. Comparison of conventional gas chromatography and comprehensive two-dimensional gas chromatography for the detailed analysis of petrochemical samples. *J Chromatogr A*. 2004;1056(1-2):155-62.
- Luong J, Guan X, Xu S, Gras R, Shellie RA. Thermal independent modulator for comprehensive two-dimensional gas chromatography. *Analyt Chem*. 2016;88(17):8428-8432.
- Beccaria M, Zou Y, Stefanuto PH, Siqueira AL, Maniquet A, Piparo M, et al. Deeper investigation of oxygen-containing compounds in oleaginous feedstock (animal fat) by preparative column chromatography and comprehensive two-dimensional gas chromatography coupled with high-resolution time-of-flight mass spectrometry. *Talanta*. 2022;238:123019.
- Lelevic A, Geantet C, Lorentz C, Moreaud M, Souchon V. Determination of vacuum ultraviolet detector response factors by hyphenation with two-dimensional comprehensive gas chromatography with flame ionization detection. *J Sep Sci*. 2021;44(20):3849-3859.
- Li J, Li K, Wang W, Wang J, Peng C, Ge M. Optical properties of secondary organic aerosols derived from long-chain alkanes under various NO_x and seed conditions. *Sci Total Environ*. 2017;579:1699-1705.
- Patel D, Taudte RV, Nizio K, Herok G, Cranfield C, Shimmon R. Headspace analysis of E-cigarette fluids using comprehensive two dimensional GC \times GC-TOF-MS reveals the presence of volatile and toxic compounds. *J Pharm Biomed Anal*. 2021;196:113930.
- Durant JL, Busby Jr WF, Lafleur AL, Penman BW, Crespi CL. Human cell mutagenicity of oxygenated, nitrated and unsubstituted polycyclic aromatic hydrocarbons associated with urban aerosols. *Mutat Res*. 1996;371(3-4):123-157.
- Lin CH, Huang X, Kolbanovskii A, Hingerty BE, Amin S, Broyde S, et al. Molecular topology of polycyclic aromatic carcinogens determines DNA adduct conformation: a link to tumorigenic activity. *J Mol Biol*. 2001;306(5):1059-1080.
- Zhao J, Zhang F, Xu L, Chen J, Xu Y. Spatial and temporal distribution of polycyclic aromatic hydrocarbons (PAHs) in the atmosphere of Xiamen, China. *Sci Total Environ*. 2011;409(24):5318-5327.
- Kuang BY, Yeung HS, Lee CC, Griffith SM, Yu JZ. Aromatic formulas in ambient PM_{2.5} samples from Hong Kong determined using FT-ICR ultrahigh-resolution mass spectrometry. *Anal Bioanal Chem*. 2018;410(24):6289-304.
- Nisbet IC, Lagoy PK. Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regul Toxicol Pharmacol*. 1992;16(3):290-300.