



Coupling of comprehensive two-dimensional gas chromatography with quadrupole mass spectrometry: Application to the identification of atmospheric volatile organic compounds



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ABSTRACT

Observation data of atmospheric volatile organic compounds (VOCs) are highly needed in air quality assessment, photochemical mechanism study, and emission control policy-making, while it has been a challenge to accurately and comprehensively measure them. Comprehensive two-dimensional gas chromatography (GC × GC) is one of the advanced techniques in analysis of complex mixtures, providing a good choice for measurement of VOCs. However, the requirement for a fast detector limits the application of quadrupole mass spectrometry (qMS) in GC × GC analysis. This paper presents a method of a common qMS detector coupled with GC × GC to the identification of atmospheric VOCs. About 125 VOCs including alkanes, alkenes, aromatics, oxygenated hydrocarbons, and halocarbons were identified in the measurement of standard gas mixtures and/or urban air samples from Beijing. The results were applied to the analysis of GC × GC–FID by one to one correspondence of peaks of the equivalent compounds between the GC × GC–FID and GC × GC–qMS chromatograms, and the retention times of the identified components in GC × GC–FID in turn undertake the qualitative analysis without the further help of MS. The wrap-around phenomenon which may confuse the match of peaks was discussed in detail. The cooperation of GC × GC–FID and GC × GC–qMS which assists the identification makes the GC × GC exploration more affordable and yet practical on both qualitative and quantitative analysis. The method and the identified results can be expanded to analyze other volatiles.

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1. Introduction

Emitted from many anthropogenic and natural sources, volatile organic compounds (VOCs) in the atmosphere are numerous, various, and ubiquitous [1,2]. Having relatively high photochemical reactivity, many VOCs contribute to photochemical smog, tropospheric ozone, and secondary organic aerosol, which are known to be harmful to human health, environment and ecosystem [3–6]. In addition, some of VOCs can affect human health directly due to their irritation and biotoxicity [7]. To be able to well understand the emission, distribution, and photochemical processes of VOCs, as well as to predict and control the related air pollution caused, it is essential to make accurate qualitative and

quantitative observations of VOCs in air over different locations and regions [8,9].

So far, there have been enormous attempts to measure VOCs. The most popular method for the speciation and measurement of VOCs is gas chromatography (GC) coupled with flame ionization detection (FID) or mass spectrometry (MS), which has greatly improved our understanding about atmospheric VOCs [9–13]. However, compared with the numerous members of the VOC family, the number of VOC species separated by one-dimensional GC is considerably fewer because of the limited separation capability of a single column. To overcome this limitation, a powerful and versatile separation technique termed comprehensive two-dimensional gas chromatography (GC × GC) was pioneered in the early 1990s [14] and introduced to the speciation of ambient VOCs early this century [15,16]. Due to orthogonal separation on two different columns jointed together by a modulator, GC × GC has a proven capability to resolve many more compounds than

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one-dimensional GC in an equivalent time, and improves the separation power greatly with respect to the chromatographic resolution, sensitivity, and capacity [17–20]. These advantages render the GC \times GC technique extremely useful for the analysis of a variety of complex mixtures [21,22], including atmospheric samples [23–26]. In a GC \times GC measurement for urban air samples, more than 500 VOCs species, including over 100 multi-substituted monoaromatic and volatile oxygenated hydrocarbons, were isolated by Lewis et al. [15]. Therefore, the authors indicated that previous assessments of reactive carbon species measured by one-dimensional GC may have underestimated the contribution of VOCs to urban pollution, particularly for VOCs with more than six carbon atoms.

Although GC \times GC is a powerful tool for analysis of complex samples, it needs a fast detector working at 50 Hz or a higher resolution because many of the GC \times GC peaks have widths typically in the range of 50–600 ms at the baseline [27,28]. In the early VOCs studies, the detection was mainly performed by FID, which is sensitive to the majority of organics. An FID has molar response factors proportional to numbers of carbon atoms in hydrocarbons, which are major components of atmospheric VOCs. Taking the advantage of such property, the concentrations of most hydrocarbons and even some oxygenated hydrocarbons can be indirectly calibrated with acceptable accuracy using standards containing only a few compounds [29–32]. In addition, FIDs are highly sensitive with large linear range, economical in purchase and operation, robust, and relatively easy to use. All these advantages make FID a favorable choice of detector in the VOCs analysis, particularly in non-targeted quantitative measurements of VOCs in air samples. However, FID cannot provide structural information for qualitative analysis as a mass spectrometer is skilled in. In recent years, reports on GC \times GC analysis coupled with a time-of-flight mass spectrometry (TOF-MS) presenting 100 or more mass spectra/s have appeared more and more frequently [24,33–36]. Compared with the expensive TOF-MS, quadrupole mass spectrometry (qMS) is far more popular and affordable in many laboratories. Though works at a low data acquisition rate of 2.43 spectra/s, a qMS detector integrated with GC \times GC provided the qualitative capability in an application to petroleum analysis by drastically slowing down the separation [37]. After that, a small number of studies on the combination of GC \times GC and qMS have been reported demonstrating not only the feasibility but also the great potential of qMS in the GC \times GC field [38–42]. These studies, however, focus mainly on analysis of much less volatile samples, such as, extracts from the roots of *Panax* (ginseng) species [38], suspected allergens in fragrances [39], essential oils of tea tree [41], and bio-oil of sugar cane straw [42], or evaluation of a novel rapid-scanning qMS detector [40].

The aim here is to describe an economical but useful GC \times GC method for analysis of atmospheric VOCs. In this paper, a common qMS was combined with GC \times GC to the purpose of the identification of VOCs in air samples, focusing on the peak matching and the qualitative analysis of GC \times GC–FID eventually. The GC \times GC–qMS methods were performed at increased spectra acquisition frequencies and qualitative acceptable GC \times GC–qMS chromatograms were obtained. About 125 components, including alkanes, alkenes, aromatics, oxygenated and halogenated hydrocarbons were identified from the standard gas mixtures and/or air samples. Based on the careful comparison of GC \times GC–qMS and GC \times GC–FID, the equivalent peaks between the two chromatograms were matched one to one. After the initial assist from GC \times GC–qMS, the subsequent qualitative analysis of GC \times GC–FID can be carried out by its own retention times, and the GC \times GC–FID chromatogram obtained at 100 Hz facilitates the quantitative analysis more accurately.

2. Experimental

2.1. Instruments and materials

The system for VOC analysis is composed of a two stage thermal desorber with an autosampler (UNITY/Ultra, Markes International Corporation, UK) and a gas chromatograph with MS/FID detection (GC–MS 6890N/5973i, Agilent Technologies, USA). To realize GC \times GC separation, the GC was retrofitted with a loop modulated GC \times GC system (KT2004, Zoex Corporation, USA). A 175-L high-pressure liquid nitrogen Dewar (XL-45, Taylor-Wharton Corporation, Malaysia) and an air compressor (DA5001D, Shanghai Dynamic Industry Co. Ltd., China) were used in combination with valves, pulse controller, heat exchange Dewar, etc., to produce cold and hot jets. The commercial pulse controller was reprogrammed, and its connection with the GC and thermal desorber was optimized to make pulse controlling more flexible and to synchronize the first modulation pulse with a certain time point after the sample injection and GC start. The synchronization can reduce the drift of retention times of VOC species on the GC \times GC chromatogram.

An HP-5MS fused silica capillary column (30 m \times 0.25 mm i.d. \times 1.0 μ m film, Agilent Technologies) and an HP-INNOWAX fused silica capillary column (2.5 m \times 0.18 mm i.d. \times 0.18 μ m film, Agilent Technologies) were used as the primary (1st dimension) and the secondary (2nd dimension) columns, respectively. A deactivated fused silica tube (1.7 m \times 0.1 mm, Agilent Technologies) was used to connect the 1st and 2nd columns and modulated by the cold and hot jets. A separate second oven housed in the GC oven was used to produce a temperature program for the 2nd column different from that for the 1st column.

In this study, both standard and air samples were tested in the separation and identification experiments. The samples were collected using stainless steel (Silcosteel coating) thermal desorption tubes prepacked with Carbograph 5TD and Carbograph 2TD (Markes International Corporation, UK), which can effectively trap organics from C₃ to C₂₀. The VOC standards tested include the Photochemical Assessment Monitoring Stations (PAMS, <http://www.epa.gov/ttn/amtic/pamsmain.html>) target list of VOCs containing 56 components (60/100 ppbC, Scott Specialty Gases, USA) and the TO-15 [43] standard containing 65 components (1 ppm, Linde Spectra Environmental Gases, USA). High purity ($\geq 99.999\%$) helium, nitrogen, hydrogen, and synthetic air (Beijing Chengweixin Gases Ltd., China) were used in the experiments. For the air sampling, an ozone scrubber (a stainless steel tube packed with anhydrous sodium sulfite and pre-purged by high purity nitrogen at 200 °C for 2 h) was installed in the front of the sampling inlet to prevent the possible reaction of VOCs with ozone.

2.2. Sample collection

Before sampling, the sample tubes were purged by high purity nitrogen gas while heated successively to 100 °C, 200 °C, 300 °C, and 325 °C, and kept for 15 min at each temperature stage. Standard VOCs mixtures were introduced onto the sample tubes either directly or after dilution with high purity nitrogen. A mass flow controller (GFC17, Aalborg Instruments & Controls Inc., USA) was used to control the flow rate. Air sampling was done on the roof of the Chinese Academy of Meteorological Sciences (39°56'N, 116°24'E), approximately 50 m high. The site represents the typical urban environment of Beijing [44]. Ambient air was drawn at 80 mL min⁻¹ through the sample tubes using a pump with an internal mass flow controller (FLEC1001, Markes International Corporation, UK). About 3 L air was accumulated for each air sample. After the sampling, the tubes were sealed with brass caps with PTFE ferrules and stored in a refrigerator until analysis.

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