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Frontier review on comprehensive two-dimensional gas chromatography for measuring organic aerosol



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ABSTRACT

Organic aerosol (OA) is a key component of atmospheric fine particles and can be composed of thousands of organic species, creating an analytical challenge to separate and identify such highly complex mixtures. Traditional offline one-dimensional gas chromatography, mostly separating molecules based on volatility, provides valuable information on the composition of OA, but is limited by insufficient separation and low peak capacity. Since its introduction in 1990s, comprehensive two-dimensional gas chromatography (GC × GC), which separates molecules by both volatility and polarity, has become an effective tool to determine the OA composition through its high molecular separation resolution and high peak capacity. Both online and offline GC × GC analyses have been applied to study OA, which extended the identification of unknown compounds and the quantification of a larger range of target compounds. Here, we review the studies using GC × GC for analyzing OA from both the ambient environment and source emissions. GC × GC coupled with mass spectrometry provides a variety of novel analysis methods, demonstrating the power of GC × GC analyzing complex aerosol samples. The development of online technologies in recent years helps to capture the dynamic temporal variations of atmospheric OA due to changes in source emissions as well as atmospheric secondary formation and meteorology.

1. Introduction

Atmospheric aerosols affect air quality, climate change, and human health (Andreae and Crutzen, 1997; Monks et al., 2009; Pope et al., 2002; Dingenen et al., 2004; Charlson et al., 1992; Lelieveld et al., 2015), within which organics can comprise over half of the total fine particulate mass (Andreae and Crutzen, 1997; Dingenen et al., 2004; Kanakidou et al., 2005; Zhang et al., 2011). Atmospheric organic aerosols (OA) are either directly emitted from biogenic and anthropogenic sources (e.g., fossil fuel combustion, biomass burning, and industrial processes) or formed in the atmosphere (secondary organic aerosol, SOA) by condensation and heterogeneous and homogeneous reactions (Jimenez et al., 2009). Measuring the chemical composition of atmospheric OA can help to quantify their origins and environmental effects.

Measurement of OA chemical composition poses an analytical challenge. There can be tens-of-thousands of different compounds present in a small sample of OA (Hamilton et al., 2004), and those compounds have a broad diversity of molecular size and functionality,

resulting in a wide range in their physicochemical properties (e.g., volatility and polarity). Additionally, the highly dynamic nature introduced by the variability of emission intensities, atmospheric reactions, and meteorological conditions adds further challenges (Jimenez et al., 2009; Hallquist et al., 2009). Analytical methods with high chemical and time resolution are required for a comprehensive characterization of OA.

Gas chromatography (GC) coupled with a detection technique, often mass spectrometry (MS) or flame ionization detection (FID) (Snyder, 2004), is capable of separating and detecting organics at the molecular level according to their volatility or polarity, thus providing structural formulae of the OA chemical composition, especially semi-volatile and low volatility organic species (Schauer et al., 2002, 1999). However, conventional one-dimensional GC usually suffers from insufficient separation when detecting complex OA samples, resulting in co-elution of compounds and unresolved complex mixtures (UCM) (Fraser et al., 1997).

Comprehensive two-dimensional gas chromatography (GC × GC), a multidimensional GC technique first introduced by Liu and Phillips three

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decades ago (Liu and Phillips, 1991), has advantages in unraveling the complex chemical composition of organic compounds in the atmosphere. GC \times GC was originally applied for complex fuel sample analysis (Liu and Phillips, 1991) until its first application for analyzing volatile organic compounds in the atmosphere in 2000 (Lewis et al., 2000). Over time it has been increasingly utilized as a method to better separate the complex organic matrix of OA. Two columns with different polarities (referred to as the ¹D column and the ²D column, respectively) are connected in series by a modulator for GC \times GC analysis. The modulator is used to periodically transfer fractions of analytes from the ¹D column effluent to the ²D column. Analytes that cannot be separated in the ¹D column due to a similar physiochemical property have the opportunity to be separated in the ²D column based on differences in other properties (Prebihalo et al., 2018). Compared to one-dimensional GC (1D GC), GC \times GC has advantages, such as higher chemical resolution, higher peak capacity and structured chromatograms with organic classes regularly distributed (Liu and Phillips, 1991; Blumberg et al., 2008). In recent years, GC \times GC has been improved in instrumentation, method optimization, and data processing (Prebihalo et al., 2018; Górecki et al., 2004; Adahchour et al., 2008; Tranchida, 2018; Shi et al., 2014).

GC \times GC coupled with MS provides full mass spectra of compounds with additional molecular separation, and thus enables various data processing methods, including target analysis, group-type analysis, and nontarget analysis (Dallüge et al., 2003). The latter two are rarely used in 1D GC due to its insufficient peak capacity. Target analysis is used specifically for analytes (identified using authentic standards) with known retention times and mass spectra as can be performed in 1D GC. Nontarget analysis is used to obtain an overall understanding of samples, including identification, classification, and quantification. Group-type analysis is used to fingerprint specific organic classes. These data processing methods have all been applied in GC \times GC–MS measurements of OA.

This study briefly reviews the application of GC \times GC for measuring OA in the atmosphere and from emission sources. Both offline and online measurements of OA by GC \times GC are discussed. Several data processing methods are presented to illustrate the advantages of OA analysis by GC \times GC compared with conventional 1D GC. In addition, challenges for analyzing atmospheric OA are discussed.

2. Experimental methods

2.1. Modulation

As shown in Fig. 1, a modulator is the key component of the GC \times GC. Based on modulation principles, modulators can be categorically divided

into thermal modulators and flow modulators (Tranchida, 2018). The thermal modulator has been extensively applied for measuring atmospheric aerosols (Hamilton, 2010). It captures effluents from the ¹D column at a lower temperature relative to the ¹D column and then releases them into the ²D column at a higher temperature (Prebihalo et al., 2018; Tranchida, 2018). Various refrigeration technologies have been used to achieve low-temperature capture, including cryogenics (Kallio et al., 2003a, 2008), heat exchangers (Libardoni et al., 2005, 2010; Panić et al., 2011), and semiconductor refrigeration (Luong et al., 2016). In recent years, consumable-free thermal modulators have been applied for online field measurements of OA due to their relatively good portability and low cost (An et al., 2020; Worton et al., 2012; Goldstein et al., 2008). Flow modulation or valve-based modulation is achieved by flushing effluent from the ¹D column to the ²D column through valve switching (Bueno and Seeley, 2004; Bruckner et al., 1998). However, its application in aerosol measurement is limited because of the high carrier gas flow rate required in the ²D column to quickly flush the sampling loop, which leads to difficulties in connecting the system with MS detectors (Tranchida, 2018).

2.2. Analytical methods

The analysis of atmospheric aerosol samples follows the sequence of pretreatment, vaporization, two-dimensional separation, ionization (for MS), and detection. Fig. 1 shows the instrumentation schematics of GC \times GC for analyzing OA. The pretreatment of off-line samples, e.g., solvent extraction, is usually time-consuming and can lead to elevated contamination and sample losses. The off-line pretreatment and vaporization can be replaced by online direct thermal desorption which directly introduces samples into the GC columns. With all thermal desorption methods, there is possibility for some decomposition of thermally labile species (Williams et al., 2016) and matrix effects (Lambe et al., 2010), but for a wide range of chemical species this method preserves the original structural information which is beneficial for nontarget analysis (Schnelle-Kreis et al., 2005; Özel et al., 2011; Waterman et al., 2000). For GC \times GC separation, a long nonpolar column (e.g. 30 m) and a short polar or medium-polarity column (generally 1–2 m) are usually used for the ¹D column and the ²D column, respectively. Such an arrangement dominantly separates molecules by volatility in the first dimension and polarity in the second dimension. Modulation frequency is set to obtain a significant number of slices across each compound as it elutes from the ¹D column in order to maintain the separation accomplished in the first dimension. Thus, separation across the second dimension requires fast separation through a shorter column.

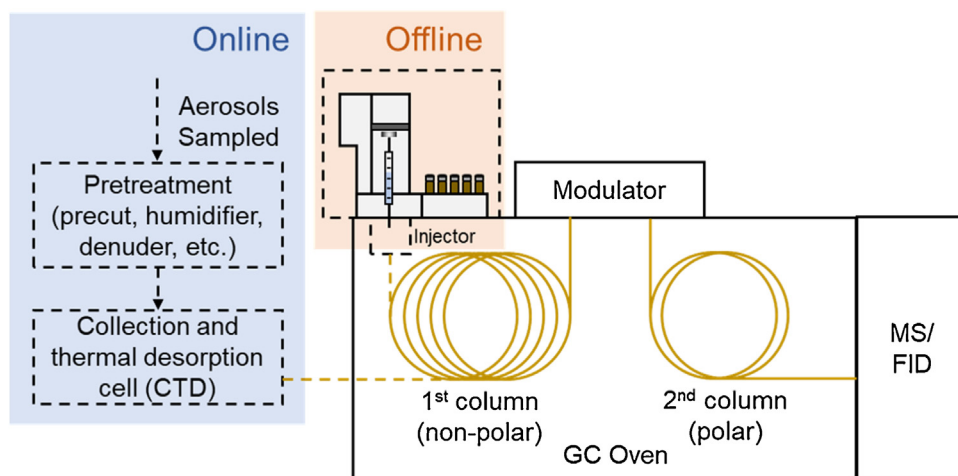


Fig. 1. Schematics of online and offline analysis of organic aerosol using comprehensive two-dimensional gas chromatography systems. Other offline technologies such as direct thermal desorption are not shown here. Offline aerosol samples are usually prepared by aerosol sample collection, extraction and derivatization, and then introduced to the GC \times GC through the injector.

For ionization, 70 eV electron ionization (EI) and soft ionization technologies (e.g. vacuum ultraviolet photoionization (Worton et al., 2017)) are often used. In recent years, GC \times GC with combined ionization technologies of 70 eV and lower energies (e.g. 10.5 eV) has been exploited for the identification of compounds in atmospheric aerosols (Worton et al., 2017; Xu et al., 2020a). Lower ionization energies reduce the fragmentation and increase the intensity of the molecular ion and thus improve the confidence in compound identification such as distinguishing isomers and aliphatic homologues (Alam et al., 2016a). Various detectors, including quadrupole mass spectrometry (Kallio et al., 2003b), time of flight mass spectrometry (Hamilton et al., 2004; Welthagen et al., 2003; Zhang et al., 2018), flame ionization detection (Lyu et al., 2017; Xu et al., 2015), nitrogen phosphorus detection (Ochiai et al., 2007), and nitrogen chemiluminescent detection (Öezel et al., 2011), have been utilized in tandem with GC \times GC for qualitative and quantitative analysis of atmospheric OA.

3. Offline measurement of organic aerosol

3.1. Atmospheric measurement

GC \times GC has been employed in measuring atmospheric OA at urban (Hamilton et al., 2004; Schnelle-Kreis et al., 2005; Öezel et al., 2011; Kallio et al., 2003b; Welthagen et al., 2003; Lyu et al., 2017; Xu et al., 2015; Vogt et al., 2007; Öezel et al., 2010; Alam et al., 2013; Chan et al., 2013; Choi et al., 2017; Lyu et al., 2019a, b; Jang et al., 2020; Lyu et al., 2019c), forested (Worton et al., 2017; Zhang et al., 2018; Kallio et al., 2006; Ruiz-Jiménez et al., 2011), and roadside sites (Xu et al., 2020a; Ochiai et al., 2007; Lyu et al., 2019c; Xu et al., 2020b) around the world. Offline analysis of total suspended particles (Kallio et al., 2003b, 2006), PM_{2.5} (particulate matter with aerodynamic diameter (AD) \leq 2.5 μ m) (Hamilton et al., 2004; Schnelle-Kreis et al., 2005; Öezel et al., 2011; Worton et al., 2017; Xu et al., 2020a; Welthagen et al., 2003; Xu et al., 2015; Vogt et al., 2007; Öezel et al., 2010; Alam et al., 2013; Chan et al., 2013; Choi et al., 2017; Lyu et al., 2019a, b; Jang et al., 2020; Xu et al., 2020b; Timkovsky et al., 2015), PM₁ (AD \leq 1 μ m) (Zhang et al., 2018), ultrafine particles (AD \leq 0.1 μ m) (Ruiz-Jiménez et al., 2011), and size resolved aerosols (Lyu et al., 2017; Ochiai et al., 2007) has been conducted both qualitatively and quantitatively.

Thousands of compounds have been detected in atmospheric OA and the positions of compound classes in the structured two-dimensional chromatograms have significant similarities across studies (Welthagen et al., 2003; Vogt et al., 2007; Weggler et al., 2019; Piotrowski et al., 2018). As shown in Fig. 2, compounds are partitioned into aliphatic and aromatic areas based on volatility and polarity. Homologues or compounds with similar properties occur as strip-shaped areas in the

two-dimensional chromatogram with increasing molecular size correlating with later retention times. The relative positions of different organic classes ratchet up in the second dimension of the chromatogram as the polarity increases gradually. Therefore, it is possible to roughly characterize the categories of compounds simply by the structure of the two-dimensional chromatogram. Detected compounds in atmospheric aerosols are from both primary emissions (e.g. alkanes, siloxanes, hopanes, steranes, and PAHs) and secondary formation (e.g. furanones, ketones, oxy-PAHs and pinic acid from α -pinene oxidation). Many of them contribute to the toxicity of atmospheric aerosols (Kishida et al., 2011; Pflieger and Kroflič, 2017; Li et al., 2020). In addition, these compounds can serve as organic tracers for source apportionment. For example, PAHs and hopanes are tracers for fossil fuel combustion and vehicle emissions, respectively.

Compared with 1D GC, GC \times GC increases the number of detected compounds by more than an order of magnitude (Blumberg et al., 2008; Hamilton, 2010). Thousands of peaks can be detected in GC \times GC, most of which would be co-eluted in 1D GC, leading to analytical difficulties. 1D GC resolved 409 peaks while GC \times GC resolved 1691 peaks when analyzing a PM_{2.5} sample from Beijing (An et al., 2020). As shown in Fig. 3, more than 86 % of the 1D GC peaks had significant co-elutions (An et al., 2020). The number of co-eluted peaks ranged from 1 to 12, among which 1–6 was the most frequent (\sim 78 %). Consequently, GC \times GC can separate the co-eluted peaks beyond 1D GC, so as to identify more compounds in OA (Alam et al., 2013).

3.1.1. Target analysis

GC \times GC is capable of improving the accuracy of the quantification of target compounds by reducing the overestimation resulting from co-elution. Our previous study showed that co-elution influenced not only the total but also the selective ion chromatogram using quantitative ions (An et al., 2020). For n-alkanes, up to 40 % of the overestimation in peak intensities was due to co-elution in 1D GC (An et al., 2020). Target analysis using external or internal standards has been widely applied for quantifying atmospheric aerosol composition (Kallio et al., 2003b; Zhang et al., 2018; Lyu et al., 2017, 2019a; Lyu et al., 2019b, c; Timkovsky et al., 2015; Jen et al., 2019; Hatch et al., 2019). Targeted organics have expanded to include almost the entire range of detected compounds, including alkanes, aldehydes, 2-ketones, PAHs, and oxy-PAHs.

3.1.2. Nontarget analysis

Nontarget analysis has been operated to identify and quantify unknown compounds within atmospheric OA. Identification is generally based on library match using retention index and mass spectra. The composition of OA was found to be distinct in different atmospheric environments. Forest aerosols are composed of more components from

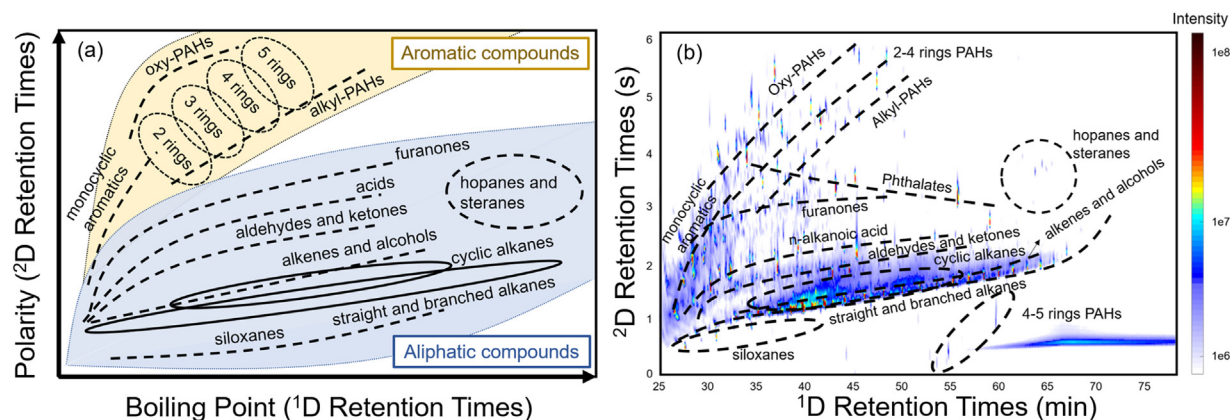


Fig. 2. (a) Conceptual two-dimensional chromatograms of atmospheric organic aerosol. Relative positions of organic classes are presented based on the nonpolar-polar column set. Common but not shown compounds include nitriles, fatty acid methyl esters, and phthalate esters. (b) Two-dimensional chromatograms of atmospheric PM_{2.5}. This sample was collected in Beijing on March 23, 2018. Details of the measurement can be found in a previous study (An et al., 2020).

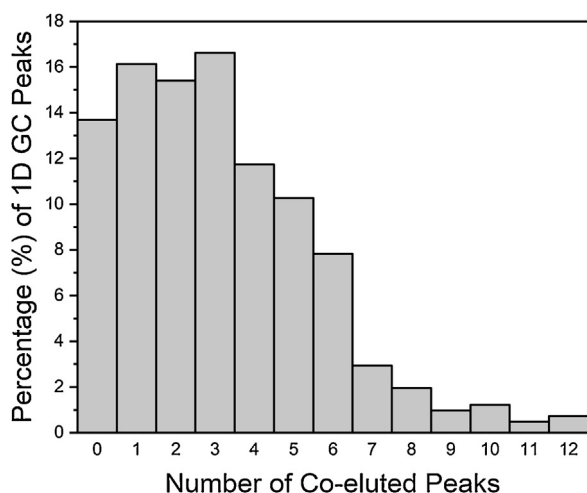


Fig. 3. Percentages of peaks in one-dimensional gas chromatography (1D GC) with different numbers of co-eluted peaks (as determined by GC \times GC analysis). Only \sim 14 % peaks in 1D GC have no obvious co-elutions. This atmospheric PM_{2.5} sample was collected in Beijing on March 16, 2018. Details of the measurement can be found in a previous study (An et al., 2020).

biogenic sources (Zhang et al., 2018; Kallio et al., 2006), while urban aerosols are dominated by components from road traffic, industry and consumer products (Alam et al., 2013). Significant nitrogen-containing compounds were found in urban OA (Özcel et al., 2011, 2010).

Quantifying nontarget compounds is also possible and can extend the range of identified compounds to the whole chromatogram. The relative response factor of each compound is related to its polarity and volatility. Based on authentic standards covering a wide range of polarity and volatility on the chromatogram, the relative response factor of this range can be determined as a function of carbon and double bond number (Zhang et al., 2018; Chan et al., 2013). This calibration has been used to quantify the concentration of UCM and secondary OA from monoterpene oxidation (Zhang et al., 2018; Chan et al., 2013). The uncertainty of this method can reach \sim 40 % when using different fitting functions. Also, there may be cases where a molecular formula can be identified by nontarget analysis, but an exact molecular structure cannot be confirmed. By matching such compounds to specific sources and including them in customized databases, they can still be utilized in source identification practices (Worton et al., 2017).

3.1.3. Group-type analysis

Visualizing organic groups enhances the understanding of unknown samples. Extracting target groups in atmospheric aerosols is based on fragmentation patterns in mass spectral data and the ¹D and ²D retention times of analytes in GC \times GC. Compounds with specific organic classes, particular elements, and functionalities, which include alkanes, alkenes and cycloalkanes, fatty acids, and various aromatic compounds, can be automatically extracted and classified with high accuracy (Hamilton et al., 2004; Welthagen et al., 2003; Vogt et al., 2007; Reichenbach et al., 2005). For example, Xu et al. Xu et al. (2020a, b) used a grouping extraction software (Reichenbach et al., 2005) and molecular ions for formula identification to assign individual compounds to specific organic groups or functionalities. Meanwhile, groups of isomers were quantified by authentic standards with the same carbon number or functionality (Alam et al., 2018).

3.2. Emission source measurement

GC \times GC has been applied to analyze OA from various sources, such as biomass burning (Jen et al., 2019; Hatch et al., 2019, 2018), motor

vehicle exhaust (Alam et al., 2018; Fushimi et al., 2012; Weggler et al., 2014; Alam et al., 2016b, 2019; Worton et al., 2014), and tobacco aerosols (Savareear et al., 2019). For biomass burning aerosols, chemical fingerprints obtained by GC \times GC showed significant diversity for different fuel types (Hatch et al., 2018). Among hundreds of compounds in biomass burning aerosols (Jen et al., 2019), catechol is the dominant compound in most samples, while hydroquinone is the dominant compound only in manzanita smoke (Hatch et al., 2018). For diesel exhaust aerosols, organic classes like alkanes, esters, ethers, substituted benzenes, PAHs, oxy-PAHs, nitro-PAHs, and methyl-PAHs were separated and determined (Alam et al., 2018; Fushimi et al., 2012; Weggler et al., 2014; Alam et al., 2016b, 2019). For tobacco emitted aerosols, hydrocarbons, oxygenated, nitrogen-containing, and miscellaneous organic groups have been identified (Savareear et al., 2019). In addition, GC \times GC can also be used to characterize indoor aerosols that are often contributed by both indoor emission sources and outdoor atmosphere.

4. Online measurement of organic aerosol

In recent years, online GC \times GC technologies for measuring OA have been developed to capture the temporal variability of atmospheric aerosols (An et al., 2020; Worton et al., 2012; Goldstein et al., 2008). Online GC \times GC for measuring OA is an improved version of one-dimensional Thermal desorption Aerosol GC-MS (TAG) with enhanced separation by an additional dimension (An et al., 2020; Worton et al., 2012; Goldstein et al., 2008). Fig. 1 shows the schematic of the online GC \times GC system (2D-TAG, two-dimensional TAG). Both 2D-TAG and TAG are capable of speciating OA in-situ at the molecular level with hourly time resolution (Williams et al., 2006). They combine a collection and thermal desorption cell (CTD) with GC \times GC-MS or GC-MS. The CTD provides aerosol sampling and in situ thermal desorption for subsequent analysis. Studies have developed CTDs based on impactors (Williams et al., 2006), metal filters (Zhao et al., 2013), and quartz filters (Cropper et al., 2017; Ren et al., 2019a, b).

The development of consumable-free and miniaturized modulators is an important prerequisite for online measurement of OA. Air-cooled thermal modulators with two-stage or single-stage modulation, achieved by alternatively heating the adjacent two areas of the air-cooled trapping capillary (Harynuk and Górecki, 2002), have been utilized for 2D-TAG systems (Worton et al., 2012; Goldstein et al., 2008). This type of modulator requires no cryogenics for trapping analytes, and thus improves the instrument portability. Recently, a solid-state thermal modulator with a miniaturized design and no requirement for cryogenics and compressed air was used for online field measurement (An et al., 2020). It uses a thermoelectric cooling device (Luong et al., 2016). Combined with a quartz filter-based TAG (Ren et al., 2019a, b), it achieved high precision of retention times and peak area with low limits of detection (An et al., 2020).

2D-TAG has been employed in field measurements of atmospheric OA and laboratory-generated aerosols (An et al., 2020; Worton et al., 2012; Goldstein et al., 2008; Isaacman et al., 2011). Hourly resolved (down to 1–2 h) chemical composition of atmospheric aerosols was obtained. Three-dimensional diagrams of ambient aerosol measurement during one day showed temporal changes in the intensity of different organic bands (Goldstein et al., 2008). Organic classes including furanones and pyranones, (alkyl-, oxy-) PAHs, phthalate esters, nitriles, ketones, aldehydes, alcohols, alkenes, hopanes, steranes, alkanes, phthalic acid, fatty acids, methylated fatty acid esters, alkyl-benzenes, chlorobenzenes, phthalimide, and amines were identified (An et al., 2020; Worton et al., 2012). The daily variation in C13-C40 n-alkane concentrations and relative contributions of emission sources were measured which provides more precise source and atmospheric chemical reaction tracking (An et al., 2020). 2D-TAG has been applied to understand the evolution of longifolene ozonolysis products and volatility distribution (Reichenbach et al., 2019). Ongoing developments of online multi-dimensional

separation systems have explored the utilization of shortened GC columns to force higher throughput of underivatized oxygenated organics. This method makes use of high-resolution mass spectrometry and advanced data processing methods (e.g. positive matrix factorization) to extend the multi-dimensional separation and identification of OA components (Martinez et al., 2016).

5. Summary and outlook

Comprehensive two-dimensional gas chromatography has been used for measuring complex OA. Compared to 1D GC, thousands of additional peaks can be detected by GC × GC with an increased peak capacity of more than an order of magnitude. Multifarious aliphatic and aromatic compounds are identified, many of which are undetectable in 1D GC due to co-elution. For target analysis, GC × GC can reduce the overestimation resulting from co-elution in 1D GC. Nontarget screening and group-type analysis provide rapid and efficient characterization of unknown samples. Chemical compositions resolved by different data processing methods demonstrate the advantages of the GC × GC in the analysis of complex aerosol samples.

Online GC × GC technologies have been demonstrated as an effective method for in-situ molecular level measurement of OA. They enable high-resolution speciation of OA with hourly time resolution. Accordingly, the variations of atmospheric processes and emission sources can be tracked.

Looking forward, GC × GC will be further improved and be widely used in online and offline OA measurements. This requires fast and robust analysis methods to process large amounts of data. Conventional target data processing methods are time-consuming and labor-intensive. New techniques such as machine learning may be capable of addressing these challenges (Reichenbach et al., 2019) and generating nontargeted features automatically. Besides, improvements are needed in method optimization with various operation parameters.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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