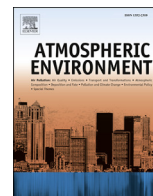




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## Using multidimensional gas chromatography to group secondary organic aerosol species by functionality

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### HIGHLIGHTS

- We developed a GC × 2GC retention diagram for 130 SOA species.
- Retention indices were estimated using the Abraham solvation parameter model.
- A DB-210/BPX90/SolGel-WAX column arrangement provided the best separation.
- A GC × 2GC retention diagram is essentially a carbon number-functionality grid.
- Multidimensional gas chromatography is a promising technique for SOA analysis.

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### ABSTRACT

A carbon number-functionality grid (CNFG) for a complex mixture of secondary organic aerosol (SOA) precursors and oxidation products was developed from the theoretical retention index diagram of a multidimensional gas chromatographic (GC × 2GC) analysis of a mixture of SOA precursors and derivatized oxidation products. In the GC × 2GC analysis, comprehensive separation of the complex mixture was achieved by diverting the modulated effluent from a polar primary column into 2 polar secondary columns. Column stationary phases spanned the widest range of selectivity of commercially available GC analytic columns. In general, separation of the species by the polar primary column was by the number of carbon atoms in the molecule (when the homologous series of reference compounds was selected to have molecular volumes and functionalities similar to the target analytes) and the polar secondary columns provided additional separation according to functionality. An algebraic transformation of the Abraham solvation parameter model was used to estimate linear retention indices of solutes relative to elution of a homologous series of methyl diesters on the primary and secondary columns to develop the theoretical GC × 2GC retention diagram. Retention indices of many of the oxidation products of SOA precursors were estimated for derivatized forms of the solutes. The GC stationary phases selected for the primary column [(50%-Trifluoropropyl)-methylpolysiloxane] and secondary columns (90% Cyanopropyl Polysilphenylene-siloxane and Polyethylene Glycol in a Sol-Gel matrix) provided a theoretical separation of 33 SOA precursors and 98 derivatized oxidation products into 35 groups by molecular volume and functionality. Comprehensive analysis of extracts of vapor and aerosol samples containing semivolatile SOA precursors and oxidation products, respectively, is best accomplished by (1) separating the complex mixture of the vapor and underivatized aerosol extracts with a (50%-Trifluoropropyl)-methylpolysiloxane × 90% Cyanopropyl Polysilphenylene-siloxane × Polyethylene Glycol in a Sol-Gel matrix arrangement and (2) derivatizing the aerosol extract and reanalyzing the sample on the GC × 2GC column combination. Quantifying groupings and organic molecular species in time series of collections of vapor- and aerosol-phase atmospheric organic matter is a promising analytic technique for measuring production of SOA and evaluating transformations of SOA precursors.

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## 1. Introduction

Organic aerosol (OA) is a complex mixture of thousands of organic species directly emitted to the atmosphere and formed through oxidation of emissions of gaseous hydrocarbons of anthropogenic and biogenic origin (Hallquist et al., 2009). Primary OA (POA) is a complex mixture of alkanes, alkanols, alkanals, alkanoids and alkenoic acids, saccharides, steroids, and polyaromatic hydrocarbons (PAHs) with varying degrees of alkylation (Rogge et al., 1993; Graham et al., 2003; Simoneit et al., 2004). Molecular markers and homolog distributions of the compound classes are characteristic of biogenic and anthropogenic sources (Doskey and Andren, 1986; Simoneit et al., 2004). Precursors of secondary organic aerosol (SOA) include volatile organic compounds (VOCs) like terpenes and terpenoids emitted by vegetation (Geron et al., 2000; Guenther et al., 2006) and monoaromatic hydrocarbons from vehicle exhaust (Lewis et al., 2000; Hamilton and Lewis, 2003), and vapor-phase, semivolatile organic compounds (SVOCs) composed of C<sub>11</sub>–C<sub>31</sub> normal, branched, and cyclic hydrocarbons emitted by gasoline- and diesel-powered vehicles (Schauer et al., 1999, 2002) and through evaporation of gasoline and diesel fuels (Gentner et al., 2012). Reactions of VOCs and vapor-phase SVOCs with hydroxyl (OH) and nitrate (NO<sub>3</sub>) radicals and ozone (O<sub>3</sub>) are dependent on molecular structure and produce a complex mixture of SOA species with nitrate (–ONO<sub>2</sub>), carboxylic acid (–COOH), alcohol (–OH), and carbonyl (C=O) functionalities and multi-functionalities (Hallquist et al., 2009).

Disagreements exist between model forecasts of SOA formation and field measurements of SOA yields and in identifying precursors and elucidating transformation pathways for locations with complex sources of SOA precursors (Heald et al., 2005; de Gouw et al., 2005; Johnson et al., 2006; Volkamer et al., 2006; Kleinman et al., 2008; Dzepina et al., 2009; Matsui et al., 2009; Hodzic et al., 2010; Tsimpidi et al., 2010; Ensberg et al., 2014). By including vapor-phase, semivolatile aliphatic and aromatic hydrocarbons in chemical mechanisms of SOA formation models discrepancies have been reduced; however, large differences remain between measured and modeled SOA (Hodzic et al., 2010; Dzepina et al., 2011). Modeling approaches that constrain OA composition by relative abundances of carbon (C), hydrogen (H), and oxygen (O) atoms (Jimenez et al., 2009; Heald et al., 2010), average C oxidation state (Kroll et al., 2011) and physicochemical properties (Pankow and Barsanti, 2009; Barsanti et al., 2011) estimated by, e.g., group contribution methods have been proposed to manage the complexity of OA species and to estimate yields of chemically, nonspecific SOA products. The two-dimensional volatility basis set (2D-VBS) framework constrains OA composition by C:O and the saturation vapor concentration of the oxidized species (Donahue et al., 2011). The carbon number-polarity grid (CNPG) approach uses the number of C atoms in the molecule ( $N_C$ ) and 20 values of total molecular polarity (tmp) of the oxidized species to characterize oxidation products (Pankow and Barsanti, 2009; Barsanti et al., 2011). Model predictions of SOA yields have been compared with chemically non-specific measurements of 2 oxygenated OA species by high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS; Zhang et al., 2007; Li et al., 2013); however, disagreements between modeled and measured SOA yields are large (Dzepina et al., 2009). Forecasts of SOA yields might be improved through organic molecular measurement of volatile and semivolatile SOA precursors in emissions and oxidation products in aerosol.

Molecular structure (i.e., normal, branched, cyclic) and functionality (e.g., unsaturated carbon bonds, –COOH, –OH, C=O, –ONO<sub>2</sub>) of OA species provide information on the origin, oxidation pathways leading to formation and evolution, and activity in

forming aerosol and as cloud condensation nuclei (Hemming and Seinfeld, 2001; Pankow, 1994; Pankow and Barsanti, 2009). However, comprehensive separation and identification of OA molecular species by gas- or liquid-chromatographic approaches coupled with various mass spectrometric detection techniques have proven difficult (Hallquist et al., 2009). Multidimensional gas chromatography (GC) is a comprehensive separation technique that resolves complex mixtures of organic compounds according to molecular volume, structure, and functionality (Seeley et al., 2001; Hamilton, 2010; Seeley and Seeley, 2013). In a GC × 2GC analysis, superior separation compared to one-dimensional GC is achieved by diverting equal volumes of the modulated effluent, typically from a non-polar primary column, which separates organic species through solute interactions with the stationary phase associated with molecular volume, into 2 polar secondary columns with unique selectivity that separate species via interactions of the solute functional groups with the stationary phases (Seeley et al., 2000). Functionality adds volume to the solute molecule and influences interactions with the GC stationary phase; however, including a homologous series of solutes with functionalities as reference compounds that are similar to the target analytes generally preserves elution order according to  $N_C$  in the chromatographic analysis (Yabumoto et al., 1977). Thus, primary and secondary columns can be selected to separate species primarily by  $N_C$ , which is a proxy for molecular volume, and by functionality, respectively, essentially making a GC × 2GC retention diagram a carbon number-functionality grid (CNFG). A shortcoming of OA analysis by GC techniques is non-quantitative transfer of mono- and multi-functional carboxylic acids, polyols, and organic peroxides through the GC system due to intermolecular interactions of the analytes with surfaces (Jennings, 1980). However, a multistep derivatization technique has been reported, which converts surface-active moieties of solutes into unique and identifiable products that are quantitatively transferred through GC systems (Kowalewski and Gierczak, 2011).

Seeley and Seeley (2007) and Seeley et al. (2009) analyzed homologous series of VOCs with various structures and mono-functionalities by GC × GC (i.e., multidimensional GC using one secondary column) and developed a model (hereafter referred to as the Seeley model) to predict retention index diagrams. The Seeley model is useful for selecting columns to optimize separation of complex mixtures by multidimensional GC analyses. The basis of the Seeley model is an algebraic transformation of the Abraham solvation parameter model, which is used to estimate linear retention indices and to develop theoretical retention diagrams for GC × GC applications that involve linear temperature-programmed operation of the GC oven (Seeley et al., 2009). The Abraham solvation parameter model is an empirical model that accounts for intermolecular interactions during partitioning of molecules between phases in, e.g., a GC column (Abraham, 1993; Abraham et al., 2004). Estimated and measured descriptors that can be used to derive GC retention factors are available for a large number of solutes and GC stationary phases (Abraham, 1993; Abraham et al., 2004; Poole and Poole, 2008a). Good agreement was observed between theoretical and experimental retention diagrams for a complex mixture of volatile mono-functional solutes (Seeley et al., 2009). However, differences were observed between measured linear and isothermal (140 °C) retention indices for cyclic hydrocarbons (Beens et al., 1998; Seeley and Seeley, 2007). Secondary OA (SOA) consists of a complex mixture of linear, branched, and cyclic hydrocarbons with mono- and multi-functionalities. Comparison of the very few measurements of solute descriptors for bi-functional species with values estimated by assuming additive behavior of functional groups indicates much poorer agreement for diols and diones than diesters (Goss et al., 2009).

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