

MichiganTech Managing the Complexity of Secondary Organic Aerosol Species Produced by Forest Emissions

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1. Introduction.

On a global scale, plants emit $\sim 1,000 \pm 600$ Tg/yr of volatile organic compounds (VOCs)¹. Isoprene (500 Tg C/yr) and monoterpenes (126 Tg C/yr) are the dominant BVOCs emitted by vegetation on a global scale^{2,3}. Sesquiterpenes are very reactive and emission rates are highly uncertain. Terpene emissions are related to leaf temperature, light intensity and other parameters such as herbivore attack⁴. Terpenes are composed of a mixture of thousands of species that are oxidized in the atmosphere by O₃, OH and NO₃ forming secondary organic aerosols (SOAs) with various functionalities that uniquely influence physicochemical properties of SOA like the uptake of water. The SOAs interact with solar radiation and change the properties of clouds which influence climate change.

Current SOA models are based on: (1) grouping compounds according to volatility into approximately 15 bins while ignoring functionality, and (2) considering all reactions of SOA precursors and the thousands of reactions of their oxidation products. Chang and Pankov⁵ developed a SOA formation model that considers the chemistry of compounds grouped according to functionality. Here we propose comprehensive multi-dimensional gas chromatography (GC \times 2GC) as an analytical technique to separate compounds in aerosol samples according to functionality. A GC \times 2GC retention index diagram is essentially a carbon number-functionality grid (CNFG), which can be used to manage the complexity of biogenic SOA.

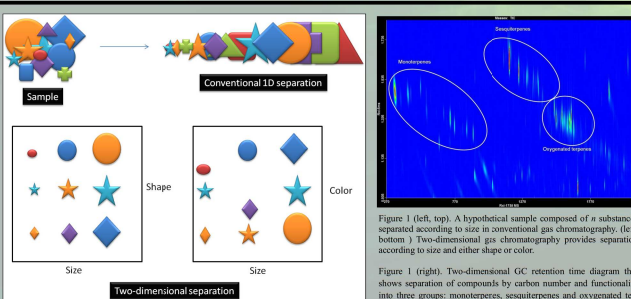


Figure 1 (left, top). A hypothetical sample composed of *n* substances separated according to size in conventional gas chromatography. (left, bottom) Two-dimensional gas chromatography provides separation according to size and either shape or color. Figure 1 (right). Two-dimensional GC retention time diagram that shows separation of compounds by carbon number and functionality into three groups: monoterpenes, sesquiterpenes and oxygenated terpenes.

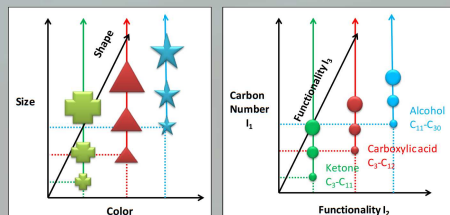


Figure 2 (left). The substances that compose the hypothetical sample in Figure 1 are separated according to size, shape and color in a three-dimensional diagram. (right). A three-dimensional retention index diagram (GC \times 2GC) composed of a primary column that separates compounds according to carbon number (*I*₁) and two secondary columns that separate compounds according to functionality (*I*₂ and *I*₃).

Research Strategy.

- 1) A mixture 85 SOA precursor oxidation products identified in chamber experiments and aerosol samples were chosen as target analytes.
- 2) Retention indices of compounds with nitrate (-ONO₂), ketone (-C=O), alcohol (-OH) and carboxylic acid (-COOH) functionalities were estimated using an algebraic transformation of the Abraham solvation parameter model⁶.
- 3) GC \times 2GC retention index diagrams were simulated using empirical relationships between the retention indices⁷ for three columns predicted to provide separation according to functionality and molecular structure^{8,9}.

2. Materials and Methods.

Solvation descriptors for the oxidation products (*S* and *E*) were estimated with the Absolv module of ADME Boxes 5.0.7. Descriptors (*s* and *e*) for the GC stationary phases (DB-210, sol-gel wax, and BPX-90) were reported by Poole and Poole⁸. Prime values of the descriptors were calculated with the algebraic transformation of the Abraham solvation parameter model⁶. Retention indices were estimated based on the following equations^{6,10}:

$$I_1 = L' + s'S' + e'E' \quad (1)$$

$$\Delta I_2 = I_2 - I_1 = \Delta s'S' + \Delta e'E' \quad (2)$$

$$\Delta I_3 = I_3 - I_1 = \Delta s'S' + \Delta e'E' \quad (3)$$

where

L dispersion interaction term of the solute.

s, S dipolarity/polarizability interaction terms of the GC stationary phase and solute, respectively.

e, E excess polarizability interaction terms of the GC stationary phase and solute, respectively.

GC \times 2GC retention index diagrams were simulated using *I*₁, 1.6⁴², and 1.6⁴³ in Equations (1)-(3) above for a system composed of a primary column DB-210 (1), and two secondary columns sol-gel wax (2) and BPX-90 (3) on the *x*, *y* and *z* axes, respectively.

4. Discussion

- Compounds oxidized in sequential reactions gain in number and variety of functionalities that can be separated.
- Compounds sharing similar functionalities undergo specific (*S* and *E* in Equations 1-3) and non-specific interactions with the GC stationary phases, allowing them to be organized into groups.
- In a GC \times GC retention index diagram with DB-210 and sol-gel wax as the primary and secondary columns, respectively, groups of compounds occupy a unique space, with the exception of groups K and V, S and Y, cD and M, and cD and X that are predicted to co-elute (Figure 3a).
- In a GC \times 2GC retention index diagram with BPX-90 as an additional secondary column, groups K and V; S and Y; cD and M, and cD and X are predicted to be separated (Figure 3b).
- Isoprene oxidation products contain -C=O and -OH functionalities, which are substances G48-49, H61-62, I68, O99 and P102 (Figure 3b).
- α - and β -pinene oxidation products are cyclic compounds containing -C=O, -COOH, and -OH functionalities and are represented in Groups cA-cH (Figure 3b).
- Oxidation compounds of monoterpenes other than α - and β -pinene contain -C=O functionality and are represented in Group G (Figure 3b).

5. Conclusions.

- 1) A GC \times 2GC retention index diagram provided separation of SOA precursor oxidation compounds into 27 groups according to carbon number and functionality.
- 2) Managing the complexity of biogenic SOA with the CNFG will (1) reduce uncertainties of SOA models that predict SOA formation based on the volatility and elemental content of precursors and oxidized products, and (2) reduce complexity of SOA models that consider the detailed chemistry of precursors and oxidation products by considering essential information regarding molecular structure only.

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3. Results.

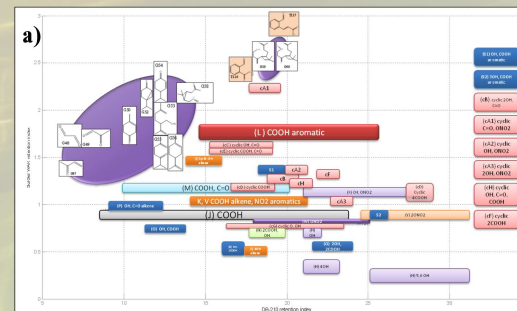
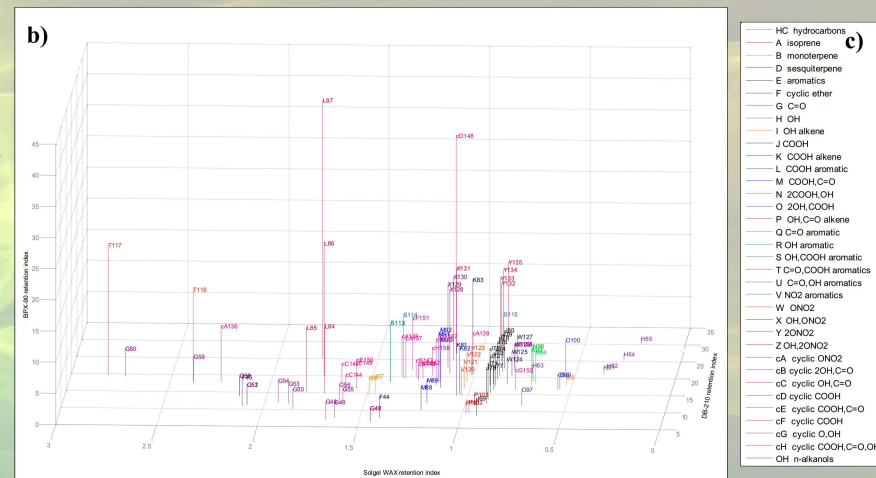


Figure 3a. Grouping of target analytes in a GC \times GC retention index diagram of DB-210 and sol-gel wax as the primary and secondary GC columns, respectively.

Figure 3b. GC \times 2GC retention index diagram of the 85 target analytes.

Figure 3c. Identification of target analyte groups in Figures 3a and 3b.



6. References.

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