

A13C-0276

Description of Organic Aerosol Diagenesis with a GC × 2GC Retention Diagram

Rosa M. Flores¹, Bo Zhang², Keenan A. Murray¹, Paul V. Doskey¹⁻³, and Judith A. Perlinger^{1,3}



mflores@mtu.edu. Michigan Technological University. ¹Department of Civil and Environmental Engineering, ²School of Forest Resources and Environmental Science, ³Atmospheric Sciences Program.

I. INTRODUCTION

The O/C ratio-volatility, H/C-O/C, carbon number (n_c)-polarity, and carbon oxidation state- n_c approaches have been developed to follow trends in the evolution of organic aerosol (OA) and to manage organic molecular data in secondary organic aerosol (SOA) models. Barstanti et al. [1] proposed a simplified approach to group SOA species by n_c and total molecular polarity [tmp, estimated as the difference between the predicted enthalpy of vaporization of the species and the enthalpy of vaporization of the corresponding hydrocarbon (ΔH_{vap})]. Perlinger et al. [2] used chromatographic theory and solute solvation descriptors that describe polar interactions to quantify tmp of SOA species. GC × 2GC technique is a multi-dimensional, gas chromatographic (GC) approach that uses an arrangement of a primary and two secondary columns to provide comprehensive resolution of complex mixtures of organic molecular species. The species are resolved by molecular structure and represented in a GC × 2GC retention index diagram, which is essentially a n_c vs. functionality grid. Here, we present (1) a selection of GC stationary phases in a GC × 2GC arrangement that comprehensively resolves a complex mixture of SOA precursors and (2) a comparison of the n_c vs. tmp and n_c vs. functionality grid approaches using products of α -pinene ozonolysis as a case of study.

II. METHODS

Molecular markers for SOA produced by the oxidation of isoprene, seven monoterpenes and one sesquiterpene, semivolatile n -alkanes, naphthalene, and alkyl-naphthalenes were identified in the literature and separated according to functionality into 28 groups. Polar moieties are derivatized prior to a GC analysis to facilitate transfer through the analytic system. Derivatization consists of a 3-step process that converts (1) carbonyl groups to methylloximes using methylloxamine, (2) carboxylic acids to methyl esters using trimethylsilyldiazomethane (TMSD), and (3) alcohols to trimethylsilyl ethers using N,O-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) [3]. Solvation descriptors were estimated with the Absolv Module of ADME Boxes v. 5.0.7 [4].

2.1 Calculation of retention indices.

Theoretical retention indices were calculated for 140 SOA precursors and products (see Figure 1) using the Abraham solvation parameter model to develop GC × 2GC retention indices [5]. The retention index of the primary (I) and each of the secondary phases (ΔI) are calculated as follows:

$$I_i = L' + s'S' + a'A' + e'E' + b'B' \quad (1)$$

$$\Delta I = I_i - I_j = \Delta s'S' + \Delta a'A' + \Delta e'E' + \Delta b'B' \quad (2)$$

where L , s , a , b and e are constants that characterize the selectivity of the GC stationary phase, and L , S , A , B and E are solvation descriptors of the solute. Prime values are obtained by correcting the data with a least square fit of hydrocarbons C_9 - C_{13} n -alkanes. GC × 2GC retention index diagrams are generated with theoretical retention indices plotted in 3-D space with the x -axis representing the primary column and the y - and z -axes representing the secondary columns.

2.2 Selection of columns.

Poole and Poole [6] evaluated the selectivity of 32 commercially available GC stationary phases using principal component analysis. The stationary phases clustered into 3 groups - polyethylene/propylene glycol (PEG), polysiloxane/trifluoropropyl (PTMS-), and cyanopropylsiloxane/phenylsiloxane (PCPS). Poole and Poole [6] suggested chemical differences between stationary phases could be assessed through a measurement of orthogonality with an angle between column vectors larger than 75° representing the desired orthogonality for optimal resolution. This approach was used to evaluate 35 stationary phases.

2.3 Comparison of n_c vs. tmp and n_c vs. functionality grids.

The n_c vs. tmp and n_c vs. functionality grids were compared using α -pinene ozonolysis products identified by Camredon et al. [7] as a case of study.

III. RESULTS AND DISCUSSION

3.1 Retention index of SOA precursors and products.

DB-210 (poly(methyl trifluoropropylsiloxane)/BPX90 (cyanopropyl polysilphenylsilo-xane)/PEG (Poly(ethylene/propylene glycol) arrangement spanned a selectivity space with individual constants $e = -0.46$, 0.027 and 0.214 and $s = 1.377$, 2.044 and 1.488 for DB-210, BPX90 and PEG, respectively, and produced optimal resolution of the 140 species.

The GC × 2GC retention index diagram which was generated with theoretically-derived retention indices (Figure 2), resolves compounds (1) by n_c (horizontal bands) on the primary column (DB-210) and (2) by molecular structure, and type and number of functional groups on the secondary columns (PEG, BPX-90). The retention time of n -alkanes (C_1 - C_{10}), represented by HC, can be used to determine Kovats retention indices of the species.

When compounds are oxidized in multiple generation reactions, they gain in number and variety of oxygenated functionalities, which can be resolved chromatographically. Reaction products occupy a space distinct from earlier reaction products in the 3-D GC × 2GC diagram. For example, tracers for second-generation oxidation reactions of isoprene include: 2C=O (species F45, F46), C=O and OH (Q104, Q105), 4OH (G59, G58), 2OH and COOH (N95), and OH alkene (H65), which fit into groups of compounds resolved according to types and number of functionalities (Figure 2). Tracers for α - and β -pinene first generation reactions are cyclic compounds that have a number of -COOH, -OH and C=O functionalities, but will be clustered into a big group of cyclic compounds (Groups eB, cC, cD, cE, cH) (Figure 2). First generation products of monoterpenes other than α - and β -pinene are cyclic, contain C=O groups and thus fit into Group F. Aliphatic hydrocarbons oxidized under high concentrations of nitrate will contain -ONO₂ and -OH groups and thus are separated into Groups R,S,T and U (Figure 2).

3.2 Comparison of n_c vs. tmp to n_c vs. functionality diagram.

Group	Functional Group	ID	Solute	Mass Fraction
1	Alc-H	A1	C ₁₀ H ₁₈ O	0.533
2	CO, COOH	B1	C ₁₀ H ₁₆ O	0.649
		B2	C ₁₀ H ₁₆ O	
		B3	C ₁₀ H ₁₆ O	
3	CO, OH	E1	C ₁₀ H ₁₆ O	0.343
		E2	C ₁₀ H ₁₆ O	
		E3	C ₁₀ H ₁₆ O	
4	CO, OH	F1	C ₁₀ H ₁₆ O	0.141
		F2	C ₁₀ H ₁₆ O	
		F3	C ₁₀ H ₁₆ O	
5	CO, OH	G1	C ₁₀ H ₁₆ O	0.423
		G2	C ₁₀ H ₁₆ O	
		G3	C ₁₀ H ₁₆ O	
6	COOH	H1	C ₁₀ H ₁₆ O	0.056
		H2	C ₁₀ H ₁₆ O	
		H3	C ₁₀ H ₁₆ O	
7	COOH	I1	C ₁₀ H ₁₆ O	0.021

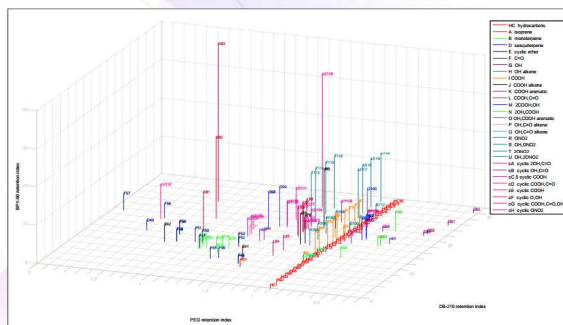


Figure 2. Theoretical retention index diagram of derivatized SOA precursors and products with a DB-210 stationary phase on the primary column, and PEG and BPX-90 stationary phases on the secondary columns in a GC × 2GC arrangement.

Tables 1 (left) and 2 (right).

The α -pinene ozonolysis products (Fig. 3a) grouped by the n_c vs. tmp (Table 1) and n_c vs. functionality grid (Table 2) approaches.

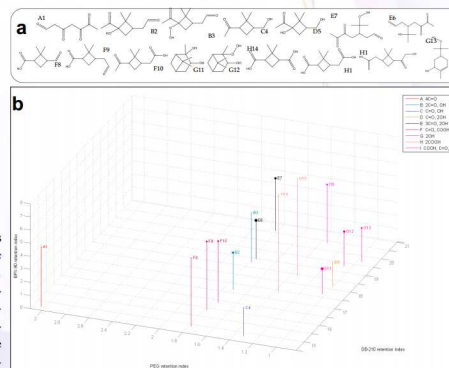
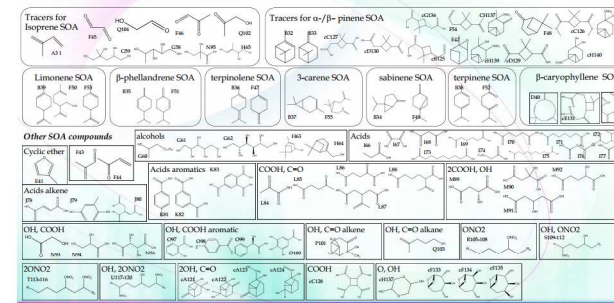


Figure 3. (a) The α -pinene ozonolysis products identified by Camredon et al. [7] and (b) theoretical GC × 2GC retention index diagram of the α -pinene ozonolysis products (Mass fractions of products are represented by the size of the bubble markers).

Fig. 1. SOA Precursors and products



IV. CONCLUSIONS

SOA precursors and products are transformed in the atmosphere through several generations of oxidation adding various types and numbers of functionalities to a molecular structure that are characteristic of the precursor oxidation pathway.

✓ A complex mixture of derivatized SOA species was theoretically resolved according to molecular structure and functionality by a GC × 2GC approach using a primary column with a DB-210 stationary phase and secondary columns with BPX90 and PEG stationary phases.

✓ As simulated using the theoretical retention diagram here, the ability to resolve molecular markers of oxidation pathways and to group SOA species by molecular structure is desirable in order to visualize OA diagenesis and to manage molecular input data to chemical transport models.

✓ The n_c vs. functionality grid, represented by a GC × 2GC retention diagram, exhibits better resolution of organic species by polarity than n_c vs. tmp grid that estimates tmp as ΔH_{vap} .

A future research involves confirming the resolution of a complex mixture of SOA species by the GC × 2GC approach reported here, which was generated with theoretically-derived retention indices, with experimentally-derived retention indices for commercially available standards and species identified in laboratory-generated SOA.

V. REFERENCES

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VI. ACKNOWLEDGEMENTS

Mexican Council of Science and Technology (CONACYT) fellowship to Rosa Flores. Ecosystem Center (ESC), Earth, Planetary and Space Sciences Institute (EPSSI) and Graduate Student Government (GSG) at Michigan Tech for travel grants.