On-line Supercritical Fluid Extraction with Gas Chromatographic - Mass Spectrometric Analysis of Biogenic SOA

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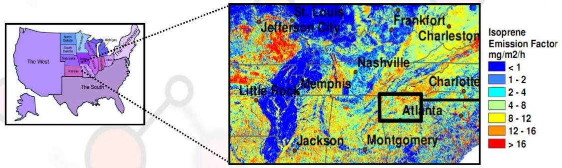
I. ABSTRACT

Secondary organic aerosols (SOA) are formed by photooxidation of volatile organic compounds (VOCs) and nucleation and condensation of the oxygenated products. The Ozarks forest in the Midwestern United States is an important global source of biogenically-derived SOA. Estimated contributions of SOA to the measured organic carbon (OC) aerosol in the St. Louis area during July were about 60% with 70% originating from isoprene. Monoterpene- and monoaromatic-derived SOA contributed about 10-20% of the OC from July through October. The overall goal of the research is to evaluate SOA produced from a variety of biogenic and anthropogenic sources of precursors in the Midwestern United States. Functional groups of organic substances comprising SOA (i.e., hydroxyl, carbonyl, carboxylic acid, sulfate, and nitrate) complicate sample processing, analysis, and identification of the characteristic aerosol products of the precursor oxidation pathways. On-line sample processing methodologies that are exhaustive and suitable for thermally labile compounds and analytic techniques that provide more complete resolution of complex mixtures for sensitive detection of molecular species are required to quantify SOA. Common extraction techniques include solvent extraction, which requires large amounts of solvent and is labor intensive, and thermal desorption, which evolves organic substances from aerosol at temperatures not suitable for thermally labile compounds. A promising technique that does not involve sample processing with solvents or high temperatures is supercritical fluid extraction (SFE). In this work, SFE was coupled to a comprehensive two-dimensional gas chromatograph with time-of-flight mass spectrometric detection (GC×GC-TOFMS) and evaluated as an on-line sample processing and analytic technique. Carboxylic and hydroxyl compounds were derivatized during static extraction conditions and identified by GC×GC-TOFMS.

II. BACKGROUND AND MOTIVATION

Midwestern USA



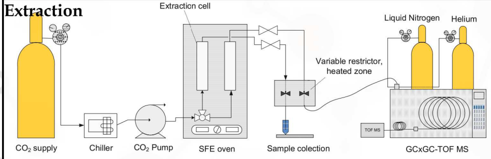
- ✓ Deciduous and coniferous forests in the Ozarks are significant sources of isoprene (> 150 mg m^{-2} d^{-1}), monoterpenes (10-40 mg m^{-2} d^{-1}) and sesquiterpenes (10-40 mg m^{-2} d^{-1}) [2]
- ✓ Contribution of SOA to particle organic carbon was 20-70% in July-November [6]
- ✓ Maximum contributions of SOA are in October with 70% originated by isoprene [6].

Method development

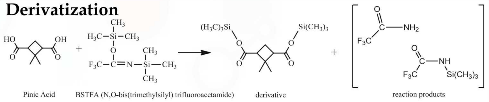
- ✓ Rapid sampling and quantitative analysis for organic molecular characterization of SOA precursors and their oxidation products.
- ✓ Evaluation of SOA models with organic molecular data to predict SOA production on a regional scale.

III. METHODOLOGY

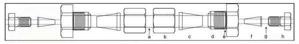
Extraction



Derivatization



SFE extraction cell (0.67 cm^3)*



(a) 4 cm– 316 stainless steel 1/14” tubing
(b-d, f, h), column end fitting 1/4” - 1/16”
(e) 1/4” 316 stainless steel frits 2mm
(f) 316 stainless steel 1/16” tubing
* Fittings were obtained from VICI Co. (Houston, TX)

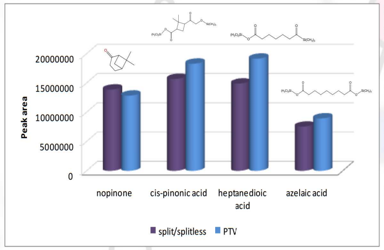
SFE Conditions

Oven temperature: 60°C
Pressure: 300 Bar
Variable restrictor temperature: 60°C
Transfer line temperature: 77°C
Static extraction time: 40 min
Dynamic extraction time: 60 min
Extraction flow: 50 ml/min

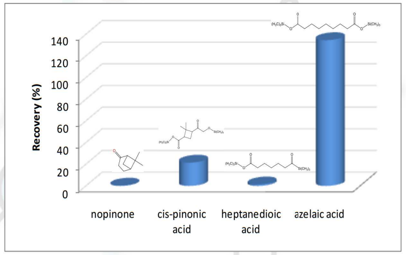
GC×GC-TOFMS conditions

GC: Agilent 6890 Gas Chromatograph
Carrier gas: Helium 1.5 ml/min
Split/splitless: 300°C
PTV trapping: silanized glass wool 32°C, 0°C
PTV desorption: 50-300°C (hold 5 min) at 12°C/s
Split ratio: 300:1
Purge time and flow: 8 min, 45 ml/min
1° column: DB-5MS, 30 m × 0.25 mm × 0.25 mm
2° column: DB17, 10m × 0.10 mm × 0.10 mm
1° oven: 30°C (5min hold) to 250°C at 15°C/min
2° oven: 25°C offset from primary oven
Modulator: 25°C offset from primary oven
MS detector: TOF-MS Pegasus 4D

IV. PRELIMINARY FINDINGS

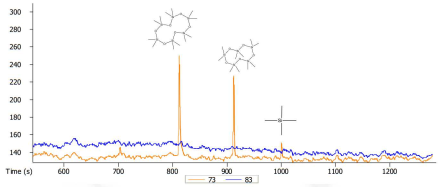


Comparison of response obtained by gas-chromatography inlets. The higher response obtained by the PTV inlet suggests that possible thermal degradation is occurring in the split/splitless inlet and thus the PTV inlet is more suitable for analysis of thermally unstable compounds [5].



SFE extraction efficiency of nopinone and derivatized compounds at a cryogenic trapping temperature of 0°C.

High recovery of azelaic acid suggests carry over from previous samples and/or sorption on active sites of the transfer line. Trapping/desorption conditions in the inlet of the GC must be refined to improve recoveries of analytes.



Transfer line cleaning. The stainless steel transfer line that allows the on-line analysis was cleaned with 3 ml of dichloromethane in order to evaluate sorption of analytes. This chromatogram shows peaks representative of bleeding of column or liner packing material but no analytes of interest.

V. DISCUSSION

- ✓ A supercritical fluid extraction unit was successfully connected to a gas chromatograph, GC×GC-TOFMS, for on-line analysis.
- ✓ Preliminary tests were performed to evaluate extraction, focusing and desorption of analytes in the cryogenic inlet of the GC×GC-TOFMS.
- ✓ Trapping of analytes was evaluated at 32, 0, -20 and –30°C. A leak in the system during –20 and –30°C induces uncertainty in the results and were not presented. It is not clear whether or not analytes were recovered at 32° C. The best recovery was obtained for azelaic acid at 0°C. Recoveries higher than 100% indicate incomplete extraction from previous samples and/or sorption of analytes on active sites of the system (e.g transfer line).
- ✓ Cleaning of the transfer line doesn’t indicate sorption of analytes, however further investigation is recommended.

VI. FUTURE WORK

- ✓Evaluate the effect of CO_2 extraction flow (e.g 25, 100, 150 ml/min) on recoveries.
- ✓ Evaluate the effect of inlet temperature (e.g –30, -60°C) on analyte trapping efficiency.
- ✓Use of a transfer line that doesn't contain active sites (e.g sulfinert, silcosteel, etc).
- ✓Perform *in situ* derivatization and extraction of ambient air samples.

VII. REFERENCES

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VIII. ACKNOWLEDGEMENTS

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