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 isomerization and condensation of the oxidized 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. Monoterpenes and monomeric-derivative-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) complexate 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 extracts organic substances from aerosol at temperatures not suitable for thermally labile compounds. A promising technique that does not involve sample processing with solvents of high temperatures is supercritical fluid extraction (SFE). In this work, SFE was applied to a comprehensive two-dimensional gas chromatography 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 Ozark KS are significant sources of isoprene (>300 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 28-70% in July-September [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.

Extraction

Derivatization

SFE extraction cell (0.67 cm)°

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 on the desorption of analytes in the cugenetic split of the GC-GC-TOFMS.

Trapping of analytes was evaluated at 32, 0°C and 40°C. A leak in the system during -20°C and -30°C. Reducing the temperature in the extraction system to 32°C yields higher recoveries, which is not possible at subzero temperatures. The best recovery was obtained at 32°C. Recovery rates 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 does not indicate sorption of analytes, however, further investigation is recommended.

VI. FUTURE WORK
- Evaluate the effect of CO₂ extraction flow (e.g., 25, 100, 150 mln m⁻²) on recovery.
- 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., sulfonated, silonized, etc.).

VII. REFERENCES

VIII. ACKNOWLEDGEMENTS
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