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Supercritical Fluid Extraction of Biogenic SOA in Northern Michigan

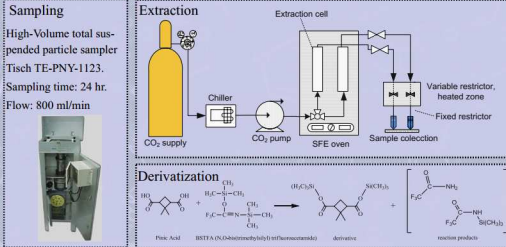
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I. INTRODUCTION

Secondary organic aerosols (SOA) are formed by photooxidation of volatile organic compounds (VOCs) and nucleation and condensation of the oxygenated products. The 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 VOC oxidation pathways. Only a very small fraction of the organic molecular species in SOA have been identified due to the complexity of precursor oxidation reactions and the need for (1) methodologies that are less labor intensive and suitable for thermally labile compounds and (2) analytic instrumentation that provides more complete resolution of complex mixtures for sensitive detection of molecular species. Extraction techniques commonly used include solvent extraction, which requires large amount 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). The main objective of this work was to develop a SFE methodology to extract compounds containing ketone and derivatized carboxylic acid functionalities. It was observed that the extraction of ketones is limited by the initial transfer to the supercritical solvent and its extraction efficiency depends on the specific conditions of temperature, pressure, extraction time, and flow rate. The dynamic extraction of low concentrations of derivatized carboxylic acids doesn't depend on extraction flow, but on extraction time, while the dynamic extraction of high concentrations of derivatized carboxylic acids depends on extraction flow (i.e. extraction efficiency increases with flow rate). Static extraction was more effective than dynamic extraction for all compounds except azelaic acid; however, complete extraction of derivatized carboxylic acids will require a combination of static and dynamic extraction. Future work will involve coupling the SFE unit to a comprehensive gas chromatograph with time-of-flight mass spectrometer (GC×GC-TOF-MS), testing of *in situ* derivatization, and extraction of atmospheric samples.

II. METHODS

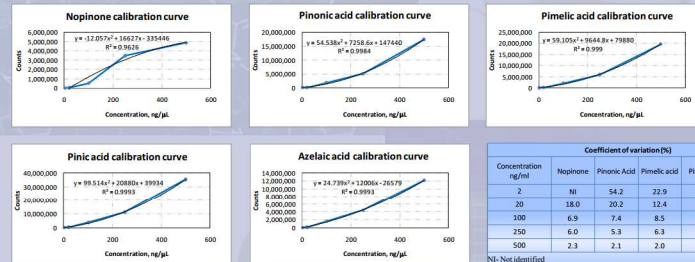


SFE Conditions
 Oven Temperature: 60°C
 Pressure: 300 Bar
 Variable restrictor Temperature: 60°C
 Static extraction time: 0-40 min
 Dynamic extraction time: 15-240 min
 Extraction flow: 25-100 mL/min

GC×GC-TOF-MS conditions
GC: Agilent 6890 Gas Chromatograph
 Inlet: Split/Splitless, 250°C
 Carrier gas: He at 1.0 mL/min
 1st column: DB-5MS, 30 m × 0.25 mm × 0.25 μm
 2nd column: DB17, 10m × 0.10 mm × 0.10 μm
 1st oven: 75°C (1min hold) to 265°C at 10°C/min and to 285°C at 20°C/min
 2nd oven: 15°C offset from primary oven
 Modulator: 15°C offset from primary oven
 Transfer line temperature: 250°C
MS detector: TOF-MS Pegasus 4D
 Ionization: EI at -70eV
 Ion Source temperature: 300°C
 Spectral acquisition rate: 200 spectra/sec
 Acquired mass range: 35-400 u
 Acquisition delay: 380 s
Data analysis and library hits:
 ChromaTOF v4.32, June 30, 2010, NIST library

III. RESULTS

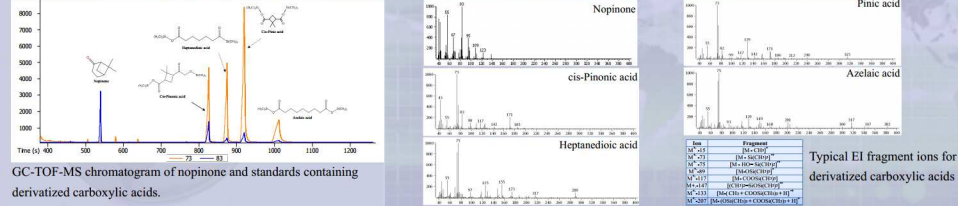
1. Calibration curves



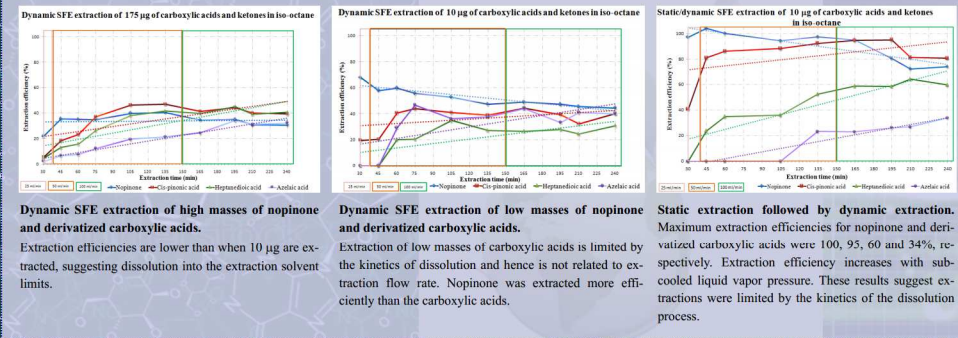
The figures show the calibration curves of nopinone and derivatized carboxylic acids by (GC-TOF-MS).

The table shows the coefficient of variation (precision) for each compound at a given concentration.

2. Chromatography and mass spectrometry



3. Optimization of SFE extraction method

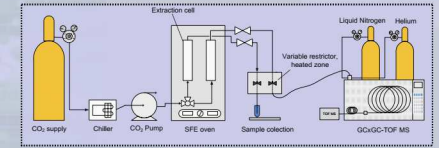


IV. PRELIMINARY FINDINGS

- ✓ Extraction of low masses of derivatized compounds with carboxylic acids is limited by the kinetics of the process (no dependence of extraction flow), while extraction of high masses of derivatized compounds depends on extraction flow rate.
- ✓ The extraction of both, low and high, masses of nopinone (not derivatized) depends on the initial transport to the supercritical fluid and is more efficient at low mass (68% vs 22% for 10 vs 175 μg, respectively).
- ✓ Extraction efficiency of low masses of derivatized carboxylic acids during static extraction considerably increased compared to dynamic extraction. Static extraction is necessary when performing *in situ* derivatization.
- ✓ Extraction efficiencies improved when static extraction was combined to dynamic extraction. However, care must be taken to improve the extraction efficiency of the least volatile compound, azelaic acid

IV. FUTURE WORK

- ✓ Optimization of the extraction method.
- ✓ Determination of the precision of the extraction method.
- ✓ *In situ* derivatization and on-line extraction (see figure below).



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Acknowledgements

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