

## Thermal/Optical Analysis of Major Elements (C, H, N, S, and O) for Particles from Different Emission Sources

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Atmospheric carbonaceous aerosols are related to adverse effects on the Earth's radiation balance, human health, visibility degradation, and material damage. Characteristic chemical information is needed for carbonaceous particles to assess their source, property, and impact. Thermal evolution methods quantify organic and elemental carbon (OC and EC, respectively) collected on filters by heating the sample at different temperatures under different oxidizing conditions. For example, the widely used IMPROVE\_A protocol (Chow *et al.*, 2007) measures eight carbon fractions (4 OC + 3 EC + OP [pyrolyzed OC]). Measurement of these thermally-resolved OC and EC fractions in aerosol emissions from gasoline- and diesel-powered vehicles enhances the ability of receptor models to discriminate between these sources (Watson *et al.*, 1994). Carbon fraction alone are usually not sufficient to differentiate sources. Due to the complex nature of carbonaceous particles, standard chemical analysis techniques such as gas chromatography-mass spectrometry (GC/MS) typically identifies less than 30% of total organic matter (OM). New technologies, such as the particle into liquid sampler (PILS), thermal desorption aerosol GC/MS (TAG)-Flame Ionization Detector (FID), and aerosol mass spectrometers, are fast developing and perfecting for in situ identification and quantification of organic compounds in aerosols (Hallquist *et al.*, 2009).

While there is tremendous complexity of carbonaceous aerosols at the molecular level, they are composed of only a few main elements (e.g., C, H, N, S, and O). Independent measurement of these elements provides new tools to study these aerosols. A Thermal Elemental Analyzer (TEA) has been developed to analyze C, H, N, S, and O on filter samples using a thermal/optical method adapted from the DRI Model 2001 Thermal/Optical Carbon Analyzer. A small punch (~0.5 cm<sup>2</sup>) from a quartz-fiber filter sample is heated in programmed heating steps, e.g., following the IMPROVE\_A protocol. Carbonaceous and other materials are volatilized, pyrolyzed, and combusted to gas phase compounds under either an inert ultrapure He atmosphere at lower temperatures (< ~600 °C) or a mixture of 98% He and 2% O<sub>2</sub> atmosphere at higher temperatures (> ~600 °C). C, H, N, and S are determined by the Pregl-Dumas method, where evolved gaseous species are oxidized in a high temperature (~900 °C) CHNS reactor containing oxidizing agents to convert organic components to CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub>/N<sub>2</sub>, and SO<sub>2</sub>. The oxidation products are measured by a quadrupole mass selective detector (MSD). Quantification of O is based on the Unterzaucher method in which O is converted to

CO in the O reactor, consisting of a nickel-coated carbon reactant. CO is then oxidized to CO<sub>2</sub> using metal oxides and is quantified by a nondispersive infrared (NDIR) sensor. Calibration of the TEA with chemicals of known quantities of C, H, N, S, and O shows that the signal and element quantity have excellent linearity. Figure 1 shows an example of the thermogram from an aerosol sample collected at the Fresno supersite. Thermally separated CHNSO fractions of particles from several sources, including gasoline- and diesel-powered vehicle exhausts, wood smoke, industrial stacks, and ship emissions, as well as ambient aerosols will be presented.

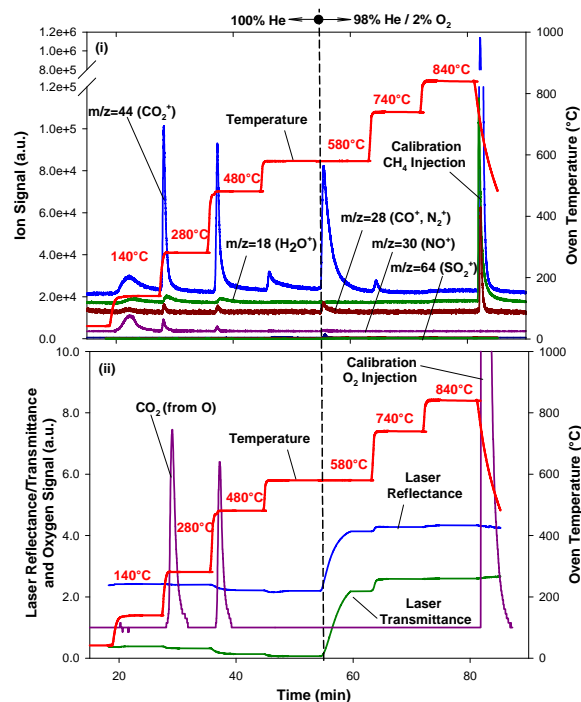


Figure 1. Thermogram of CHNS (top panel) and O and optical signal (bottom panel) for an ambient aerosol sample from Fresno, CA.

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Chow, J.C., Watson, J.G., Chen, L.-W.A., Chang, M.C.O., Robinson, N.F., Trimble, D. and Kohl, S.D. (2007) *J. Air Waste Manage. Assoc.*, **57**(9), 1014-1023.

Hallquist, M. *et al.* (2009) *Atmos. Chem. Phys.*, **9**(14), 5155-5236.