

## **Development of an optimum tracer set for apportioning emissions of individual power plants using highly time-resolved measurements and advanced receptor modeling**

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Grant No. DE-FG26-06NT42738

Elemental concentrations of eleven elements have previously been determined in 30-minute aerosol samples collected with the University of Maryland Semi-Continuous Elements in Aerosol Sampler (Kidwell and Ondov, 2001, 2004; SEAS-II) of extended periods at more than five locations. At this time resolution, plumes from stationary high temperature combustion sources are readily detected as large excursions in ambient concentrations of elements emitted by these sources. Selected periods of this dataset have been exploited by Park et al. (2005 and 2006) who have developed an advanced Pseudo-Deterministic Receptor Model (PDRM). The model employs positions of known sources relative to prevailing wind angles in what may be considered a Gaussian filter, to eliminate contributions from sources for which wind direction and dispersion conditions obviates their influence on air quality at the receptor site. As posed, the PDRM determines average emission rates of particle constituents and emitted gases from individual stationary sources, their time-dependent meteorological dispersion factors, and the source-resolved concentrations of these pollutants induced at the receptor site.

The objectives of our project are to expand the data set by increasing the number of elements from eleven to twenty seven including both major elements Ca, Na, K, and Mg and trace elements. It is believed the larger dataset will provide additional marker species and improve the resolving power of the model to effectively target individual plants with scrubbers and/or different coal sources.

An Inductively Coupled Plasma Mass Spectrometer (ICP-MS) is employed to provide a larger element set and improved analytical capabilities for analysis of SEAS-II slurry samples at ppb and sub-ppb levels while decreasing analysis time. Much of the progress completed on the project has involved the development of analytical protocols both for instrumental methods and in sample preparation.

The poster presents key developments in both instrumental and sample preparatory methods. Instrumental methods incorporate the use of Collision Cell Technology with Kinetic Energy Discrimination (CCT-KED) and include: the determination of correction equations for doubly-charged interferences and oxides, the development of consistent tuning procedures to ensure that low, mid, and high masses are over certain sensitivity thresholds while minimizing polyatomic (including oxides) and doubly charged interferences, and the inclusion of an internal standard set to minimize drift encountered during experiments, thus enhancing reproducibility of results.

These methods were tested with excellent results on NIST SRM 1640, "Trace Elements in Natural Water", and have been found to give highly reproducible results on pooled sample slurries.

Sample preparatory methods are needed to ensure that slurry samples are adequately digested prior to analysis with the ICP-MS. Results show that heating of the samples in Teflon vials under elevated pressure in low concentrations of HNO<sub>3</sub> and HF has increased elemental yields in slurry analysis for refractory elements such as Al, Cr, Fe, La, Ni, and Ti, whilst minimizing blank concentrations. These results have been verified with a total dissolution procedure successfully developed and tested with an interim Urban Fine particulate SRM and adapted for slurry analysis to give percent recoveries for our preparation procedures.

In addition to developments in the analysis protocol, the poster will present completed sampling work on samples collected at sites in St. Louis, Windsor, Tampa, and Birmingham. Modeling results from expanded Tampa set will be included with 16 extra elements.