

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

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BACKGROUND

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.

OBJECTIVES

Expand the data set by increasing the number of elements from 11 to 27.

Elements include:

- Major elements Ca, Na, K, and Mg
- Trace elements

It is believed the Objective will:

- Provide additional marker species
- Improve the resolving power of the model

Which in turn will effectively target individual plants:

- with scrubbers
- with different coal sources.

METHODS

Instrumental. Inductively Coupled Plasma Mass Spectrometer (ICP-MS) with the use of Collision Cell Technology with Kinetic Energy Discrimination (CCT-KED) for analysis of SEAS-II slurry samples

Advantages of Methods:

- Larger element set
- Improved analytical capabilities
- ppb and sub-ppb levels
- decreasing analysis time

Collision Cell Technology with Kinetic Energy Discrimination (CCT-KED):

Sampled ions are focused into a hexapole collision/reaction cell via ion lenses before entering the mass analyzer. Collision cell gas (He/H₂) is bled into the cell and collides with ions in the focused beam. The collision will alter the path and kinetic energy of interfering ions (reducing noise more than signal), which are then filtered from the sampled ion beam by KED barrier. The filtered beam then proceeds to the analyzer.

Reproducibility of Methods:

- Consistent Tuning Procedures to ensure that low, mid, and high masses are over certain sensitivity thresholds whilst minimizing polyatomic (including oxides) and doubly charged interferences.
- Internal Standardization used to monitor drift encountered during experimental runs and correct values accordingly.

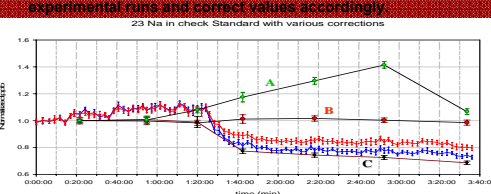


Figure 1. Graph of check standards corrected with differing software correction methods (A, B, C). Correction B provides linear results, despite the evidence of a strong drift occurring in our internal standards (red and blue lines in backdrop).

Methods verification: 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 and are shown in Table 1.

Table 1. Analyses of SRM 1640, Natural Water, ppb

Elements (CCT)	m/z	This work ¹		NIST certified or informational value ²		% Deviation
		mean	±	mean	±	
Al	27	51	± 1.8	52	± 1.5	2.4%
As	75	25.89	± 0.60	26.67	± 0.41	3.0%
Ba	137	1.89	± 3	1.88	± 2.2	0.4%
Ca	44	7006	± 108	7045	± 89	0.6%
Cd	111	22.40	± 1.63	22.79	± 0.96	1.7%
Ce	144	23.21	± 0.62			-1.8%
Co	59	20.13	± 0.48	20.28	± 0.31	0.7%
Cr	52	37.4	± 0.7	38.6	± 1.6	3.2%
Cu	63	86.7	± 4.7	86.6	± 1.6	-1.8%
Cu	65	86.1	± 3.9	85.2	± 1.2	-1.1%
Fe	56	34.4	± 1.7	34.3	± 1.6	-0.4%
K	39	956	± 22	994	± 27	3.9%
Mg	24	9776	± 58	9819	± 56	0.7%
Mn	55	120.3	± 1.8	121.5	± 1.1	1.0%
Mo	95	47.37	± 3.89	46.75	± 2.6	-1.3%
Na	23	29220	± 188	29350	± 310	0.4%
Ni	60	27.1	± 1.2	27.4	± 0.8	1.0%
Pb	121	13.61	± 0.34	13.79	± 0.42	0.9%
Sb	78	20.94	± 0.82	21.96	± 0.51	4.3%
Se	78	20.94	± 0.82	21.96	± 0.51	4.3%
Sr	88	123.3	± 1.5	124.2	± 0.7	0.8%
V	51	12.75	± 0.79	12.99	± 0.37	1.9%
Zn	66	55.5	± 4.2	53.2	± 1.1	-4.2%

¹ - Determined at 1/10 dilution in 0.2% high purity nitric acid, along with routine sample analysis. Values in italics are not certified by NIST, but are provided by NIST as "reference" values.

Sample Preparatory Methods

Despite highly reproducible results for most elements in slurries, it was found that the elements Al, Cr, Fe, La, Ni, and Ti increased in concentration upon re-analysis after acidification. It is hypothesized that these refractory elements are associated with crustal dust and may need further digestion prior to analysis. In order to investigate this, a Total Dissolution Method was developed and tested on NIST interim atmospheric fine-particle SRM with good (± 7%) agreement to their values.

Percent Yields of In-vial Sample Digestion

The process was then adapted to digest a filtrate of the same material in hopes that it would behave much like a mock slurry sample collected with the SEAS-II. When comparing the Total Digestion of the slurry filtrate to the undigested slurry filtrate (Table 2), the majority of elements fell within ± 8% of the total digestion value. Co, Ni, and Pb showed significant increases in the undigested slurry, suggesting that some material may have been lost and Al, Cr, Fe, La, and Ti all showed significantly less concentrations in undigested slurry and supports our hypothesis that these elements are incompletely digested.

Table 2. Comparisons of percent yield of partial digestion techniques to Total Digestion Method on SRM filtrate

	SRM Total Digestion Net (ppb)		SRM 0.2% HNO ₃ no heat % yield		SRM 2.0% HNO ₃ post heat % yield	
	ave x	prop s	ave x	prop s	ave x	prop s
27Al	266 ± 70		0.46 ± 0.12		0.52 ± 0.14	
52Cr	2.75 ± 0.72		0.61 ± 0.16		0.63 ± 0.17	
56Fe	2.64 ± 12		0.58 ± 0.07		0.72 ± 0.03	
139La	0.35 ± 0.04		0.70 ± 0.10		0.83 ± 0.11	
47Ti	54.1 ± 59.7		0.09 ± 0.11		0.08 ± 0.10	

In-vial sample digestion methods of heating slurry samples in differing acid strengths was tested as a means to quickly increase percent yields of these elements. Heating the samples to 85°C for 19 hours increased percent yields of Fe and La by 14%, Al and Ti by 6-8%, and Cr by 2%.

These in-vial sample methods were then applied to pooled slurry samples collected near a Pittsburgh coke oven and showed strikingly similar results, presented in Table 3.

Table 3. Percent (%) Increase in Elemental Concentration with heating in Clairton Slurry experiment

Acid	Time (hr)	27Al ratio	56Fe ratio	52Cr ratio	47Ti ratio	139La ratio	60Ni ratio	140Ce ratio	44Ca ratio
0.2% Heating	0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
	22	1.26	0.24	1.51	0.09	1.22	0.38	1.22	0.81
	92	1.46	0.29	1.69	0.11	1.18	0.33	1.24	0.69
2.0% Heating	0	1.07	0.16	1.21	0.13	0.98	0.51	0.95	0.93
	22	1.00	0.22	1.81	0.14	1.20	0.53	1.22	1.02
	92	1.84	0.34	1.96	0.16	1.20	0.51	1.26	1.05

In addition to observed increases in Al, Cr, Fe, La, and Ti, results from the coke oven slurry also showed increases in Ca, Ce (not analyzed for the SRM filtrate), and Ni. Degrees of the percent increase were also observed to be much larger, especially in 2.0% HNO₃.

Leaching of Blank

It was also found that significant yellowing of the vials occurred in vials heated up to 92 hours in 2.0% HNO₃, and that this effect was accompanied by leaching of Al, Ca, Mg, and Ti from the polypropylene vials in which the samples were digested. The leaching effects were drastically reduced in samples acidified to 0.2% HNO₃, while considerable increases in yields of the refractory elements were still observed: 80% in Fe, 40% in Ni, ~35% in Al and La, 20% in Cr and Ce, and no significant increase in Ca.

Ca and Al concentrations were the most dramatically affected (95±13 ppb Ca and 63±8 ppb Al in blanks) by vial leaching and may contribute to the high increases (30% for Ca and 125% for Al) observed despite the application of blank corrections. Blank concentrations in 0.2% HNO₃ heated for 92 hours were reduced to 3±0.7 ppb for Ca and 1±0.1 ppb for Al. It is hypothesized that heating samples in-vial for 44 hours in 0.2% HNO₃ may produce sufficient percent yields for routine analysis, but first needs to be verified with a Total Dissolution on the coke oven slurry as soon as problems concerning procedural detection limits can be addressed.

RESULTS

A set of 18 samples spanning a 8.5 hour sampling period at Sydney, FL (near Tampa) were previously analyzed using a Graphite Furnace Atomic Absorption Spectrometer with Zeeman Background Correction (GFAAS) and modeled using the PDRM. Results were published by Park et al, 2005. This sample set was re-analyzed using our ICP-MS methods and results were compared to the previous values and then run in the PDRM model. The number of elements included in the model was increased to 19 including: Al, As, Ba, Ca, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, V, and Zn.

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GFAAS v. ICPMS Results

Elemental trends and fluctuations of concentrations from ICP-MS analysis appear to mirror those obtained by GFAAS for most elements. However, anomalies in these trends do exist. For most of the elements, ICP-MS values were somewhat greater (1.2-2 times) than values obtained in GFAAS analysis. It is hypothesized that these differences are attributed to:

- more rigorous sample heating procedures before ICP-MS analysis
- statistical sampling of suspended particles (always a concern for GFAAS analysis)
- possible breakdown of particles stored in the slurry over long periods of time.

New Peak at 19:00

Of the observed differences, the most interesting comes at 19:00 hours when the wind is coming from 251°, corresponding to the TECO Gannon (coal) plant and FPC Bartow (oil) plant at a direction of 253°. A large excursion is observed in Ca, Cu, K, Na, Ni, Pb, Sb, and Zn that was not observed in GFAAS results. Initially thought to be an artifact of contamination, upon closer analysis, element to Se ratios seem to suggest that the excursion is related to plumes from a Coal-fired power plant. Figure 2a shows a logarithmic graph of elements ratioed to Se for the excursion.

At 19:00, these compare well to Literature values from plume measurements (Figure 2b) sampled from plants equipped with Electrostatic Precipitators (ESP). TECO Gannon is also equipped with an ESP.

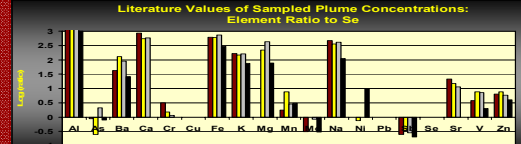
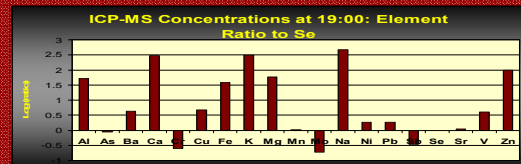
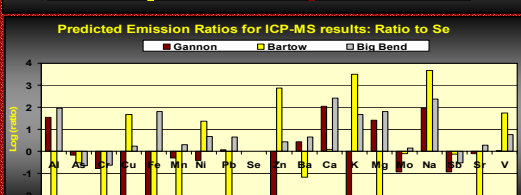
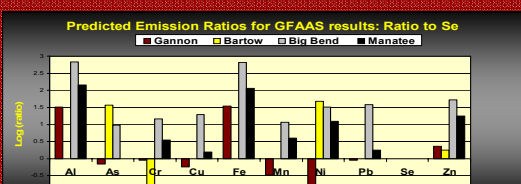


Figure 2a and 2b. Logarithmic Graph of Elemental ratio to Se at 19:00 sample from Tampa data, and from 2b) published plume measurements from stack equipped with ESPs (Ondov et al., 1975, 1979, 1989). Cu and Pb were not determined in published studies.

Similarities in these two graphs are noticeable, especially in sub-Se concentration ratios observed in As, Mo, and Sb. Differences in the ratios of our results and the literature ratios include less Al, Cr, Fe, Sr, and Zn.

Modeled Results:

As the excursion at 19:00 is beginning to look like a coal plume, results are run in the PDRM and emission rates are obtained. Figures 3a and 3b show the emission rates as ratios to Se. Figure 3a shows the predicted emission rates from the GFAAS data, and there are apparent changes observed by running the ICP-MS data.



Figures 3a and 3b. Logarithmic Graph of PDRM predicted elemental emission rates ratios to Se using GFAAS values (3a) and ICP-MS values (3b). Predicted Se from Manatee plant was so small that the log of ratios all exceeded 4 and were not plotted.

Emission Rates obtained from the ICP-MS PDRM run imply that many element excursions observed at 19:00 are likely from the FPC Bartow plant, including: Cu, K, Na, Ni, V, & Zn. Further investigations are needed to assess these changes and it is possible that an external source could influence observed elemental concentrations as well.

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