SIZE-SELECTED AEROSOL FILTER ANALYSIS USING ELECTROSTATIC CLASSIFICATION AND LIBS

Quantitative elemental composition analysis is possible using size-selected aerosol samples collected on a filter. This is accomplished by combining size-selection using a TSI Model 3080 Electrostatic Classifier with elemental analysis using the TSI® Model 3464-01 LIBS Desktop Analyzer. A method is described for loading filters, collecting spectra, and determining calibrations for individual elements in a multi-component mixture. This technique offers a fast and robust way of conducting filter analysis to predict element loadings.

Sampling Setup

The sampling setup is shown in Figure 1. A metal solution is aerosolized, and the particles are dried using a diffusion drier. Size-selected metal particles (D_m = 200 nm) are collected onto a 47 mm polycarbonate filter. Mass loading is calculated based on the filter area, mass concentration, volume flow and exposure time.
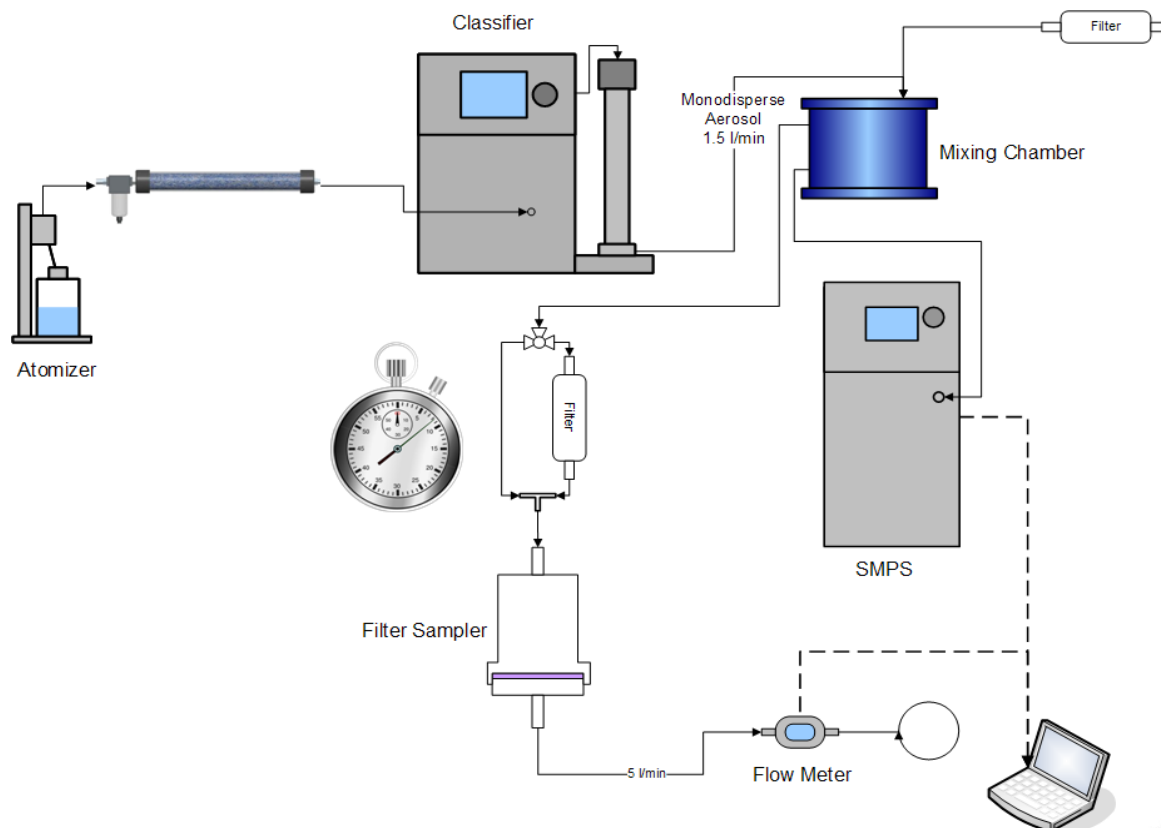

Figure 1: Sampling Setup

Sample Preparation

A sample solution containing ~20 mg/l of eight different metals (High Purity Standards, Charleston, SC) was prepared and aerosolized. Resulting aerosol mass concentrations and filter loading (per metal) ranged from 18 to 32 $\mu g/m^3$ and 20 to 370 ng/cm^2 for exposure times that ranged from 0.75 to 18.5 hours, respectively. The metal concentrations are given in Table 1.

Table 1: Metal Concentrations in Multi-Component Sample Solution ($\mu mol/l$)

Li	Na	K	V	Mo	Ag	Ba	Pb
3200	980	580	440	230	210	160	110

Aerosol Size Distribution

Figure 2 shows the mass-weighted size distribution of the 200 nm classified metal particle aerosol measured with a TSI Model 3034 SMPS™ spectrometer. 327 scans covering more than 16 hours were averaged. The calculated total mass concentration was 30.2 $\mu g/m^3$. The bimodal distribution was likely caused by a) some doubly-charged dimmers being classified as 200 nm, and b) coagulation of particles in the mixing chamber. The intensity of the larger peak is more pronounced in the mass weighted graph.
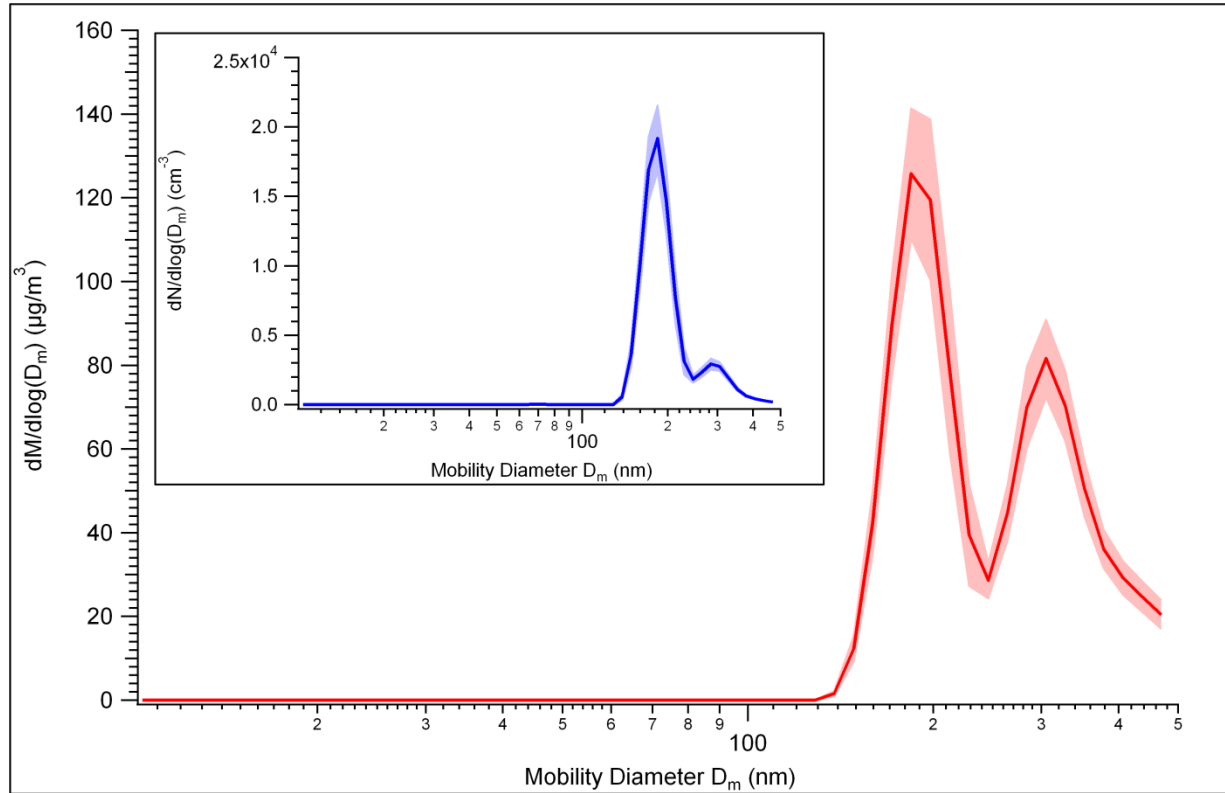
Figure 2: Mass-Weighted Size Distribution of 200 nm Classified Metal Particles. Graph Shows Average ± 1 Standard Deviation of 327 Scans. Insert Shows Number-Weighted Size Distribution

Sample Analysis

The filter samples were analyzed with a Model 3464-01 LIBS Desktop Analyzer, using a 50 mJ, 1064 nm Nd:YAG laser and a 4 channel broadband spectrometer. Instrument settings were as follows:

- Laser output: 60% (~30 mJ/pulse)
- Spot size: 100 μm
- Sample shots: 1 (shot per spot)
- Layout: 15 x 15 grid (225 spots total)
- Spacing: 1.5 mm x 1.5 mm
- Acquisition delay: 1 μs

Data Analysis and Results

Acquired spectra were analyzed for metal content at different loadings in order to develop a calibration for each metal type. One or several peaks for each metal were selected, integrated after baseline subtraction, and normalized against a carbon background peak. The selected peaks for the different elements are shown in Table 2.

Table 2: Element Peaks Chosen for Calibration

Element	Wavelength (nm)	Element	Wavelength (nm)	Element	Wavelength (nm)
Li	610.3542	V	292.4017	Ag	328.068
Li	670.7775	V	310.2292	Ag	338.2887
Na	588.995	V	311.0709	Ba	455.4033
Na	589.5924	Mo	277.5402	Ba	614.1713
K	766.4899	Mo	281.6158	Ba	649.6898
K	769.8964	Mo	390.2953	Pb	220.3534
		C	247.8561		

For each metal, calibration curves were developed for normalized peak area versus surface loading. Figure 3 shows a calibration curve for silver. Linear calibrations for all eight elements were found. Correlation coefficients for each metal are given in Table 3.
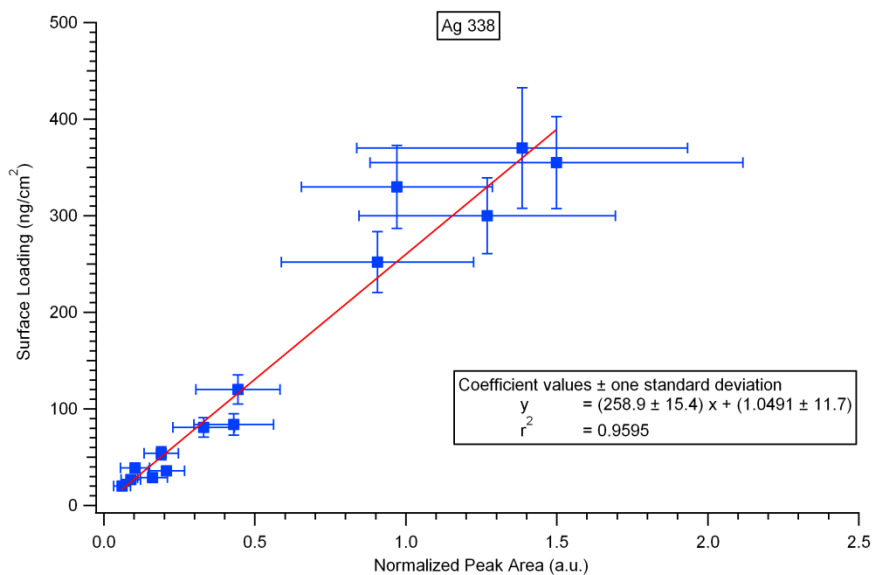

Coefficient values ± one standard deviation
y = (258.9 ± 15.4) x + (1.0491 ± 11.7)
r² = 0.9595

Figure 3: Calibration Curve for Silver, using the 338.29nm Line

Potential sources of error in the y-axis surface loading values include:

- SMPS spectrometer measurement error
- Error in surface area calculation
- Error in volume flow measurement
- Error in exposure time measurement
- Error in particle density determination

Estimates for these errors are as follows:

SMPS measurement: Estimated ±10%
One aspect of this error is the limited size range of the SMPS spectrometer, i.e. the mass weighted size distribution extends past 500 nm. To evaluate this error, two log-normal functions were fitted to the data. The total mass was calculated from the fit and compared with the measured values. The fit was then extended to ~1 μm, and the "extra" mass was calculated. The error between calculated and measured mass values was between 0.1 and 0.3%, and the extra mass between 4.3 and 12.5%.

Surface area: The diameter can easily be measured within ±1 mm, with an exposed diameter of 43 mm, this equals ±5% in area (rounded)

Volume flow: The 4140 flow meter is specified at 2% error.

Exposure time: As a worst case, exposure time was controlled with 15 seconds. This equals a total error of <0.6%.

Particle density: Not a source of error in this work because the same particle type was used for all measurements.

Assuming an SMPS measurement error of 10%, the total error ranges from 12 to 17%. The y-error bars shown in Figure 3 indicate these error calculations.

Table 3: Correlation Coefficients r^2 for Predicted Values Versus Measured Values

Line	Value	Line	Value	Line	Value
Li 610	0.9247	V 292	0.9176	Ag 328	0.9499
Li 670	0.9234	V 310	0.9255	Ag 338	0.9595
Na 588	0.9427	V 311	0.9248	Ba 455	0.9375
Na 589	0.8918	Mo 277	0.9343	Ba 614	0.9361
Na comb.	0.9274	Mo 281	0.9369	Ba 650	0.9377
K 766	0.9478	Mo 390	0.9245	Pb 220	0.9430
K 769	0.9446				

The calibrations were used to predict surface loadings using the "leave-one-out" method of cross validation. Calibrations were built using 13 of the 14 data points for each metal and then the calibration was applied to the normalized peak area of the omitted point. Typical prediction results are shown in Figure 4 which compares the known surface loading to the predicted loadings for Mo and Ag, resulting in average prediction errors of 28% and 21%, respectively, and limits of detection around 20 ng/cm^2 for each metal. Similar results were obtained for the other metals.

The average slope of the correlations was calculated as 0.937 ± 0.013, indicating an under-prediction of ~6%.
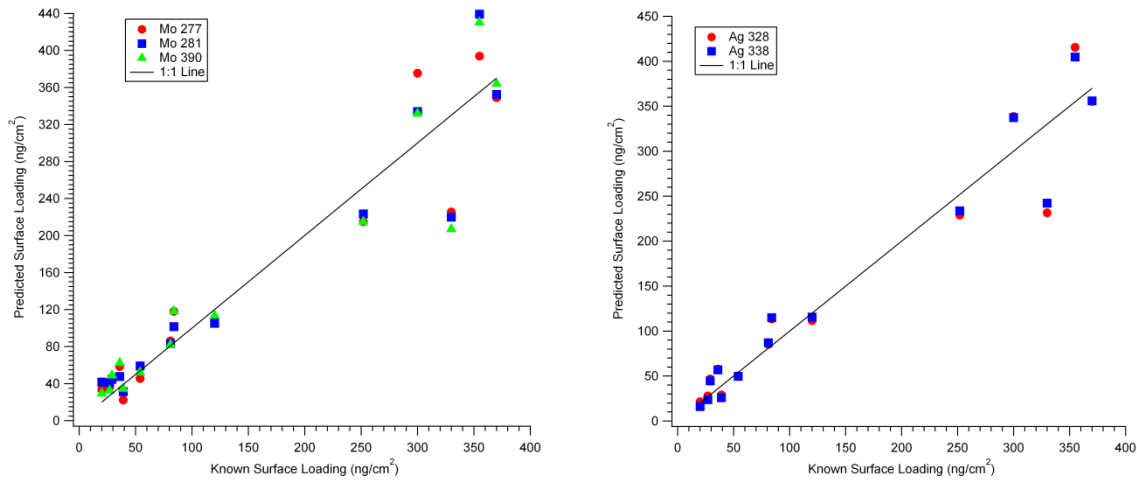
Figure 4: Plots of Predicted Values (y-axis) Versus Measured Values (x-axis) of Surface Loading

Ambient Measurements

Based on a detection limit of 20 ng/cm^2, detection limits for ambient air can be calculated. Volume flow and sample time are variable, and the use of a 47 mm filter is assumed for these calculations. Table 4 below shows the detection limits (in ng/m^3) for flows of 1, 5 and 16.7 l/min, and sampling times between 1 and 24 hours. Higher flows and longer sampling times will lower the required concentration in the aerosol.

Table 4: Ambient Detection Limits (in ng/m^3)

Sample Flow		Sample Time (hr)			
m^3/hr	l/min	*1*	*4*	*12*	*24*
0.06	*1*	4841	1210	403	202
0.3	*5*	968	242	81	40
1	*16. 7*	290	73	24	12

Conclusions

- Size-segregated aerosol material collected on polycarbonate filters was quantified for metal concentrations using the combination of aerosol classification and LIBS.

- Simple linear calibration models were fairly accurate in predicting concentrations. Better results may be obtained using more sophisticated models.

- Even in this straightforward method, limits of detection as low as 20 ng/cm^2 could be achieved.

- LIBS analysis provided an easy method to perform quantitative elemental analysis with little required sample preparation and quick data acquisition and analysis.

- The light element capability of LIBS allowed for straightforward normalization using carbon peak data.

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