



APPENDIX AVAILABLE ON REQUEST

Research Report 133

Characterization of Metals Emitted from Motor Vehicles

Appendix A. Synopsis of UW-Madison Aerosol Trace Element Protocols

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The following is a summary of the analytical methods used for measurement of the elemental composition of aerosol particulate matter. Summarized are our approaches for contamination control, recovery of analytes from the particulate matter, and quantification of the target analytes.

I. CONTAMINATION CONTROL

A. Clean Lab Environment

All preparation steps (filter and supply/equipment cleaning, aerosol digestion/leaching) and analyses are performed in HEPA filtered, dedicated trace metal clean labs by personnel with extensive experience in trace level techniques (Shafer et al. 1999; Hurley et al. 1996). Our two clean labs were purpose-built for trace metal analyses from non-metallic materials. Critical sample and equipment handling (bottle/vial drying, sub-sampling, and dilutions) are performed under polypropylene/acrylic laminar-flow benches (recirculating or exhausting). To further isolate samples from potential contamination sources, the ICP-MS auto-samplers are positioned under acrylic enclosures within the clean lab.

B. Compatible Materials

Samples contact only trace metal compatible materials (TFE, FEP, PFA -Teflon, polypropylene, or polyethylene), exhaustively prepared in multi-step acid leachings. Teflon supplies are prepared by leaching in 16N nitric acid for 24 hours at 80°C in large Teflon acid baths. After leaching the Teflon is thoroughly rinsed with Milli-Q, and then filled/immersed in 2% nitric acid until needed. Polyolefins are cleaned by successive leaching in 2.5 N HCl, 3.2 N HNO₃, and 0.3 N high purity HNO₃; each step for a minimum of two-days. We have documented that bottles prepped using these protocols do not introduce trace metal contaminants (above our ICP-MS LOD's) to either blanks or samples stored for periods of at least 6 months.

Aerosols are collected on Teflo[®] filters. These Teflon filters were selected because of their relatively low blank levels and compatibility with the rigorous bomb-digestion procedure. The encircling polypropylene ring is removed prior to digestion. To ensure the lowest possible method detection levels, trace contaminants in the Teflo[®] filters are removed via a cleaning protocol incorporating sequential flow-through leaches with 2N HCl, 2N HNO₃ and MQ water.

C. Handling

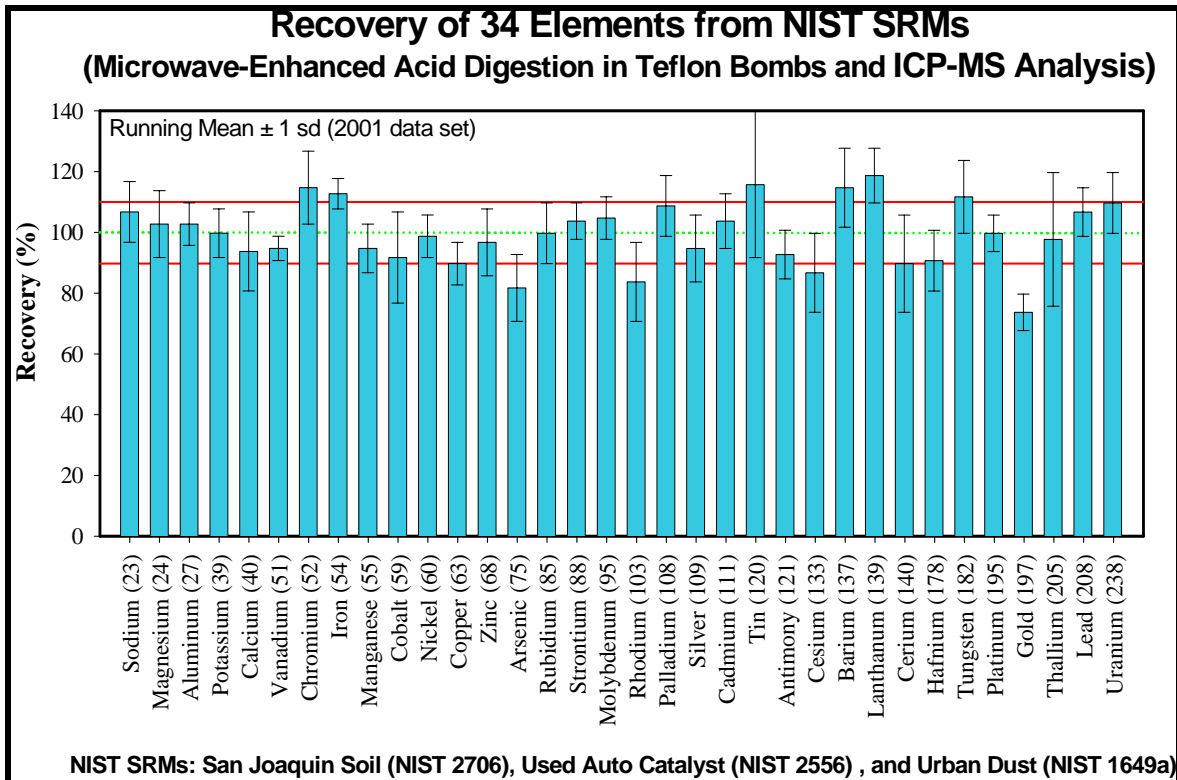
Equipment and supplies are protected by double-bagging in plastic zip-lock bags in the clean lab. Field manipulations are minimized by pre-packaging field supplies. Double-bagged supplies are handled using clean-hands dirty-hands techniques by personnel wearing polyethylene gloves.

II. AEROSOL SOLUBILIZATION

Full realization of the unique capabilities/advantages of ICP-MS is contingent upon the application and coupling with an unbiased, precise, and efficient aerosol solubilization method. Lack of a suitable solubilization method for the complete suite of elements comprising atmospheric particulate matter has been a barrier to the use of all solution nebulization techniques, including ICP-MS, for the analysis of aerosols. Concerns have included extraction efficiency, volatilization losses, contamination, and issues of dilution and sensitivity. The digestion protocols used in this work have been developed to overcome these problems. We have focused our efforts in several key areas: (1) minimization of **contamination** during handling and digestion, including reduction of filter blank levels (2) optimization for the traditionally difficult **platinum and noble metal** groups (3) address the influence of the **acid matrix** on **polyatomic interferences** in the mass spectrum (4) maximize sensitivity.

Total dissolution of aerosols collected on pre-cleaned Teflon membranes is effected by microwave-assisted acid digestion in Teflon bombs. An automated, temperature (and pressure)-regulated, trace analysis microwave system (Milestone Ethos+) is utilized. The acid chemistry employs a mix of ultra-high purity acids (1.5 mL 16N HNO₃, 0.5 mL 12N HCl, 0.2 mL 28N HF). We are able to use a single addition (step) mix of the required acids without degradation of detection levels because of the advanced capabilities of the ICP-MS system and nebulizer front-end. The method is efficient and rapid, with digestion of a 36 sample batch completed in 20 minutes. Traditionally difficult elements (Cr, noble metals, platinum group) and compounds (aluminosilicates, quartz) are completely solubilized. A typical batch consists of 22 unknowns, 6 standard reference materials (SRMs), 4 matrix blanks, 2 method blanks, and 2 matrix spikes. The SRMs used to monitor digestion performance were selected to represent phases that represent actual aerosols or significant aerosol components. These included the NIST SRMs: Recycled Auto Catalyst (#2556), Urban Dust (#1649a), and San Joaquin Soil (#2709). The Figure on the following page presents a summary of the recoveries of 34 chemical elements in the aforementioned SRM's.

The polymethylpentene support rings are removed from the Teflon filters, and the filter membranes were placed in a digestion bomb with a mixture of 1.5 mL 16N HNO₃ (Ultrex grade, Fisher Scientific), 0.2 mL 28N HF (Optima grade, J.T. Baker), and 0.5 mL 12N HCl (Optima/trace metal grade, J.T. Baker). The samples are digested in closed Teflon digestion vessels using a programmable microwave digestion unit (ETHOS, Milestone). The digestion protocol is comprised of a 9 minute ramp to 180°C followed by a 10 minute hold at 180°C and one hour of ventilation/cooling. Digestates were diluted to 30 mL with high purity water (18 MΩ cm⁻¹) generated by a Milli-Q system (Millipore, Bedford, MA, USA), and were stored in low-density polyethylene (LDPE) bottles. To minimize contamination, all Teflon tubes and vessels were cleaned before use by soaking in an 8N hot nitric acid bath for at least 24 hours, followed by a Milli-Q rinse. LDPE digestate storage bottles were soaked in 4N HCl for 48 hours, 3N HNO₃ for 48 hours, and rinsed with Milli-Q.



III. INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY ANALYSIS

A. Background

Inductively-Coupled Plasma Mass Spectrometry (ICP-MS) is a powerful tool for the determination of the elemental composition of atmospheric aerosols. In addition to exhibiting extreme sensitivity and high signal to noise, the technique offers other unique capabilities including: high precision, extremely wide dynamic range, a large element menu, and elemental isotopic capability. These features significantly advance the state-of-the art (making it the method of choice for most applications) over traditional aerosol analysis techniques. However, realization of these advantages is contingent upon several key factors: 1. Full integration of clean techniques into collection/processing/analysis methods (section I) 2. Application of efficient, unbiased, and precise solubilization methods (section II) and 3. Minimization of polyatomic interferences during ICP-MS analysis (briefly discussed in this section).

The significantly enhanced detection limits of ICP-MS, compared with traditional techniques, brings with it major advantages for aerosol characterization including:

- a. the ability to work with much smaller sample masses*
- enabling shorter sampling intervals (improved temporal resolution and event sampling)
- enabling lower volume samples (e.g. personal samplers less cumbersome)
- enabling detailed size-fractionated mass characterization (e.g. Moudi impactors)

b. expansion of number of routine elements that are quantifiable

- leading to improved source characterization
- enhanced potential for identification of unique source and process tracer
- greatly reduced error component for more traditional elements

Because the ICP-MS technique as normally implemented is solution-based, detection levels can typically be further improved by such techniques as filter compositing (if filters are properly cleaned) and by post-solubilization concentration techniques such as volume reduction, solid-phase extraction, and liquid-liquid extraction.

B. Method

Our research group, with over a decade of experience in trace level ICP-MS analysis, operates two ICP-MS systems, both installed in a dedicated trace metal clean room at the State Lab of Hygiene. The ICP-MS system used in this study, a Thermo Instruments PQ-ExCell, is a collision-cell equipped instrument, optimized for high signal to noise ratios, which when coupled with a comprehensive program of contamination control, enabled high accuracy, high precision, analysis of complex, low concentration, aerosol digests. When operated with pneumatic aspiration 80 to 100 MHz/ppm sensitivity is observed with backgrounds typically in the range of 0.5 to 2 cps. To eliminate molecular isobars which compromise the analysis of an important group of light elements (refer to Table 2) when traditional ICP-MS is applied, the "cool"-plasma, shielded torch mode of the ExCell ICP-MS was utilized. In "normal" hot plasma mode (Table 2) isotopes of an additional 26 elements were examined. In both modes, a micro-concentric nebulizer (Cetac, MCN-6000), served as the ICP-MS front-end. This desolvating nebulizer/spray chamber prevents the formation of many interfering polyatomic species, especially oxides, and is ideal for trace analysis in the limited volume aerosol digestates because of the low sample consumption (80-100 $\mu\text{L min}^{-1}$) rate. Additionally, since all wetted components of the MCN are constructed entirely of inert Teflon, the nebulizer is ideal for the aggressive acids used in the solubilization protocols. Instrumental detection limits (3 sigma IDL) are in the low to sub- ng L^{-1} range (equivalent to 0.1-10 $\text{pg} / 14 \text{ m}^3$ air sample) (refer to **Table 2**). Metal quantification was typically performed using external standards with internal normalization (using Ga, In, Bi as internal standards). Isotopes were acquired in peak jumping mode, and where possible the element menu included multiple isotopes of each element (**Table 2**). A minimum of three replicate 180 second analyses were performed on each sample after a 45 second uptake and stabilization period. A long (360 second) rinse with 2% high purity nitric acid is performed between samples to virtually eliminate carry-over and to recondition the sampler cone. A typical MCN-ICP-MS batch will include 25 actual samples, 2 matrix spikes, 6 SRM's, 3 matrix blanks and a set of check blanks (CCB's) and calibration verification checks (CCV's) that are run at frequent intervals during the batch sequence.

A detailed discussion of our routine ICP-MS quality assurance plan can be found in the EPA document: Shafer and Overdier 1996; Analysis of Surface Waters for Trace Elements by Inductively-Coupled Plasma Mass Spectrometry, Revision 5, 1996 (University of Wisconsin-Madison).

Table 1. ICP-MS General Operating Parameters

| Parameter | Normal Mode | Cool Plasma Mode |
|---|--------------------|-------------------------|
| RF power (watts) | 1350 | 370 / 650 |
| Sample uptake rate ($\mu\text{L}/\text{min}$) | 80 | 80 |
| Dwell time / mass (μs) | 10,000 | 10,000 |
| Number of sweeps | 60 | 60 |
| Number of main runs | 4 | 4 |
| Expansion pressure (mbar) | 1.6 | 1.6 |
| Analyzer pressure (mbar) | 1×10^{-6} | 1×10^{-6} |
| Cool gas flow rate (L/min) | 13.0 | 10.7 |
| Auxiliary gas flow rate (L/min) | 1.0 | 1.5 |
| Nebulizer gas flow rate (L/min) | 0.90 | 0.95 |
| Sweep gas flow rate (L/min) | 3.2 | 2.6 |
| Indium sensitivity (5 ppb) | 350,000 - 450,000 | 30,000 |

Table 2. ICP-MS Element Menu

| Normal Plasma Elements | | | | | | | |
|------------------------|-------------|--------|---------|----------------|----------|--------|---------|
| Element | Isotopes | IDL ** | MDL *** | Element | Isotopes | IDL ** | MDL *** |
| Antimony (Sb) | 121, 123 | 1.5 | 0.4 | Niobium (Nb) | 93 | 3 | 0.9 |
| Arsenic (As) | 75 | 2 | 0.1 | Osmium (Os) | 189, 188 | 1.5 | 0.06 |
| Barium (Ba) | 135, 137 | 7 | 0.6 | Palladium (Pd) | 105, 108 | 1.5 | 0.1 |
| Beryllium (Be) | 9 | 5 | 0.3 | Platinum (Pt) | 194, 195 | 1 | 0.04 |
| Bismuth (Bi) | 209 | IS* | ---- | Rhodium (Rh) | 103 | 0.4 | 0.02 |
| Cadmium (Cd) | 111, 114 | 1 | 0.08 | Rubidium (Rb) | 85 | 3 | 0.4 |
| Cerium (Ce) | 140 | 0.4 | 0.06 | Ruthenium (Ru) | 101 | 0.5 | 0.05 |
| Cesium (Cs) | 133 | 0.4 | 0.05 | Silver (Ag) | 107, 109 | 0.2 | 0.02 |
| Chromium (Cr) | 52, 53 | 3 | 0.5 | Selenium (Se) | 78, 82 | 3 | 0.1 |
| Cobalt (Co) | 59 | 1 | 0.1 | Strontium (Sr) | 88 | 5 | 0.5 |
| Copper (Cu) | 63, 65 | 2 | 0.6 | Tantalum (Ta) | 181 | 3 | 1.4 |
| Gallium (Ga) | 71 | IS* | --- | Tellurium (Te) | 125, 130 | 4 | 0.3 |
| Gold (Au) | 197 | 1.5 | 0.08 | Thallium (Tl) | 205 | 1 | 0.3 |
| Hafnium (Hf) | 178 | 0.6 | 0.3 | Tin (Sn) | 118, 120 | 8 | 1.7 |
| Holmium (Ho) | 165 | IS* | --- | Titanium (Ti) | 47, 50 | 25 | 0.4 |
| Indium (In) | 115 | IS* | --- | Tungsten (W) | 182, 184 | 1.5 | 0.1 |
| Iridium (Ir) | 191, 193 | 0.2 | 0.02 | Uranium (U) | 238 | 0.2 | 0.02 |
| Lanthanum (La) | 139 | 0.3 | 0.05 | Vanadium (V) | 51 | 4 | 0.8 |
| Lead (Pb) | 206,207,208 | 0.2 | 0.1 | Ytterbium (Yb) | 172 | IS* | --- |
| Manganese (Mn) | 55 | 7 | 0.9 | Yttrium (Y) | 89 | IS* | --- |
| Molybdenum (Mo) | 95, 98 | 5 | 0.5 | Zinc (Zn) | 66, 68 | 6 | 1.1 |
| Nickel (Ni) | 60, 62 | 7 | 2.4 | Zirconium (Zr) | 90 | 9 | 0.6 |

| Cool Plasma Elements | | | | QA/QC Isotopes | |
|----------------------|------------|--------|---------|----------------|------------|
| Element | Isotopes | IDL ** | MDL *** | Species | Isotopes |
| Aluminium (Al) | 27 | 11 | 17 | ArCl | 77 |
| Calcium (Ca) | 40, 44 | 25 | 1.4 | Krypton (Kr) | 83 |
| Iron (Fe) | 54, 56 | 5 | 0.4 | Xenon (Xe) | 130 |
| Lithium (Li) | 7 | 0.5 | 0.06 | Cerium Oxide | 156 |
| Magnesium (Mg) | 24, 25, 26 | 6 | 0.3 | Background | 8, 99, 220 |
| Potassium (K) | 39 | 20 | 0.8 | | |
| Sodium (Na) | 23 | 20 | 1.3 | | |

* Internal Standard

** Instrumental Detection Limit (ng L^{-1} : 3 sigma, 95% confidence, 7 replicate reagent blanks)

*** Method Detection Limit (ng m^{-3} : 3 sigma, are based on 14 m^3 sample collected on pre-cleaned 47mm Teflon membrane substrate).

C. Minimization of Interferences

Polyatomic interferences can impose significant limitations on the accurate quantification of several elements of interest. These interferences are classified into three general groups based upon their primary source: (a). digest matrix-sourced, (b). aerosol matrix-sourced; and (c). plasma sourced. Multiple tools and strategies are available to minimize and/or prevent their formation. These approaches include: **(a)** modified digestions to avoid polyatomic-prone acids; **(b)** front-end control through the use of desolvation (MCN or USN or cold spray chamber), micro-volume, enhanced efficiency nebulizers, or automated SPC; and **(c)** control by the ICP-MS itself with modes such as cool plasma / shielded torch operation or collision / reaction cells. The later two approaches, specifically the use of a microconcentric desolvating nebulizer front-end, and use of the cool plasma/shielded torch mode of the ICP-MS were used in this study to greatly minimize the effect of polyatomic interferences.

These techniques when properly applied enable the accurate quantitation of certain key elements which otherwise would be severely compromised. In addition these approaches significantly improve the detection limits for an additional group of elements. The reductions in polyatomic interferences brought about by these techniques also bring important benefits to isotope ratio and isotope dilution analyses, as well as a simplified solubilization method.

IV. Inductively-Coupled Plasma Optical Emission Measurements

Where levels of the light elements: Al, Ca, Fe, K, Mg, Mn, Na, S, Si, and Zn allow, Inductively-Coupled Plasma - Optical Emission Spectrometry is a viable and attractive option to "cool-plasma" ICP-MS. The method is quite robust and accurate for the above listed elements when concentrations exceed a few ppb.

The elements Al, Ca, Fe, K, Mg, Mn, Na, S, Si, and Zn are determined on a Perkin Elmer 4300 DV Inductively-Coupled Plasma Optical Emission Spectrometer (ICP-OES). This is a CCD-based, simultaneous reading instrument with a typical optical resolution of 0.007 nm. All emission data are acquired in axial-viewed mode for significantly enhanced sensitivity. Multiple emission lines for each element were viewed to ensure spectral purity. The optical bench is purged with argon to improve low-UV performance. The spectrometer is interfaced with an acid resistant, polymer-based, Scott-type spray-chamber and an alumina GEM-TIP nebulizer, operated at room temperature. The demountable quartz torch is fitted with a sapphire injector. This "front-end" enabled the determination of silicon in the HF-containing digests. Six mL sub-samples of the 30 mL total volume digestates from the microwave-assisted acid digestion of the aerosol samples were utilized for the analysis. Samples and standards are transferred to trace metal clean polypropylene tubes for automated analysis (AS-91 autosampler). Before analysis the spectrometer is optimized to produce >800,000 emission counts for a 1 mg L⁻¹ Mn standard (257.610 nm). Calibration standards are acid matrix matched (nominally 0.8N HNO₃, 0.2N HCl, 0.2N HF), though our earlier studies demonstrated no detectable difference between standard response in 0.1N HNO₃ and the digest matrix for these elements. A standard four-point external calibration scheme is employed and linearity of the calibration curves at each element line was uniformly excellent (typical r² of at least four-nines). Six replicate acquisitions are obtained for each sample. Sensitivity and background are monitored with check standards and blanks every 9 samples. Over all instrument performance is verified (also every 9 samples) using the Canadian Research Council's Standard Reference Water Sample, SLRS-4. Accuracy and precision as inferred from repeated analysis of the SRM was excellent, with all recoveries within the certified ranges, and precision on the order of ~ 1-2%. Specific operating details follow:

| | |
|---------------------|---------------------------|
| Plasma Gas Flow: | 15 L min ⁻¹ |
| Auxillary Gas Flow: | 0.2 L min ⁻¹ |
| Nebulizer Gas Flow: | 0.58 L min ⁻¹ |
| Sample Uptake: | 1.35 mL min ⁻¹ |
| Emission Quant: | Area Counts |

Emission Wavelengths (nm):

| | |
|------------------------------|---------------------------------------|
| Al: 394.401 , 396.153 | Mn: 259.372 , 257.610 |
| Ca: 317.933 , 315.887 | Na: 589.592 , 588.995 |
| Fe: 238.204 , 259.939 | S: 180.669 , 181.975, 182.563 |
| K: 766.490 | Si: 251.611 , 252.851, 288.158 |
| Mg: 285.213 , 279.077 | Zn: 213.857 , 202.548 |