



# Continuous measurement of elemental composition of ambient aerosol by induction-coupled plasma mass spectrometry

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## ABSTRACT

There is presently no instrumentation that can provide (near) real time information on elemental composition of atmospheric aerosols. We describe an arrangement where air is sampled through a cyclone @30 L/min with a 50% cutoff @ ~250 nm. The particles deposit into a cup through which deionized water is continuously flowing. High purity HNO<sub>3</sub> is added downstream and the mixed stream optionally flows through a quartz photo reactor (185 nm, ~90 °C, t<sub>R</sub> ~1.2 min) and is aspirated by an induction coupled plasma mass spectrometer (ICP-MS). Comparative batch experiments in which samples were not photodigested at all or thermally digested off-line for an extended period indicated no statistically significant difference in the results. This observation agrees with early theoretical and experimental work. Some 22 elements were quantifiable (S/N ≥ 10) at all times in the aerosol samples collected in our highly urban sampling location; an additional 4 elements were quantifiable at times of construction activity in the general area. Presently attained system limits of detection (LODs) are orders of magnitude higher than the instrumental LOD, both because of the purity of the acid and pump-induced contamination. These aspects can be vastly improved and will need to be improved to determine background concentrations.

## 1. Introduction

An average adult breathes 13 m<sup>3</sup> air/day, representing a mass of ~15 kg, substantially more than the total mass of food and beverages consumed, emphasizing the importance of air contamination [1]. The size fraction of particulate matter (PM) of concern is generally considered to be ≤ 2.5 μm aerodynamic diameter (PM<sub>2.5</sub>) [2], although various parameters may affect the exact intake fraction [3] and there is currently special interest in the very fine particles (≤1.0 μm).

Metals are of particular interest; they can range from essential to toxic. In ambient aerosols, they can be present as the element or as a pure compound, in soluble or insoluble form, or be complexed to other soluble or insoluble components [4]. While soluble material can pass through the alveoli and deposit in the parenchyma [5], insoluble materials may stay deposited in the lower respiratory tract much longer and be released only slowly [4]. Metals in anthropogenic aerosols generally occur in more soluble forms than in crustal aerosols [6]. Trace metal solubility depends more on the metal than on the particle size and differences in various literature reports may in part be due to different extraction procedures [7]. One recent paper suggests that sulfate plays a key role in producing highly acidic fine aerosols

capable of dissolving primary transition metals and this may account for sulfate-health associations reported in past studies [8].

Chromium, Cd, As, Ni, Mn and Pb are classified as mobile source air toxics by the USEPA [9]. Cu and Fe are redox-active metals that lead to in-vivo generation of reactive oxygen species. Iron, Ni, V, Co, Cu, Cr in/on inhaled aerosols are linked to cellular oxidative stress in airway cells [5]. The extent of oxidative damage to DNA in A549 human lung cells was related to metals in PM<sub>2.5</sub> [10]. Zinc may cause cellular inflammation [5,11] and has been correlated with lung problems. Soluble metals in PM affect blood coagulation, exacerbate thrombotic diseases [12] and reduce infant birth weights, possibly through deposition in fetal tissues and affecting fetal growth [13].

Typically heavy metals are present in ambient aerosols in the low to sub ng/m<sup>3</sup> range, necessitating long (often 12–24 h) sample collection periods resulting in poor time resolution [14]; filter collection on a variety of available media are used. Laboratory analysis of such filters involve obligatory manual handling steps with potential contamination. Some efforts, dedicated to a single metal, have automated the analysis process [15] but the filter collection step remains the bottleneck. For example, we have previously demonstrated automated 15 min resolution filter collection and analysis, but only for soluble Cr (VI) [16].

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Prior to our work, Kidwell and Ondov devised a system sampling at 170 L/min to which steam was introduced at 5 g/min for particle growth. Particles were then collected as a slurry by a virtual impactor and a fraction collector [17], the collection efficiency for 0.5  $\mu\text{m}$  particles was 40% and decreased with decreasing particle size, falling below 30% for 0.1  $\mu\text{m}$  particles. Later the authors used this system to collect 30 min samples that were subjected to multi-element analysis by graphite furnace atomic absorption spectrometry [18]. The only multi-element work we are aware of is due to Chang et al. [19], who introduced aliquots of cigarette smoke aerosol in a flow injection mode from a smoking machine directly into an inductively coupled plasma mass spectrometer (ICP-MS) by consecutively puffing a burning cigarette. A complex valving system accomplished this and they looked primarily at As, Pb, Cd, and Hg. Considering the origin, some of these metals were likely already in gaseous form or at best present as nanoparticles; in any case, thankfully the metal concentrations in ambient air is far smaller than those in cigarette smoke.

Reported techniques for the measurement of aerosol metals include proton-induced X-ray emission [20], inductively coupled plasma mass spectrometry (ICP-MS) by itself [7,21], or with laser ablation [22] and optical emission spectrometry (ICP-OES) [4], ion chromatography [9], X-ray fluorescence [12], atomic absorption spectrometry [2], etc. Herein we describe a novel integrated system: A mini-cyclone is operated at a high sampling rate with the estimated 50% cutoff being  $\sim 250$  nm. Deionized water continuously flushes the cyclone bottom. High purity  $\text{HNO}_3$  is added to the effluent particle suspension; the mixed stream flowed into an ICP-MS detector, in most cases through a photochemical reactor to aid digestion (but this was later proved unnecessary).

## 2. Material and methods

Standards and reagents are described in detail in the SI.

### 2.1. Instrumentation

The experimental arrangement is shown in Fig. 1. An inverted funnel sample inlet located  $\sim 8$  m above ground level, extending 0.5 m from the exterior wall of the laboratory building (at University of Texas at Arlington, 32.7050°N, 97.1228°W was connected by a electrically grounded metal encased PFA Teflon conduit (total length  $\sim 2$  m, including the wall traverse) to a cyclone (Teflon<sup>®</sup> coated Aluminum mini-cyclone: 50% cutoff,  $d_{50}$ , 2.5  $\mu\text{m}$  @ 3 LPM, URG-2000-30ED, [www.urgcorp.com](http://www.urgcorp.com)). The manufacturer provides  $d_{50}$  values up to 21 LPM (370 nm). Two different extrapolation methods (see Supporting Information, Fig. S1) indicate  $d_{50}$  @ 30 LPM to be  $245 \pm 11$  nm. The precise cut-off is not considered particularly important as the total mass in the sub-300 nm region is relatively insignificant. The upper cut off is estimated from the inlet geometry to be  $\sim 12$   $\mu\text{m}$ . A custom PTFE sample collection cup was machined in-house and was equipped with two polytetrafluoroethylene (PTFE) tubes (0.86/1.68 mm i.d./o.d., 20 SW, [www.zeusinc.com](http://www.zeusinc.com)) to function as Milli-Q water (0.45 mL/min) inlet and exit. The cyclone air exit was followed by a glass wool-flask water trap, a mass flow controller (UNIT model 3050 A, 50 standard liters per minute (SLPM) full scale, [www.brooksinstrument.com](http://www.brooksinstrument.com)) and an air pump (Model DOA-P707-AA, [www.Gastmfg.com](http://www.Gastmfg.com)) aspirating air at 30 SLPM. A three-way solenoid valve SV (P/N 100T3WMP12-54, 20 psi, [www.bio-chemvalve.com](http://www.bio-chemvalve.com)) normally permitted 7.9 M  $\text{HNO}_3$  to be mixed with the aerosol slurry in water at a tee. The flow rates of nitric acid to the tee and milli-Q water input to the cyclone varied in the range 0.37–0.45 mL/min giving a total flow of 0.74–0.90 mL/min to match the liquid aspiration rate into the ICPMS by adjusting the peristaltic pump flow rate as needed. The valve SV was incorporated such that the stream can be segmented to minimize dispersion by alternately turning it on and off to aspirate air bubbles. The mixed stream proceeds through a 1 mm i.d. quartz digestion coil ( $\sim 0.7$  mL

volume). The 5-mm inner diameter of the coil snugly fit the 15 cm fused quartz mercury pen lamp (L, Analamp 81–1025-01, 17.5-cm lighted length, powered by a dedicated power supply (P/N 90-0001-01, both from [www.bhkinc.com](http://www.bhkinc.com)) capable of transmitting the 185-nm Hg line. The digestion coil was fixed to the lamp housing in four places by thermally conductive ceramic adhesive. Aluminum foil was then wrapped around the assembly both for preventing onlooker/operator exposure and more efficient utilization of the light by creating a reflecting cavity. The outside was then insulated with glass fiber padding. The ends of the quartz coil were terminated in PTFE tubing using heat-shrink FEP sleeves.

An X Series II ICP-MS ([www.thermo.com](http://www.thermo.com)) was used in the direct infusion mode. The instrument utilizes a Peltier-cooled (3 °C) nebulizer and has an enhanced mass resolution of 0.7 amu. The operating conditions can be found in the Supporting Information in text and Table S1. All results are reported as average  $\pm$  standard deviation ( $n = 3$ ) and are based on the peak area calculations for specific elements.

### 2.2. Adequacy of Limited Time On-line Digestion

For comparison with on-line vs. prolonged batch mode digestion, mg quantity of ambient aerosol was collected by sampling through the cyclone with its original collection cup for 48 h. The collected sample was suspended into a slurry using 5 mL water and ultrasonication. Four 1-mL aliquots from this continuously agitated suspension were transferred to clean 5 mL PFA Teflon vials ([www.saville.com](http://www.saville.com)) while momentarily turning off the agitation when pipetting off an aliquot. To each of two vials, 1 mL 7.9 M  $\text{HNO}_3$  was added; they were then loosely capped and incubated at 90 °C for 8 and 24 h, respectively. After this digestion step, the contents were transferred to a volumetric flask and made up to 25 mL. Control blanks consisted of 1 mL 7.9 M  $\text{HNO}_3$  added to water in similar Teflon vials and incubated in the same manner (one 8 h and one 24 h). The aliquots to which no acid was added were respectively transferred to volumetric flask and made up to 25 mL just before analysis as follows.

The batch samples above were analyzed by replacing the cyclone in Fig. 1 with a 6-port all-PTFE rotary injector equipped with a 100  $\mu\text{L}$  loop. The contents of all six volumetric flasks above (including two controls) were analyzed in triplicate; the flask contents were poured into a sample cup and ultrasonicated immediately before the injection aliquot was taken by direct aspiration into the valve. The incubated control blank values,  $< 1\%$  than the incubated sample data, were nevertheless subtracted from the sample results before consideration.

## 3. Results and discussions

### 3.1. Contamination. Pumps and tubing

It was anticipated that the levels of many of the metals of interest in the sample seen by the ICP-MS will be very low. Hence it was vital to keep contamination levels as small as possible. We therefore designed the system such that the sample comes in contact with only PTFE and quartz after collection. This does not however solve the problem of other reagents, notably  $\text{HNO}_3$ , potentially acquiring contamination through the pumping system. Metallic pumps are obviously unsuitable and PEEK is not compatible with strong oxidizing acids. The pump should also have an infinite reservoir, i.e., it should not need to frequently refill itself (as in a syringe pump). Based on these criteria we chose a peristaltic pump. Commonly used silicone pump tubing was known beforehand to be incompatible with  $\geq 2$  M  $\text{HNO}_3$ ; poly(vinyl) chloride (PVC) tubing could be used for very limited periods. Our choice was then based on plasticized fluorocarbon (Viton<sup>®</sup>) and cross-linked EPDM rubber-polypropylene tubing (Santoprene<sup>™</sup>). The levels of metals leaching from the tubes were dramatically reduced by boiling the pump tubes in 2 M HCl for 4 h and using them after thorough washing. The metal concentrations observed by the ICP-MS for the two

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