

# Measuring the Trace Elemental Composition of Size-Resolved Airborne Particles

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A new method to measure the trace elemental composition of size-resolved airborne particles that uses acetone extraction followed by ICPMS analysis is compared to three other established methods: copper anode XRF, molybdenum anode XRF, and an ICPMS method that uses HF digestion. The method detection limit (MDL), accuracy, and precision of each method is studied through the analysis of ambient samples collected in California. The MDLs of the new acetone-ICPMS method are similar to MDLs for the established HF-ICPMS method. Both sets of ICPMS MDLs are 1–3 orders of magnitude lower than XRF MDLs for approximately 50 elements other than the light crustal elements such as silicon, sulfur, calcium, and zinc. The accuracy of the acetone-ICPMS method was verified by comparison to measurements made using ion chromatography and the HF-ICPMS method. The acetone-ICPMS analysis method was more precise than the conventional HF-ICPMS method for collocated measurements. Both ICPMS methods were more precise than XRF for most elements. The size distribution of 21 elements contained in ambient particles collected with cascade impactors could be measured with good precision using the new acetone-ICPMS analysis method: lithium, sulfur, potassium, titanium, vanadium, manganese, iron, gallium, germanium, arsenic, selenium, bromine, rubidium, strontium, cadmium, tin, antimony, barium, thallium, lead, and bismuth. It is likely that the size distribution of an additional 9 elements could also be measured when concentrations are sufficiently high: phosphorus, molybdenum, niobium, palladium, cesium, europium, holmium, platinum, and uranium. None of the conventional methods were able to measure the size distribution of these elements with acceptable precision under the conditions studied. The new acetone-ICPMS method should provide useful data for the study of the health effects of airborne particles.

## Introduction

Epidemiological studies have identified a correlation between airborne particle mass and increased health risk (1), but attempts to definitively link these health effects to more

detailed measures of particle size and/or composition have been inconclusive (2). The ability to identify strong correlations between health effects and the size resolved composition of airborne particles may be limited by the resolution of the conventional techniques used to measure particle composition. Traditional methods for the measurement of elemental particle composition such as Proton Induced X-ray Emission (PIXE) and X-ray Fluorescence (XRF) have primarily focused on the most abundant elements in the particles (see for example refs 3–6) that usually include significant contributions from windblown soil. While this approach helps achieve mass closure in source apportionment studies (see for example refs 7–12), it may ignore elements derived from combustion sources that make up a small fraction of particle mass but that have significant health impacts. This problem is exacerbated in smaller size fractions such as PM<sub>0.1</sub> (airborne particles smaller than 0.1  $\mu\text{m}$ ) because mass concentrations are typically much lower in this part of the distribution, pushing concentrations below the minimum detection limits. The abilities of different methods to determine the composition of airborne particles across a broad range of elements must be clearly understood before the relationship between particle composition and health can be determined.

In this study, a new method to measure the trace elemental composition of size-resolved airborne particulate matter that uses acetone extraction followed by Inductively Coupled Plasma Mass Spectrometry (ICPMS) analysis is compared to three other established methods: copper anode XRF, molybdenum anode XRF, and an ICPMS method using HF digestion. The precision of each technique for the measurement of elements in different particle size fractions will be evaluated through the analysis of collocated samples. The accuracy of each technique is studied using internal consistency checks, comparison to other measurement methods, and validation against standard reference materials where possible.

## Methods

An Agilent 7500i ICPMS operated with a MicroMist nebulizer (Glass Expansion, AR50) was used to analyze samples of airborne particulate matter at the University of California, Davis, and a Thermo-Finnigan Element II Magnetic Sector ICPMS operated with a microconcentric nebulizer (Cetac, MCN-6000) was used to analyze samples at the University of Wisconsin, Madison. The Agilent 7500i ICPMS is capable of routine measurements of elemental concentrations in the range of parts per trillion by mass. The Thermo-Finnigan ICPMS has even lower detection limits and can resolve very small fractional mass-to-charge ratio ( $m/z$ ) differences that can be used to separate analyte  $m/z$  from interfering plasma molecular ions. The overall sensitivity of both ICPMS instruments is limited by the ability to transfer the particulate matter sample into a solution that can readily be analyzed. Airborne particles are often collected on Teflon membrane filters that have low background contamination. Teflon is hydrophobic, and so direct dissolution of the sample in water is not possible. Teflon can be wetted with a substance such as ethanol to improve aqueous contact, but many of the particles that contain elements of interest are not water soluble and remain trapped in the filter. The sample dissolution step represents the true challenge of measuring elemental composition of airborne particles using ICPMS.

An aggressive digestion technique has been developed at the University of Wisconsin, Madison, to remove airborne particulate matter trapped on a Teflon filter and place it into

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an acidic solution suitable for ICPMS analysis. The PTFE ring surrounding the stretched Teflon membrane is first removed, and the remaining portion of the filter is then placed in a Teflon pressure vessel with a mixture made from 1.5 mL of 16 N HNO<sub>3</sub>, 0.5 mL of 28 N HF, and 0.2 mL of 12 N HCL. The samples are then heated with a microwave oven to 180 °C in 9 min, followed by a 10 min hold at that temperature, and 1 h of ventilation/cooling. After cooling, digests are diluted to 30 mL with high purity water prior to ICPMS analysis. This digestion method has been used to prepare samples for the study of the elemental composition of traffic-related aerosols (13). Similar digestion methods have yielded good results for the analysis of PM10 standard reference materials (14). This digestion technique requires adequate safety measures when working with HF at high temperature and pressure. The digestion vessels also require rigorous cleaning between samples to avoid "carry-over" contamination (15).

A new method for the removal of airborne particulate matter from Teflon membrane filters that does not employ HF at high temperature and pressure has been developed at the University of California, Davis. The underlying principles for the method are based on the observations that organic solvents can be used to remove airborne particulate matter from filters in preparation for organics analysis (16, 17), and that the ICPMS can quantitatively analyze many elements contained in aqueous particles up to 1  $\mu$ m in diameter without the need for complete dissolution (18, 19). An organic solvent that frees particles smaller than 1  $\mu$ m in diameter from the Teflon membrane should therefore produce a solution that can be analyzed directly by the ICPMS. The extraction efficiencies of ethyl acetate, hexane, toluene, 2-propanol, and acetone were evaluated separately using ambient airborne particulate matter collected on Teflon filters (R2PJ047, Pall Corp.). Dichloromethane (DCM) is another solvent commonly used for organics extraction, but it was not considered because chlorine radicals produced from the DCM attack the ICPMS, and toxic byproducts such as phosgene (CCl<sub>2</sub>O) would be expected from the reaction of excess chlorine in the plasma. 2-Propanol and acetone were found to have good extraction efficiency from the Teflon membrane filters. Acetone was eventually picked as the best solvent because it is available in relatively pure form and has a high vapor pressure allowing the sample to be concentrated in subsequent handling steps. Ketones larger than acetone may also be efficient extraction solvents, but they are not miscible with water and are less volatile. In the current study, half of each Teflon filter was sonicated for 20 min in a 50 mL polypropylene vial (Corning Corp.) containing 30 mL of solution made from 75% acetone (Fisher Optima grade) and 25% 1 N nitric acid (Fisher Trace Metal Grade diluted with ultrapure water). The resulting extract was decanted into a second 50 mL polypropylene vial to prevent particles from adsorbing back onto the filter. The sample extract was then heated to approximately 45 °C, and pure nitrogen (99.997%) was passed over it to evaporate acetone using a Reacti-Vap Evaporator (Pierce Corp) equipped with Teflon coated needles. After the sample volume was reduced to 4 mL, the extract was transferred to a 15 mL polypropylene (Corning Corp.) vial that could be loaded into the ICPMS autosampler (Cetac Technologies, ASX500). All bottles, Corning vials, and other sample handling materials were triple rinsed with ultrapure water prior to use. Elemental standards (SPEX Certiprep, Metuchen, NJ) were diluted in a solution of 75% acetone, 25% 1 N HNO<sub>3</sub> that had already been concentrated 7.5-fold and were analyzed alongside samples for calibration.

Two types of XRF systems at the UC Davis Crocker Nuclear Laboratory (CNL) were used for sample analysis during the current study. Both systems are optimized to work with samples that have high areal density. The first XRF system

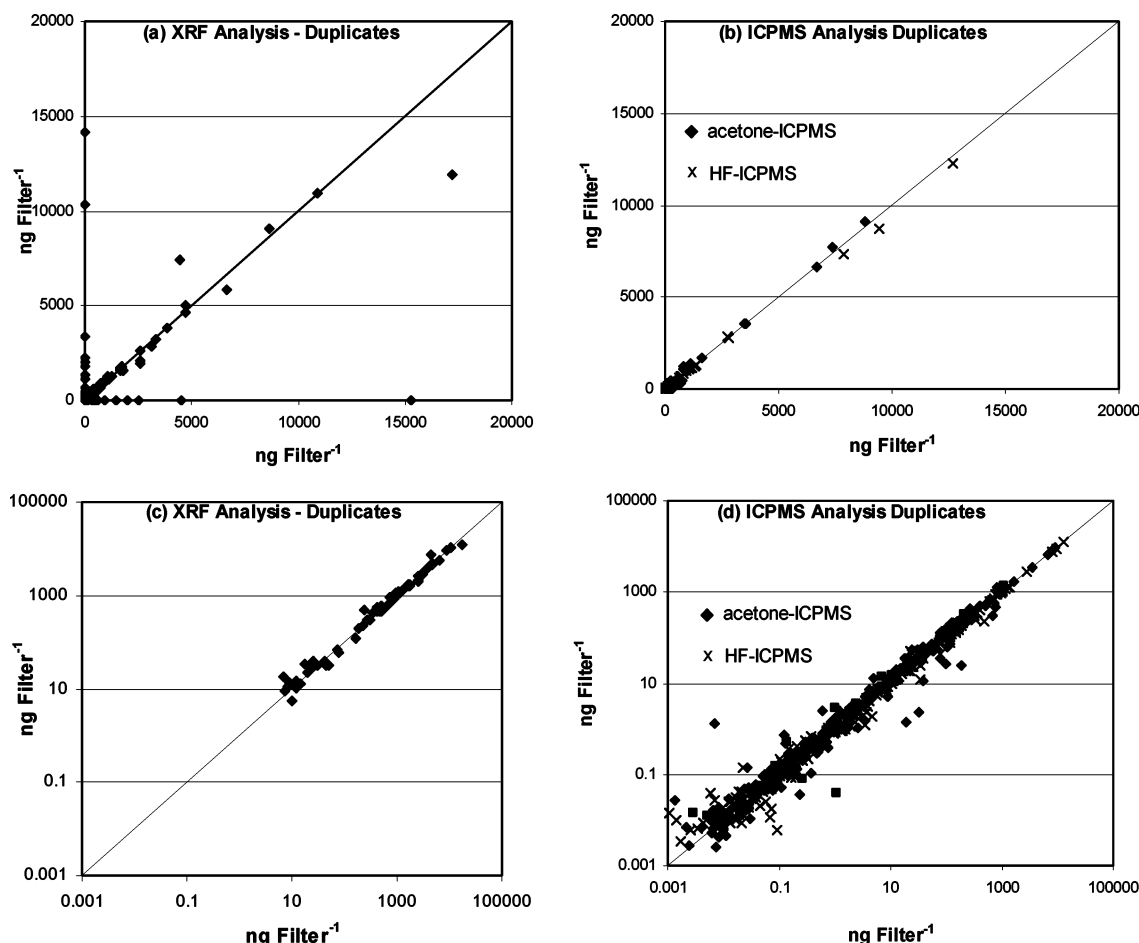
was equipped with a General Electric grounded anode diffraction type X-ray tube with a molybdenum anode (moly-XRF), while the second XRF system used a copper anode (copper-XRF). The copper-XRF system was used to measure elements lighter than iron, while the moly-XRF system was used to measure elements heavier than iron. The copper-XRF system has lower detection limits than a PIXE system available at CNL (20) for elements heavier than silicon and lighter than iron (21). No comparison was made between ICPMS and PIXE analytical methods in the current study, since PIXE statistics are inferior to those of the copper-XRF system. The XRF systems were calibrated prior to analysis using pure elemental standards.

The precision and accuracy of the four analysis techniques (abbreviated copper-XRF, moly-XRF, HF-ICPMS, acetone-ICPMS) was explored using ambient samples of airborne particulate matter collected with Reference Ambient Air Samplers (RAAS) (Andersen Instruments, Smyra GA) and Micro Orifice Uniform Deposit Impactors (MOUDIs model #110) (MSP Corporation, Shoreview, MN). An upstream AIHL-design cyclone (22) was used to remove particles with diameter larger than 1.8  $\mu$ m before sample collection. The smallest aerodynamic diameters of particles collected on stages 5–10 of the MOUDIs were 1.0, 0.56, 0.32, 0.18, 0.1, and 0.056  $\mu$ m, respectively. Collection times ranged from 8 to 48 h with flow rates of 10 L min<sup>-1</sup> and 30 L min<sup>-1</sup> for RAAS and MOUDI, respectively. Samples collected in California at Bakersfield, Bodega Bay, Davis, Modesto, Sacramento, and Sequoia during the California Regional Particulate Air Quality Study (CRPAQS) between December 2000–February 2001 (23) were analyzed using copper-XRF, moly-XRF, and acetone-ICPMS. Samples collected at UC Davis during February 2005 were analyzed with HF-ICPMS and acetone-ICPMS. The performance of each analysis technique is discussed below.

## Results

Method detection limits (MDLs) and/or method blank levels were calculated for each analysis technique. The variability of acetone-ICPMS method blanks was  $\leq$  the variability of HF-ICPMS method blanks for 36 of 49 elements, suggesting that the sensitivity of the two methods is comparable. The MDLs of the acetone-ICPMS method were lower than the XRF MDLs (typically by several orders of magnitude) for 20 of 23 elements where a direct comparison was possible. Generally, elements with high atomic weight had lower ICPMS MDLs, while elements with lower atomic weight such as Si, S, and Ca had lower XRF MDLs. A complete description of the MDLs is provided in the Supporting Information.

Figure 1 illustrates the agreement of duplicate laboratory measurements of element concentrations in ambient airborne particles collected on Teflon filters. Each sample was analyzed multiple times on the same day using one set of calibration curves to produce duplicate data points. Figure 1a,c shows the results of duplicate copper-XRF analysis for 15 elements in 10 samples, while Figure 1b,d shows the results of duplicate acetone-ICPMS analysis for 55 elements in 65 samples and HF-ICPMS analysis for 55 elements in 5 samples. The two top panels show the results on a linear scale (with 0 values), while the lower panels show the results on a log scale (without 0 values). Figure 1a shows that copper-XRF measurements of elements present at relatively high concentrations are reproducible, with most of the data points detected above MDL falling close to the 1:1 line. Duplicate copper-XRF measurements of sulfur, calcium, iron, and nickel had normalized RMS error <10%, while the remaining copper-XRF elements had normalized RMS error >10%. The precision of copper-XRF analysis becomes poor for those concentrations that are close to the MDL because the first copper-XRF measurement may detect a concentration, while the second measurement of the same sample falls below the



**FIGURE 1. Precision of duplicate analysis of ambient particulate matter samples collected on Teflon filters using acetone-ICPMS and XRF. Each sample was analyzed twice on the same day with the same set of calibration standards. Panels (a, b) show the results on a linear scale, while panels (c, d) show the results on a log scale (without 0 values).**

MDL and is therefore determined to be zero. This problem produces data points on the horizontal and vertical axes in Figure 1a. Based on expected MDLs and the diminishing abundance of heavier elements in the environment, it is likely that heavier elements analyzed by XRF would have similar or worse precision. The lowest concentration that can be reliably measured with copper-XRF is approximately 10 ng filter<sup>-1</sup> using a collection area of 10 cm<sup>2</sup>. Figure 1b shows that the corresponding results of duplicate analysis using ICPMS do not suffer from the “on-off” effect seen in the copper-XRF data. All 55 elements measured with ICPMS had a normalized RMS error less than 10% with the exception of titanium, germanium, and some rare earths which had a normalized RMS error between 10 and 13%. The trends at very low concentrations can be better viewed in Figure 1c,d that use a log scale. ICPMS can make precise duplicate measurements down to 0.01–0.1 ng filter<sup>-1</sup> or lower. Additional statistics summarizing the duplicate measurements can be found in the Supporting Information.

Table 1 shows the linear correlation coefficients ( $R^2$ ) and slopes between collocated PM<sub>1.8</sub> samples collected during CRPAQS. These samples were collected with RAAS filter samplers loaded with identical Teflon filters in two separate sampling legs. These collocated samples exhibit concentration differences caused by variability in sample handling, collection, and analytical precision. Forty-seven collocated samples were analyzed using acetone-ICPMS, but only six collocated samples were analyzed with XRF due to the limited availability of resources at CNL.

Good agreement between collocated samples is defined to be  $R^2 \geq 0.7$  combined with slopes of  $1.0 \pm 0.3$ . Twenty-

seven elements show good agreement between collocated samples analyzed using acetone-ICPMS. Six elements meet these criteria with copper-XRF and moly-XRF analysis. Of these, only collocated calcium and iron measurements are significantly more consistent with XRF than with acetone-ICPMS analysis. Plasma molecular ions interfere with the ICPMS measurement of silicon, calcium, and iron. Dust contamination during sample handling also introduces random uncertainty in the measurement of light crustal elements. Duplicate analysis of the same sample does not identify this problem because the ICPMS method reliably reports the same concentrations (including the contamination). Dust contamination could be minimized in future studies by processing the samples in a dedicated clean room. In the current study, a dedicated clean room was not available for acetone ICPMS analysis, and a few outliers were detected in the measured concentrations using Grub's Test. When 4, 3, and 1 outliers were removed from the 47 samples of iron, strontium, and silver concentrations, respectively, these elements pass the internal consistency criteria ( $R^2_{\text{Fe}} = 0.75$ , slope<sub>Fe</sub> = 0.94;  $R^2_{\text{Sr}} = 0.93$ , slope<sub>Sr</sub> = 0.81;  $R^2_{\text{Ag}} = 0.85$ , slope<sub>Ag</sub> = 1.01). Magnesium and sodium are found in large sea salt aerosol, and the statistics in Table 1 are dominated by 9 samples with high concentrations that were measured at Bodega Bay during on-shore flow conditions. The  $R^2$  for these elements is 0.99, but the slope is 0.66, suggesting that the flow rate for one of the sampling legs was incorrect at this location. Without these 9 high concentration samples the statistics for Na and Mg are  $R^2_{\text{Na}} = 0.65$ , slope<sub>Na</sub> = 0.85;  $R^2_{\text{Mg}} = 0.56$ , slope<sub>Mg</sub> = 0.82. Other elements, such as the rare earths and tungsten, did not pass the consistency criteria because

**TABLE 1: Precision of Collocated Analysis of Ambient Particulate Matter Samples Collected on Teflon Filters Using Acetone-ICPMS and XRF<sup>a</sup>**

	acetone-ICPMS ( <i>n</i> = 47)		XRF ( <i>n</i> = 6)	
	filter sample 1 vs 2		filter sample 1 vs 2	
	<i>R</i> <sup>2</sup>	slope	<i>R</i> <sup>2</sup>	slope
lithium	<b>0.94</b>	<b>0.96</b>		
sodium	0.99	0.66	0.37	-0.14
magnesium	0.99	0.66	0.09	-0.19
aluminum	0.00	0.01	0.09	-0.29
silicon	0.05	0.23	0.40	-1.13
phosphorus	<b>0.84</b>	<b>0.80</b>	0.00	0.00
sulfur	<b>0.88</b>	<b>0.93</b>	<b>0.98</b>	<b>0.96</b>
chlorine				
potassium	<b>0.96</b>	<b>0.89</b>	<b>1.00</b>	<b>1.00</b>
calcium	0.00	0.03	<b>0.93</b>	<b>1.08</b>
titanium	<b>0.70</b>	<b>0.95</b>	0.07	-0.74
vanadium	<b>0.99</b>	<b>1.01</b>	0.39	0.63
chromium	0.28	0.54	0.04	-0.56
manganese	<b>0.86</b>	<b>1.01</b>	<b>0.76</b>	<b>0.95</b>
iron <sup>b</sup>	0.40	0.59	<b>0.72</b>	<b>0.95</b>
cobalt	0.01	0.04	<MDL	<MDL
nickel	0.01	0.02	0.00	0.00
copper	0.01	0.02	0.54	0.72
zinc	0.14	0.16	0.32	1.59
gallium	<b>0.97</b>	<b>1.06</b>	0.05	0.59
germanium	0.53	0.54		
arsenic	<b>0.90</b>	<b>1.02</b>	0.01	-0.15
selenium	<b>0.94</b>	<b>0.89</b>	0.91	0.59
bromine	<b>0.93</b>	<b>0.70</b>	<b>0.97</b>	<b>0.70</b>
rubidium	<b>0.91</b>	<b>0.90</b>	0.50	0.84
strontium <sup>b</sup>	0.72	0.63	0.32	0.40
yttrium	0.33	0.56	0.62	1.57
zirconium	0.45	2.36	0.20	-0.22
niobium	<b>0.87</b>	<b>1.05</b>		
molybdenum	<b>0.98</b>	<b>1.00</b>		
palladium	<b>0.91</b>	<b>0.83</b>		
silver <sup>b</sup>	0.69	1.03		
cadmium	<b>0.91</b>	<b>0.86</b>		
tin	<b>1.00</b>	<b>0.98</b>		
antimony	<b>0.98</b>	<b>1.02</b>		
cesium	<b>0.90</b>	<b>1.00</b>		
barium	<b>0.96</b>	<b>1.06</b>		
lanthanum	0.38	0.79		
cerium	0.38	0.84		
praseodymium	0.16	0.68		
neodymium	0.25	0.68		
samarium	0.54	0.49		
europium	<b>0.91</b>	<b>0.93</b>		
gadolinium	0.64	0.92		
dysprosium	0.42	0.73		
holmium	<b>0.98</b>	<b>0.81</b>		
erbium	<MDL	<MDL		
thulium	<MDL	<MDL		
ytterbium	<MDL	<MDL		
lutetium	<MDL	<MDL		
tungsten	0.02	0.30		
platinum	<b>0.90</b>	<b>1.25</b>		
thallium	<b>0.90</b>	<b>0.96</b>		
lead	<b>0.89</b>	<b>0.87</b>	0.38	0.68
bismuth	<b>0.99</b>	<b>1.07</b>		
thorium	0.75	1.56		
uranium	<b>0.86</b>	<b>0.95</b>		

<sup>a</sup> Collocated samples were collected simultaneously in separate channels of a PM<sub>1.8</sub> filter sampler. Missing values indicate that the element was not measured by the technique. *R*<sup>2</sup> values greater than 0.7 coupled with slopes equal to 1.0 ± 0.3 are deemed consistent and are shown in bold. <sup>b</sup> Fe statistics would improve to 0.75 and 0.94 if 4 outliers were removed. Sr statistics would improve to 0.93 and 0.81 if 3 outliers were removed. Ag statistics would improve to 0.85 and 1.01 if a single outlier was removed.

sample concentrations were negligible or so close to the MDL that accuracy was compromised.

**TABLE 2: Average Normalized Dot Product of Collocated MOUDI Size Distributions Analyzed Using Acetone-ICPMS and HF-ICPMS<sup>a</sup>**

	<i>n</i> = 6		<i>n</i> = 4
	acetone-ICPMS	HF-ICPMS	acetone-ICPMS vs HF-ICPMS
lithium	<b>0.98</b>	0.00	0.06
sodium	0.43	0.01	0.36
magnesium	0.54	0.67	0.48
aluminum	0.49	0.69	0.57
phosphorus		0.73	
sulfur	<b>0.90</b>	0.17	0.43
potassium	<b>0.98</b>	<b>0.94</b>	0.81
calcium	0.00	0.24	0.01
titanium	<b>0.90</b>	0.69	<b>0.86</b>
vanadium	<b>0.93</b>	0.67	0.84
chromium	0.00	0.17	0.05
manganese	<b>0.99</b>	<b>0.95</b>	<b>0.93</b>
iron	<b>0.87</b>	<b>0.88</b>	<b>0.88</b>
cobalt	0.65	0.57	0.82
nickel	0.69	0.64	0.64
copper	0.68	0.80	0.64
zinc		0.39	
gallium	<b>0.98</b>	0.68	0.74
germanium	<b>0.96</b>		
arsenic	<b>0.96</b>	<b>0.87</b>	<b>0.88</b>
selenium	<b>0.92</b>	0.00	0.05
bromine	<b>0.97</b>		
rubidium	<b>0.98</b>	0.68	<b>0.85</b>
strontium	<b>0.94</b>	0.61	0.73
yttrium			
zirconium	0.46		
niobium	0.76	0.43	0.75
molybdenum	<b>0.98</b>	0.68	0.74
palladium		0.38	
silver	0.53	0.09	0.32
cadmium	<b>0.92</b>		
tin	<b>0.97</b>		
antimony	<b>0.95</b>	0.80	0.83
cesium		0.26	
barium	<b>0.98</b>	0.81	<b>0.91</b>
lanthanum	0.16	0.35	0.21
cerium		0.65	
praseodymium			
neodymium			
samarium			
europium			
terbium			
dysprosium		0.58	
erbium		0.49	
thulium			
ytterbium			
lutetium	0.00		
tungsten	<b>0.93</b>	0.82	0.78
platinum			
thallium	<b>0.98</b>	0.62	0.80
lead	<b>0.97</b>	0.73	<b>0.86</b>
bismuth	<b>0.96</b>		
thorium			
uranium		0.47	

<sup>a</sup> Values greater than 0.85 indicate consistency and are shown in bold.

Size-resolved measurements of airborne particulate matter are more difficult than bulk filter analysis because the same amount of mass is divided between multiple size fractions. Table 2 shows an analysis of the consistency of size-resolved measurements from four collocated MOUDI samples collected at UC Davis in February 2005. Samples from MOUDI stages 5–10 were cut in half after collection. One-half of each sample was analyzed using acetone-ICPMS at UC Davis, while the second half was analyzed using HF-ICPMS at the University of Wisconsin, Madison. Samples were shipped to Madison in Petri dishes sealed with Teflon tape in multiple layers of sealed packaging to prevent



**TABLE 3: Agreement between Collocated Analysis of Ambient Particulate Matter Samples Collected on Teflon Filters Using Filter-Based Samplers and MOUDIs Analyzed Using Acetone-ICPMS and HF-ICPMS<sup>a</sup>**

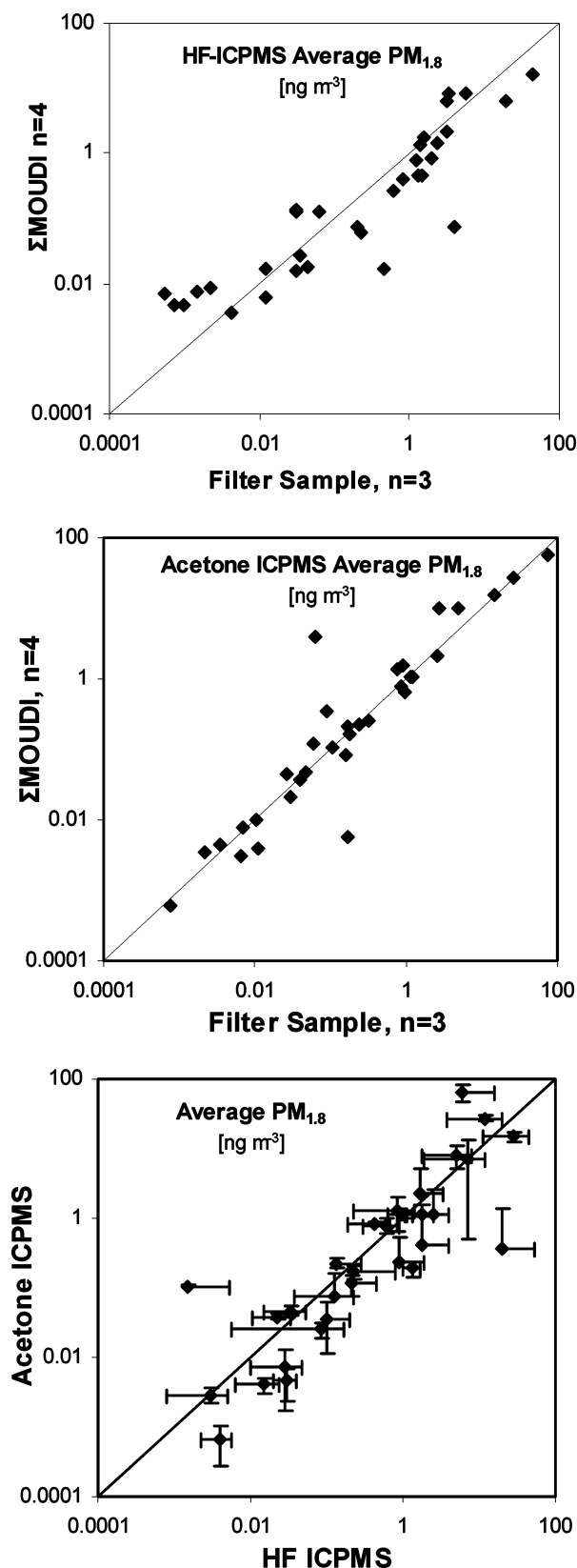
	average PM <sub>1.8</sub> acetone-ICPMS [ng m <sup>-3</sup> ]			average PM <sub>1.8</sub> HF-ICPMS [ng m <sup>-3</sup> ]		
	filter sample n = 3	ΣMOUDI n = 4	all n = 7	filter sample n = 3	ΣMOUDI n = 4	all n = 7
lithium	0.11 ± 0.01	0.11 ± 0.01	0.11 ± 0.01	0 ± 0	0 ± 0.01	0 ± 0
sodium	0.06 ± 0.11	3.82 ± 3.25	2.21 ± 3.06	1.58 ± 1.76	1.75 ± 2.02	1.68 ± 1.76
magnesium	0.09 ± 0.15	0.34 ± 0.34	0.23 ± 0.29	1.49 ± 1.4	0.46 ± 0.27	0.9 ± 1
aluminum	2.72 ± 1.28	10.24 ± 7.17	7.02 ± 6.51	<b>5.58 ± 3.05</b>	<b>8.01 ± 6.46</b>	<b>6.97 ± 5.07</b>
phosphorus	<MDL	<MDL	<MDL	2 ± 1.1	0.82 ± 0.27	1.33 ± 0.92
sulfur <sup>b</sup>	<b>74.6 ± 11.7</b>	<b>66 ± 7.4</b>	<b>70.3 ± 9.9</b>	3.4 ± 6	8 ± 12.2	6.1 ± 9.6
potassium	<b>26.7 ± 1.4</b>	<b>27.4 ± 3.5</b>	<b>27.1 ± 2.6</b>	19.2 ± 6.4	6.4 ± 3.3	11.9 ± 8.1
calcium	0 ± 0	0.64 ± 1.29	0.37 ± 0.97	0 ± 0	35.5 ± 38.95	20.28 ± 33.45
titanium	<b>0.17 ± 0.06</b>	<b>0.2 ± 0.04</b>	<b>0.19 ± 0.05</b>	<b>1.4 ± 0.38</b>	<b>1.3 ± 0.32</b>	<b>1.34 ± 0.32</b>
vanadium	<b>0.03 ± 0</b>	<b>0.04 ± 0.03</b>	<b>0.04 ± 0.02</b>	0.06 ± 0.02	0.13 ± 0.14	0.1 ± 0.11
chromium	0 ± 0	0.74 ± 1.48	0.42 ± 1.12	4 ± 0.86	0.07 ± 0.09	1.76 ± 2.16
manganese	<b>1.14 ± 0.03</b>	<b>1.07 ± 0.08</b>	<b>1.1 ± 0.07</b>	2.38 ± 0.75	1.4 ± 0.3	1.82 ± 0.71
iron	<b>14.6 ± 0.8</b>	<b>15.6 ± 3.3</b>	<b>15.2 ± 2.4</b>	44.1 ± 13.1	16.6 ± 5.1	28.4 ± 16.9
cobalt	0.01 ± 0.01	0 ± 0	0.01 ± 0.01	0.04 ± 0	0.02 ± 0.02	0.03 ± 0.02
nickel	0.76 ± 0.62	1.37 ± 1.93	1.11 ± 1.45	<b>3.1 ± 1.06</b>	<b>2.18 ± 1.84</b>	<b>2.57 ± 1.52</b>
copper	<b>0.92 ± 0.11</b>	<b>1.57 ± 0.8</b>	<b>1.29 ± 0.67</b>	1.34 ± 0.6	0.45 ± 0.17	0.83 ± 0.6
zinc	5.03 ± 0.06	10.23 ± 0.27	8 ± 2.79	3.18 ± 0.75	6.2 ± 3.78	4.91 ± 3.16
gallium	<b>0.09 ± 0</b>	<b>0.06 ± 0.01</b>	<b>0.08 ± 0.02</b>	<b>0.01 ± 0.01</b>	<b>0.02 ± 0.01</b>	<b>0.01 ± 0.01</b>
germanium	<b>0.01 ± 0</b>	<b>0.01 ± 0</b>	<b>0.01 ± 0</b>			
arsenic	<b>0.24 ± 0.02</b>	<b>0.22 ± 0.04</b>	<b>0.23 ± 0.03</b>	0.23 ± 0.2	0.06 ± 0.04	0.13 ± 0.15
selenium	<b>0.18 ± 0.04</b>	<b>0.17 ± 0.04</b>	<b>0.17 ± 0.04</b>	0 ± 0	0.39 ± 0.78	0.22 ± 0.59
bromine	<b>2.53 ± 0.19</b>	<b>2.15 ± 0.1</b>	<b>2.31 ± 0.24</b>			
rubidium	<b>0.04 ± 0</b>	<b>0.04 ± 0</b>	<b>0.04 ± 0</b>	0.03 ± 0.01	0.02 ± 0.01	0.02 ± 0.01
strontium	<b>0.03 ± 0</b>	<b>0.02 ± 0</b>	<b>0.03 ± 0.01</b>	0.03 ± 0.01	0.13 ± 0.09	0.09 ± 0.08
yttrium	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
zirconium	0.06 ± 0.03	0.12 ± 0.06	0.09 ± 0.06	0 ± 0	0 ± 0	0 ± 0
niobium	<b>0.0008 ± 0.0003</b>	<b>0.0006 ± 0.0005</b>	<b>0.0007 ± 0.0004</b>	<b>0.0043 ± 0.0006</b>	<b>0.0036 ± 0.0023</b>	<b>0.0039 ± 0.0017</b>
molybdenum	0.16 ± 0.02	0.08 ± 0	0.12 ± 0.04	0.46 ± 0.07	0.02 ± 0.01	0.21 ± 0.24
palladium	<MDL	<MDL	<MDL	0.03 ± 0.01	0.13 ± 0.06	0.09 ± 0.07
silver	0.17 ± 0.03	0.01 ± 0.01	0.08 ± 0.09	0.2 ± 0.06	0.07 ± 0.07	0.13 ± 0.09
cadmium	<b>0.05 ± 0.01</b>	<b>0.05 ± 0.01</b>	<b>0.05 ± 0.01</b>	<b>0.04 ± 0.01</b>	<MDL	n.a.
tin	<b>0.32 ± 0.02</b>	<b>0.26 ± 0.01</b>	<b>0.28 ± 0.03</b>	<MDL	<MDL	<MDL
antimony	<b>0.86 ± 0.04</b>	<b>0.79 ± 0.05</b>	<b>0.82 ± 0.06</b>	0.62 ± 0.21	0.27 ± 0.1	0.42 ± 0.23
cesium	<MDL	<MDL	<MDL	0 ± 0	0.01 ± 0.01	0 ± 0.01
barium	<b>0.99 ± 0.03</b>	<b>0.65 ± 0.1</b>	<b>0.79 ± 0.19</b>	0.83 ± 0.26	0.41 ± 0.17	0.59 ± 0.3
lanthanum	0 ± 0	0 ± 0	0 ± 0	0.002 ± 0.001	0.009 ± 0.009	0.006 ± 0.008
cerium	<MDL	<MDL	<MDL	0.011 ± 0.003	0.006 ± 0.003	0.008 ± 0.004
praseodymium	<MDL	<MDL	<MDL	0.001 ± 0	<MDL	n.a.
neodymium	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
samarium	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
europium	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
terbium	<MDL	<MDL	<MDL	0 ± 0	<MDL	n.a.
dysprosium	<MDL	<MDL	<MDL	0.001 ± 0	0.005 ± 0.002	0.003 ± 0.002
erbium	<MDL	<MDL	<MDL	0.001 ± 0	0.007 ± 0.006	0.005 ± 0.005
thulium	<MDL	<MDL	<MDL	0 ± 0	<MDL	n.a.
ytterbium	<MDL	<MDL	<MDL	0 ± 0	<MDL	n.a.
lutetium	<MDL	<MDL	<MDL	0 ± 0	<MDL	n.a.
tungsten	0.007 ± 0.001	0.003 ± 0.002	0.005 ± 0.002	<b>0.03 ± 0.01</b>	<b>0.03 ± 0.01</b>	<b>0.03 ± 0.01</b>
platinum	<MDL	<MDL	<MDL	0 ± 0	<MDL	n.a.
thallium	<b>0.0022 ± 0.0001</b>	<b>0.0034 ± 0.0005</b>	<b>0.0029 ± 0.0007</b>	0.0007 ± 0.0006	<MDL	n.a.
lead	<b>1.21 ± 0.07</b>	<b>1.05 ± 0.05</b>	<b>1.12 ± 0.1</b>	<b>1.22 ± 0.39</b>	<b>0.79 ± 0.12</b>	<b>0.97 ± 0.34</b>
bismuth	<b>0.0068 ± 0.0004</b>	<b>0.0077 ± 0.0025</b>	<b>0.0074 ± 0.0018</b>			
thorium	0 ± 0	0 ± 0	0 ± 0	0.0006 ± 0.0002	0.0039 ± 0.0023	0.0025 ± 0.0024
uranium	<MDL	<MDL	<MDL	0 ± 0	0 ± 0.01	0 ± 0.01

<sup>a</sup> Values consistent across methods within 30% are shown in bold. Missing values indicate elements that were not analyzed for. <sup>b</sup> Three samples used for average MOUDI sum.

contamination or loss. XRF analysis was not sensitive enough to reliably detect elemental concentrations under the current sampling conditions. The consistency of the four collocated size distributions measured using the two ICPMS techniques was evaluated using a dot product defined by eq 1

$$\text{dotproduct} = \sum_{i=5}^{10} \frac{m_i^1}{\sqrt{\sum_{i=5}^{10} (m_i^1)^2}} \frac{m_i^2}{\sqrt{\sum_{i=5}^{10} (m_i^2)^2}} \quad (1)$$

where  $m_i^1$  represents the elemental mass measured on stage  $i$  by impactor 1, and  $m_i^2$  represents the elemental mass measured on stage  $i$  by impactor 2. Two identical size distributions have a dot product of 1.0, while completely dissimilar size distributions have a dot product of 0.0. Dot products differ from 1.0 because each impactor has slightly different collection efficiency and each sample experiences different levels of random handling contamination. An average dot product  $\geq 0.85$  has been chosen to represent reasonable agreement between collocated size distribution measurements. Columns 2 and 3 in Table 2 show the average



**FIGURE 2.** Precision of collocated filter vs  $\Sigma MOUDI$  concentrations for (a) HF-ICPMS and (b) acetone-ICPMS. Panel (c) shows a direct comparison of  $PM_{1.8}$  concentrations measured by HF-ICPMS and acetone-ICPMS. Uncertainty bars are one standard deviation of all measurements. Missing uncertainty bars indicate measurements where the standard deviation was greater than the measurement.

dot product agreement between the six unique combinations of the four collocated measurements using acetone-ICPMS

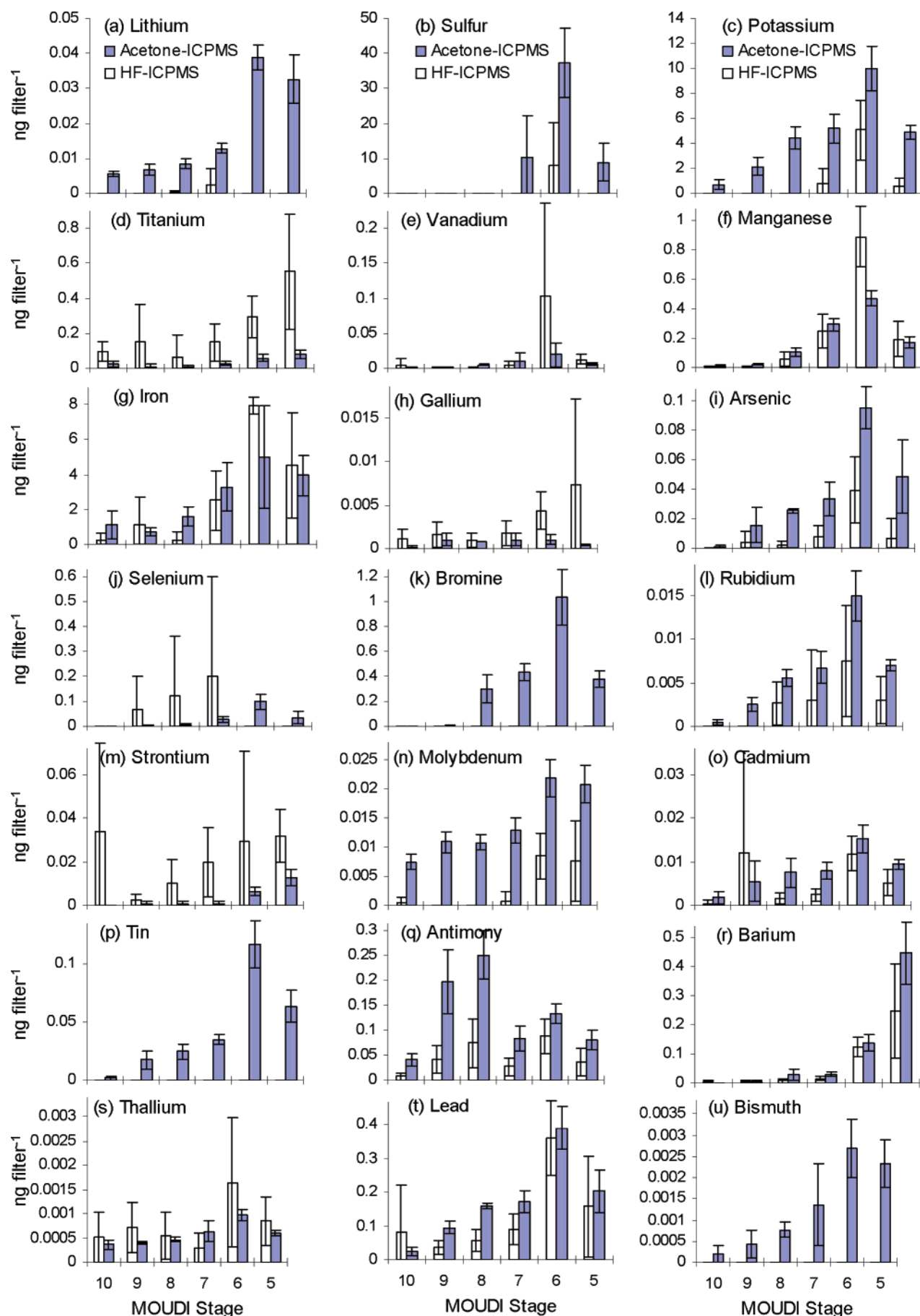
and HF-ICPMS, respectively. The last column in Table 2 is the average dot product between four corresponding MOUDI size distributions measured with different ICPMS methods. The dot products in the final column are not influenced by MOUDI collection efficiency because comparisons are only made between corresponding halves of the same sample that were analyzed using different methods.

The results shown in the first column of Table 2 indicate that acetone-ICPMS size distribution measurements were consistent for 23 elements. Many of the elements with inconsistent measurements had concentrations below the MDL during the current sampling event. Laboratory contamination appears to be less of an issue for iron and strontium measurements in the size-resolved comparison shown in Table 2 than the bulk filter comparison shown in Table 1. The results shown in the second column of Table 3 indicate that the HF-ICPMS size distribution measurements were consistent for four elements. Size distributions of phosphorus, copper, antimony, barium, tungsten, and lead measured with HF-ICPMS all had dot products  $>0.7$ , suggesting that these elements could be measured precisely if they were present at slightly higher concentrations. Lead measurements made by the HF-ICPMS analysis would pass the size-resolved consistency check if a single outlier was removed. The results shown in the third column of Table 2 suggest consistency in the normalized shape of the measured size distribution between the two ICPMS methods for titanium, manganese, iron, arsenic, rubidium, barium, and lead. Both ICPMS methods fail the size-resolved consistency check for the elements calcium, nickel, and zinc (these elements that may be important for source apportionment and health-effects studies).

Table 3 summarizes a comparison of absolute  $PM_{1.8}$  concentrations of individual elements collected at Davis in February, 2005. Average concentrations measured from three collocated filter samplers and four collocated MOUDIs are shown separately and in combined form in the different columns of Table 3. MOUDI  $PM_{1.8}$  concentrations are calculated by summing all stages to produce the integrated concentration of particles smaller than  $1.8 \mu m$  in diameter. The uncertainty shown in Table 3 reflects the standard deviation of the collocated measurements. Reasonable precision in  $PM_{1.8}$  concentration has been defined as both MOUDI and filter sample varying less than 30% from the average of all measurements with mean reported concentrations greater than the uncertainty.

Passing the consistency checks in Tables 2 and 3 requires that both the shape of the size distribution and the absolute concentration of the size distribution are reproducible between collocated measurements. Using the acetone-ICPMS method, the following 21 elements are judged to have precise size distribution measurements using collocated samplers: lithium, sulfur, potassium, titanium, vanadium, iron, manganese, gallium, germanium, arsenic, selenium, bromine, rubidium, strontium, cadmium, tin, antimony, barium, thallium, lead, and bismuth. Based on the results shown in Tables 1 and 2, it is likely that the size distribution of an additional 9 elements could also be measured when concentrations are sufficiently high: phosphorus, niobium, molybdenum, palladium, cesium, europium, holmium, platinum, and uranium. While several individual elements from the size distributions analyzed using HF-ICPMS pass either the consistency check for Table 2 or 3, no element passes both.

Figure 2 illustrates the MOUDI vs filter concentrations reported in Table 3 for HF-ICPMS (2a) and acetone-ICPMS (2b). Filter and MOUDI measurements analyzed using acetone-ICPMS show strong agreement, with almost all measurements within a factor of 2 except for sodium and silver. A linear correlation analysis for acetone-ICPMS



**FIGURE 3.** Size distribution of elements contained in airborne particles collected with MOUDIs at Davis California in February 2005 measured with acetone-ICPMS and HF-ICPMS. Uncertainty bars represent one standard deviation of four collocated measurements.

measurements without sodium and silver yields correlation coefficients ( $R^2$ ) of 0.75, 0.9, and 0.98 for concentration ranges  $<0.01$ , 1.0, and  $100 \text{ ng m}^{-3}$ , respectively. Filter and MOUDI measurements made using HF-ICPMS look less consistent at lower concentrations, with significant overprediction of MOUDI values for multiple elements below  $0.01 \text{ ng m}^{-3}$ . A linear correlation analysis of HF-ICPMS measurements yields correlation coefficients ( $R^2$ ) of 0.32, 0.71, and 0.76 for concentration ranges  $<0.01$ , 1.0, and  $100 \text{ ng m}^{-3}$ , respectively. This trend may reflect some source of contamination during the sample digestion phase. Background contamination is magnified by a factor of 2 in MOUDI  $\text{PM}_{1.8}$  measurements relative to filter-based measurements because six values are summed to produce the total, and the flow rate of the MOUDI is three times larger than the RAAS filter sampler.

The internal self-consistency checks discussed in Tables 2 and 3 convey accuracy because they measure the same concentration using techniques that have different artifacts. Another method to evaluate accuracy would be to analyze a standard reference material (SRM) that is certified by an agency such as the National Institute of Standards and Technology (NIST). The acetone-ICPMS method is applicable for particles with diameter smaller than  $1.0 \mu\text{m}$ , but a NIST  $\text{PM}_{1.0}$  (or smaller) SRM does not exist. The HF-ICPMS analysis technique is not limited to particles with diameter smaller than  $1.0 \mu\text{m}$ , and several NIST SRMs are routinely analyzed alongside other samples [Recycled Auto Catalyst (#2556), Urban Dust (#1649a), and San Joaquin Soil (#2709)]. Since the HF-ICPMS technique routinely undergoes this accuracy check, a comparison of the absolute concentration of the elements measured by the two ICPMS methods will verify the accuracy of the new acetone-ICPMS technique. Figure 2c shows average  $\text{PM}_{1.8}$  concentration of ambient airborne particulate samples analyzed with acetone-ICPMS and HF-ICPMS. The uncertainty ranges shown in Figure 2c constitute one standard deviation of the seven collocated measurements. Almost all data points are within one standard deviation of the 1:1 line. The measurements made using the two different ICPMS analysis techniques are correlated across a concentration range spanning from  $0.01$  to  $100 \text{ ng m}^{-3}$ . Furthermore, the acetone-ICPMS method appears to be more internally self-consistent than the HF-ICPMS method under the conditions encountered in the current study. The final check of accuracy for the acetone-ICPMS technique was made by direct comparison to ion chromatography measurements.  $\text{PM}_{1.8}$  samples collected on Teflon 47 mm filters during CRPAQS were divided in half so that they could be separately analyzed by both techniques (23). A linear correlation analysis between the measurements yields the following statistics for sodium, potassium, and sulfur:  $\text{slope}_{\text{Na}} = 1.11$ ,  $R^2_{\text{Na}} = 0.96$ ,  $\text{slope}_{\text{K}} = 0.82$ ,  $R^2_{\text{K}} = 0.87$ ,  $\text{slope}_{\text{S}} = 0.96$ ,  $R^2_{\text{S}} = 0.76$  ( $n = 145$ ). These results provide further evidence that the acetone-ICPMS method is accurate.

Figure 3 shows the size distributions measured in airborne particles in February 2005 for the 20 elements that pass the precision and accuracy consistency checks illustrated in Tables 1–3. Molybdenum has also been included. Each panel of Figure 3 shows the average of four collocated MOUDI measurements with uncertainty bars representing one standard deviation in those measurements. Within the uncertainty bars there is generally good agreement between the acetone-ICPMS and HF-ICPMS measurements. Good agreement is also seen in stage 5 of the MOUDI which contains particles with diameters between 1 and  $1.8 \mu\text{m}$ , suggesting the acetone-ICPMS method also works for  $\text{PM}_{1.8}$ . For elements where the difference between acetone-ICPMS and HF-ICPMS is larger than the calculated uncertainty, the shape of the size distributions is often still similar. Examples include titanium, arsenic, and individual stages of manganese and antimony. Many elements (Li, K, S, Mn, Fe, As, Br, Rb,

Cd, Sn, Th, Pb, Bi) have a concentration peak in MOUDI stage 6 ( $\text{Dp} = 0.56\text{--}1.0 \mu\text{m}$ ), but some elements peak at larger sizes (Ti, Ba) suggesting different emissions sources and possible environmental impacts. The concentrations of numerous elements (Li, K, Ti, Fe, Rb, Mo, Pb) are present above uncertainty levels in the ultrafine particle size range ( $\text{Dp} < 0.1 \mu\text{m}$ ).

## Discussion

Previous studies have indicated that traditional XRF analysis of airborne particles is more accurate than HF-ICPMS analysis for Al, Si, P, S, Cl, K, Ca, Sc, Ge, Se, Br, I, and Ce (13). Based on the results from the current study, XRF analysis appears to be more sensitive than the new acetone-ICPMS analysis for Si, S, Ca, Ni, Zn, and Cu. The benefit of the acetone-ICPMS analysis method is to measure more than 20 additional elements with improved accuracy and precision relative to current techniques. The acetone-ICPMS analysis method should provide useful measurements of size-resolved trace elements contained in ambient airborne particles that can be compared to health effects information.

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## Supporting Information Available

Method detection limits and blank levels for acetone-ICPMS, HF-ICPMS, and XRF (Table S1) and the precision of duplicate laboratory measurements using acetone-ICPMS and XRF (Table S2). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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