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# Accurate and Precise Zinc Isotope Ratio Measurements in Urban Aerosols

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We developed an analytical method and constrained procedural boundary conditions that enable accurate and precise Zn isotope ratio measurements in urban aerosols. We also demonstrate the potential of this new isotope system for air pollutant source tracing. The procedural blank is around 5 ng and significantly lower than published methods due to a tailored ion chromatographic separation. Accurate mass bias correction using external correction with Cu is limited to Zn sample content of approximately 50 ng due to the combined effect of blank contribution of Cu and Zn from the ion exchange procedure and the need to maintain a Cu/Zn ratio of approximately 1. Mass bias is corrected for by applying the common analyte internal standardization method approach. Comparison with other mass bias correction methods demonstrates the accuracy of the method. The average precision of  $\delta^{66}\text{Zn}$  determinations in aerosols is around 0.05‰ per atomic mass unit. The method was tested on aerosols collected in São Paulo City, Brazil. The measurements reveal significant variations in  $\delta^{66}\text{Zn}_{\text{Imperial}}$  ranging between  $-0.96$  and  $-0.37$ ‰ in coarse and between  $-1.04$  and  $0.02$ ‰ in fine particular matter. This variability suggests that Zn isotopic compositions distinguish atmospheric sources. The isotopic light signature suggests traffic as the main source. We present further  $\delta^{66}\text{Zn}_{\text{Imperial}}$  data for the standard reference material NIST SRM 2783 ( $\delta^{66}\text{Zn}_{\text{Imperial}} = 0.26 \pm 0.10$ ‰).

Multicollector inductively coupled plasma mass spectrometry allows high precision isotope ratio measurements of Zn despite its high first ionization efficiency and enables us to use this isotope system to study geochemical and environmental problems.<sup>1–4</sup>

Recent studies demonstrated isotopic variations of  $\sim 2$ ‰<sup>4</sup> for  $\delta^{66}\text{Zn}$  in biological and geological materials, where

$$\delta^{66}\text{Zn}_{\text{standard}} = \left( \frac{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{sample}}}{(^{66}\text{Zn}/^{64}\text{Zn})_{\text{standard}}} - 1 \right) \times 1000 \quad (1)$$

Of particular interest is the application to source tracing of atmospheric pollution as Zn is emitted to the atmosphere in greater amounts than any other trace metal worldwide<sup>5</sup> and sources remain often unidentified.<sup>6</sup> Preliminary work suggests that source tracing is feasible with Zn isotopes.<sup>5–9</sup>

However, the low degree of ionization results in low sensitivity and high detection limits, and relatively large amounts of Zn are required to obtain good precision, typically around 100 ng.<sup>10</sup> This is a serious challenge to isotope ratio determinations in aerosol samples because, in general, metal concentrations are between 1 and 200 ng/mg, and collected samples have a maximum weight of approximately 350  $\mu\text{g}$  but are often lower. Furthermore, isobaric interferences and mass bias effects from the complex aerosols matrix should pose a major challenge.<sup>11–15</sup>

Good separation of Zn from the matrix using ion exchange chromatography is coupled to the need of low procedural blanks and quantitative recovery if standard sample bracketing is used for mass bias correction.<sup>16,17</sup> The first ion exchange procedures

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focused on geological materials with abundant Zn.<sup>2,16,18</sup> To reduce the blank in environmental applications, acid and resin volumes were minimized but this resulted often in incomplete separation needing an additional chromatographic step<sup>10</sup> or the matrix affected the quality of the subsequent isotope measurements.<sup>19</sup> Borrok and co-workers developed a method for river waters that reduced the blank values to around 20 ng for Zn.<sup>20</sup>

Techniques for the correction of mass bias include double spike,<sup>14</sup> external normalization using a Cu dopant,<sup>13,18,21,22</sup> and direct standard sample bracketing.<sup>23</sup> The external normalization is most widely applied but is challenged by the matrix,<sup>14,19</sup> interferences,<sup>11</sup> and accurate definition of the dopant/element mass fractionation relationship.<sup>10,13,18</sup> To address the latter, the common analyte internal standard (CAIS) method<sup>24</sup> was successfully applied to Zn isotope measurements.<sup>10,13</sup>

Given these analytical challenges, the aim of this study was to develop a low blank analytical method for accurate and precise Zn isotope measurements in aerosols and explore the suitability of this isotope system for pollution source tracing. This was achieved (i) by scaling down acid and resin volumes in the ion exchange procedure and thus reducing blanks, (ii) determining the best Cu/Zn ratio during doping and minimizing Zn content needed for accurate  $\delta^{66}\text{Zn}$  determination, (iii) quantifying precision and testing accuracy using different mass bias correction schemes plotting data in three isotope space, and (iv) testing the method by assessing variability of  $\delta^{66}\text{Zn}$  in aerosols and potential sources in São Paulo, Brazil.

## MATERIALS AND METHODS

**Samples and Reagents.** The work was conducted under clean room conditions at the University of São Paulo (USP) and Imperial College London (ICL). Ultrapure reagents (sub-boiling distillation in Quartex and water purified on Milli-Q, >18.2 M $\Omega$ /cm) were used for sample digestion and ion exchange chromatography. Ultrapure single element standards (Romil Ltd., Cambridge, U.K.) were used during the mass spectrometry.<sup>11</sup> The in-house isotope standard solution (denoted as Imperial Zn thereafter) was prepared from a Johnson Matthey Purotronic Zn metal (supplied through Alfa Aesar, Karlsruhe, Germany) batch no. NH 27040 as described elsewhere.<sup>11,12</sup> Imperial Zn was used as the normalization standard (see eq 1). All results are reported relative to this standard. The widely used Zn standard JMC 3-0749 L<sup>18</sup> has an isotopic composition relative to Imperial Zn

$$^{66}\text{Zn}_{\text{JMC3-0749L}} - ^{66}\text{Zn}_{\text{Imperial}} = -0.09 \pm 0.05\% \quad (2s, n = 12) \quad (2)$$

BCR-1 (basalt from the U.S. Geological Survey), the aerosol standard reference material NIST SRM 2783, and aerosol samples collected at the campus of USP in São Paulo City, Brazil, during September of 2006 were used during the method development.

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**Table 1. Six Different Procedures (A–F) Evaluated during This Study Varying Column Diameter (Bio-Rad with 8 mm Inner Diameter and Shrink Column with 4 mm Inner Diameter), Resin Volume (0.6 mL, 1, and 2 mL), and Acid Volume (Between 19 and 41 mL)**

procedure			A	B	C	D	E	F
column type (diameter)			Bio-Rad (8 mm)		shrink Teflon (4 mm)			
resin volume (mL)			2	0.6	1	0.2	0.6	0.2
step	fraction acid		volume (mL)					
1	column	HCl 7M	7	2	3	2	3	3
2	sample	HCl 7M	1	1	1	1	1	1
3	matrix	HCl 7M	6	4	4	4	4	2
4	Cu + Fe	HCl 2M	14	6	8	6	6	6
5	Zn	HCl 0.1M	10	4	6	4	4	4
6	wash	HNO <sub>3</sub> 0.5 M	3	3	3	3	3	3
volume (excluding step 6)			38	17	22	17	18	16

The aerosols were separated in coarse and fine particles (aerodynamic diameter between 2.5 and 10  $\mu\text{m}$  and below 2.5  $\mu\text{m}$ , respectively) and dissolved using 3 mL of 7.7 M HNO<sub>3</sub> for 48 h on a hotplate at 110 °C. After evaporation, 2 mL of 6 M HCl were added and the sample was dried down and redissolved in 1 mL of 7 M HCl. The basalt was digested using HF/HNO<sub>3</sub>/HClO<sub>4</sub> acid digestion on a hotplate at 140 °C.

**Development of Ion Exchange Experiments.** Six different procedures (A–F, Table 1) were tested using three different resin volumes (1.0, 0.6, and 0.2 mL), two column types with different diameters (a Bio-Rad with 8 mm diameter and a heat-shrink Teflon tubing with 4 mm diameter), and various acid volumes ranging between 16 and 38 mL (excluding the wash step). The anionic exchange resin used was the AG MP-1 from Bio-Rad. Next to the aerosol samples and the BCR-1, we used an artificial solution with Zn (1  $\mu\text{g/mL}$ ), Cu (1  $\mu\text{g/mL}$ ), Fe (2  $\mu\text{g/mL}$ ), and Ti (2  $\mu\text{g/mL}$ ). Titanium was chosen because it forms important polyatomic interferences in the Cu–Zn mass range<sup>11</sup> and Fe due to its reported effect on the ion exchange performance of the resin.<sup>16</sup> The 2/1 weight ratio for Fe/Zn was representative for the aerosols measured later during this study. For the subsequent isotope ratio measurements, the residual chloride was removed by re-evaporating in 50  $\mu\text{L}$  of ultrapure concentrated HNO<sub>3</sub>. Concentrations of the solutions were determined before and after the column using ICP-AES.

**Instrumentation.** Isotope measurements were made using the IsoProbe MC-ICP-MS (Thermo Instruments, U.K.) at ICL. A Cetac Aridus desolvating nebulizer (Cetac Technologies, Omaha) was used for sample introduction. The instrument settings are given in Table 2. The instrument was used in the “hard extraction” mode. This leads to an increase in the sensitivity to approximately 24 V/ $\mu\text{g/mL}$  compared to 7 V/ $\mu\text{g/mL}$  when using the “soft extraction” mode. This strategy increases <sup>64</sup>Ni interferences; however, signal contributions from the cone were insignificant. Instrumental background and acid matrix blank corrections were performed using on-peak acid blank measurements taken before every sample and standard.

## RESULTS AND DISCUSSION

**Development of the Ion Exchange Chromatography Procedure.** Figure 1 shows the elution curves for Zn, Cu, Fe, and Ti for procedures A and B. Procedure A was the starting point as it is

**Table 2. Typical Operating Conditions of the Isoprobe MC-ICP-MS and CETAC Aridus Desolvating Nebulizer**

Instrument Parameters	
coolant Ar flow	14 L/min
auxiliary Ar flow	1.0–1.4 L/min
nebulizer Ar flow	0.9–1.1 L/min
extraction voltage (hard)	600 V
torch power	1336 W
cones	Ni
sensitivity for Zn	24 V/ $\mu\text{g/mL}$
Sample Introduction	
spray chamber temperature	70 °C
desolvator temperature	160 °C
Ar sweep gas flow	2.5–3.5 L/min
sample uptake rate	$\sim 50 \mu\text{L/min}$

applied to geological and biological material in our laboratory to separate Cu and Zn in low concentration samples.<sup>19</sup> Procedures B (Figure 1), C, and E (chromatograms not shown) separated Zn quantitatively with less resin (1 and 0.6 mL) and acid volume (down to 20 mL) than procedure A. Copper and Fe were discharged together. The advantage of procedure B to procedure E was the time as the Bio-Rad columns showed a better through flow. The procedures D and F did not separate Zn quantitatively from the matrix elements due to the small resin volume.

Procedure B was consequently tested on natural samples using two aerosols (sample ID 337, coarse (C) and fine (F) fraction) and the basalt sample BCR-1 (Table 3). The Zn fractions of 337F and 337C showed both 100% recoveries, were successfully isolated from Ti, and had minor contributions of Cu (less than 3 ng). Iron, however, leached into the Zn fraction ( $\sim 300$  ng). The Zn fraction of BCR-1, in contrast, showed good separation from Cu but

**Table 3. Application of Procedure B to Four Aerosol Samples (Fine and Coarse Fraction Denoted as F and C) and BCR-1<sup>a</sup>**

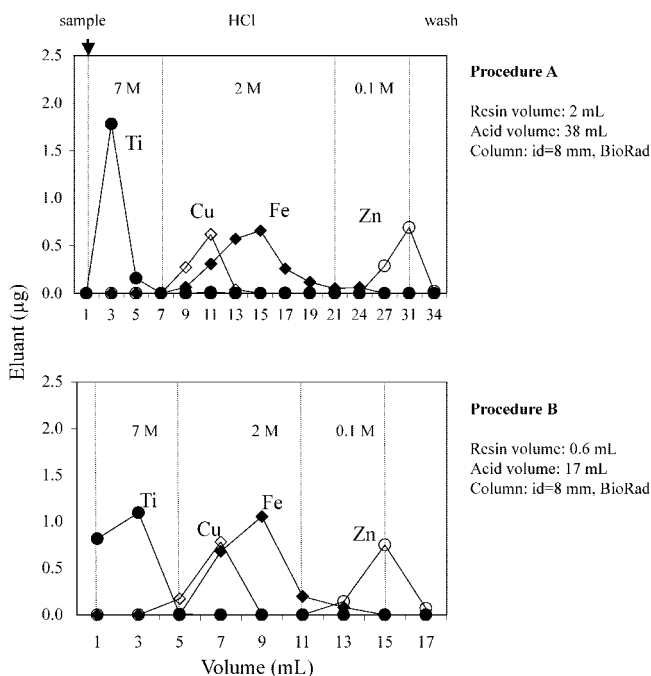
sample ID	fraction	$\mu\text{g}$				recovery (%)
		Cu	Fe	Ti	Zn	
337F	Cu	0.052	0.936	0	0	75
337F	Zn	0.003	0.200	0	0.397	100
337C	Cu	0.050	1.712	0	0	81
337C	Zn	0.002	0.296	0	0.226	100
BCR-1	Cu	0.058	319	1.148	0.010	68
BCR-1	Zn	0.002	14.3	0.035	0.532	85

<sup>a</sup> Shown are the contents of Cu, Zn, Fe, and Ti (in  $\mu\text{g}$ ) in the Cu and Zn fractions (steps 4 and 5, see Table 1) and the recovery rate for Cu and Zn.

**Table 4. Final Procedure Using the Bio-Rad Column with 8 mm Inner Diameter, a Resin Volume of 0.6 mL, and Total Acid Volume of 21 mL<sup>a</sup>**

step	fraction	acid	volume (mL)
1	column conditioning	HCl 7 M	3
2	sample	HCl 7 M	1
3	matrix	HCl 7 M	3
4	Cu + Fe	HCl 2 M	7
5	Zn	HCl 0.1 M	7
6	wash	HNO <sub>3</sub> 0.5 M	3
volume (excluding step 6)			21

<sup>a</sup> Slightly more 2 M HCl is used in step 4 to eliminate the Cu tail found in the Zn fraction using procedure B (see Tables 1 and 3).



**Figure 1.** Elution curves for a solution containing 1  $\mu\text{g}$  Zn/mL (○), 1  $\mu\text{g}$  Cu/mL (◇), 2  $\mu\text{g}$  Fe/mL (◆), and 2  $\mu\text{g}$  Ti/mL (●) using procedures A and B (see also Table 1). Shown is the recovery of the eluant in micrograms. A volume of 1 mL of sample was loaded onto the column. The variables assessed were column diameter, resin volume, and acid volume.

unsatisfactory recovery (85%) or separation from Ti ( $\sim 35$  ng). Also the iron concentrations were significantly higher. BCR-1 represents a very complex matrix and is affected by a high Fe/Zn weight ratio of  $\sim 560$ . Blank contributions from the ion exchange chromatography using procedure B were smaller than 5 ng (average of  $2.81 \pm 1.92$  ng,  $n = 10$ ).

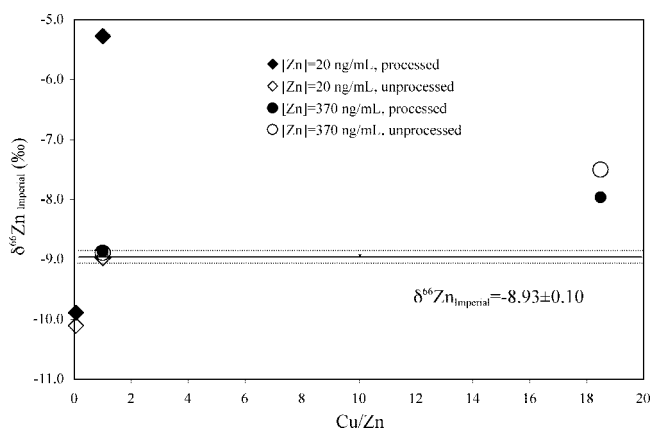
The final procedure used for the subsequent aerosol study is shown in Table 4. We increased the acid volume for the (Cu + Fe) fraction to 7 mL to entirely remove the Cu.

**Effect of Dopant/Analyte Ratio and Concentrations on Zn Isotopes Ratio Measurements.** A major concern regarding isotope ratio determinations at low concentrations is the effect of the dopant element itself and the blank correction. Adding low Cu concentrations to guarantee an equal dopant/analyte ratio results in a low Cu signal which is threatened by the procedural blank. Spiking the samples with higher dopant concentrations changes the mass bias behavior of the analyte<sup>12</sup> and can lead to abundance sensitivity effects if standard and samples are not doped with the same ratio.<sup>25</sup>

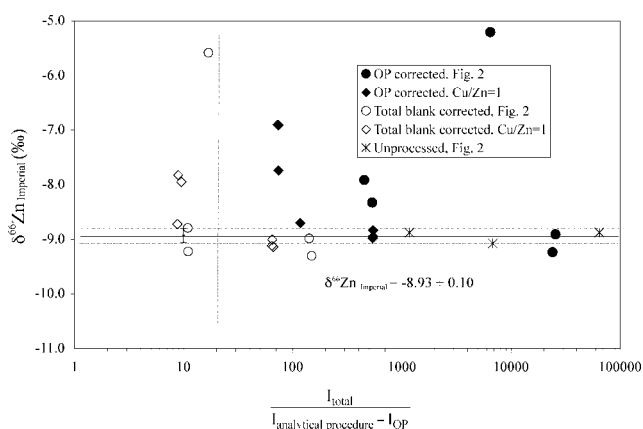
To characterize the effect of the Cu addition, we conducted a set of experiment where Zn single element solutions (denoted as Romil Zn) with concentrations of 20 and 370 ng Zn/mL (this corresponds to the expected concentration range in processed aerosol samples) were spiked with Cu to final concentrations of 20, 50, and 370 ng Cu/mL. Aliquots of these solutions were processed through the ion exchange column. Figure 2 shows the  $\delta^{66}\text{Zn}_{\text{Imperial}}$  of the different solutions versus the Cu/Zn ratio.

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**Figure 2.**  $\delta^{66}\text{Zn}_{\text{Imperial}}$  for Romil Zn solutions with 20 and 370 ng Zn/mL (diamonds and circles, respectively) and doped with 20, 50, and 370 ng Cu/mL (resulting in Cu/Zn ratios varying between 0.05 and 18.5). Of each solution, two aliquots were measured, one unprocessed (open symbols) and one processed (closed symbols) through the ion exchange column. Shown for reference is the  $\delta^{66}\text{Zn}_{\text{Imperial}}$  value (mean  $\pm 2\sigma$ ) estimated from repeated measurements of unprocessed solutions.



**Figure 3.**  $\delta^{66}\text{Zn}_{\text{Imperial}}$  vs  $(I_{\text{total}})/(I_{\text{analytical procedure}} + I_{\text{OP}})$  for the Romil Zn solutions shown in Figure 2. Total signals were corrected using on peak (OP corrected, closed symbols) or analytical procedure (total blank corrected,  $\circ$ ) signals. Samples with Cu/Zn = 1 (diamonds) and unprocessed (\*) are plotted separately. The dashed line indicates the critical  $\text{ratio}_{\text{blank}}$  needed (20) to ascertain accurate measurements. Shown for reference is the  $\delta^{66}\text{Zn}_{\text{Imperial}}$  value of Romil Zn.

We see strong effects of the dopant/analyte ratio and the ion exchange procedure. Low and high Cu/Zn ratios lead to inaccurate results independently if samples were processed through columns or not. However, if the Cu/Zn was approximately 1, low concentration solutions passed through the

column were inaccurate while the higher concentration samples were accurate. (Shown for reference is the  $\delta^{66}\text{Zn}_{\text{Imperial}} \pm 2\sigma$  value of unprocessed Romil Zn solutions measured during this study. This value agrees with previously published ones<sup>12</sup>). Low concentration samples not passed through the column were accurate, suggesting an effect of the Cu and/or Zn blank from the ion exchange procedure.

Consequently, we assessed blank correction and the minimum Zn content needed to guarantee accurate  $\delta^{66}\text{Zn}$  values. Measured total signal intensity ( $I_{\text{total}}$ ) is composed of contributions from the instrument ( $I_{\text{instrumental}}$ ), the acid matrix ( $I_{\text{acid matrix}}$ ), the analytical procedure ( $I_{\text{analytical procedure}}$ ), and the sample ( $I_{\text{sample}}$ ):

$$I_{\text{total}} = I_{\text{instrumental}} + I_{\text{acid matrix}} + I_{\text{analytical procedure}} + I_{\text{sample}} \quad (3)$$

Instrumental and acid matrix contribution can be corrected for using on peak measurements ( $I_{\text{OP}}$ ):

$$I_{\text{OP}} = I_{\text{instrumental}} + I_{\text{acid matrix}} \quad (4)$$

Thus

$$I_{\text{OP}} + I_{\text{analytical procedure}} = I_{\text{total}} - I_{\text{sample}} \quad (5)$$

At low Zn concentrations,  $I_{\text{OP}}$  and  $I_{\text{analytical procedure}}$  become significant in the term of  $I_{\text{total}}$ .

To assess the blank effects, we can define the  $\text{ratio}_{\text{blank}}$ :

$$\text{ratio}_{\text{blank}} = \frac{I_{\text{total}}}{I_{\text{analytical procedure}} - I_{\text{OP}}} \quad (6)$$

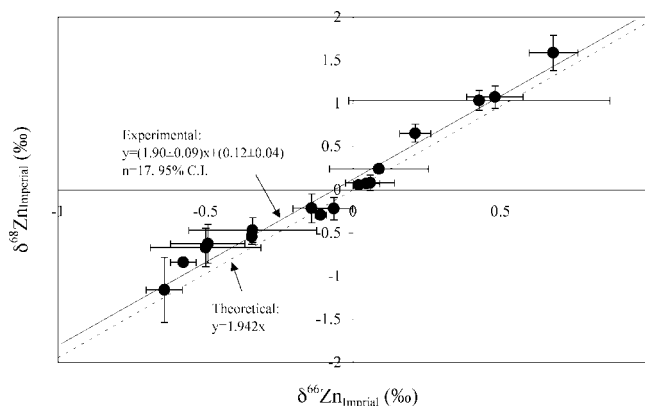
Figure 3 plots the calculated  $\text{ratio}_{\text{blank}}$  versus the  $\delta^{66}\text{Zn}_{\text{Imperial}}$  of the same Romil Zn solutions shown in Figure 2, corrected using the on peak signal only (OP corrected) or using the analytical procedure signal (total blank corrected). Solutions with Cu/Zn = 1 and unprocessed samples are plotted separately. We find that accurate data are achieved for the same samples with an order of magnitude lower  $\text{ratio}_{\text{blank}}$  if the analytical procedure blank is used for correction. This significantly enhances the working range of our aerosol study. Furthermore, we can define that the  $\text{ratio}_{\text{blank}}$  has to be  $\geq 20$  and Zn concentrations  $\geq 50$  ng/mL to obtain accurate results.

**Accuracy and Precision of the New Procedure.** To assess the accuracy and the precision of the new procedure, we determined the  $\delta^{66}\text{Zn}_{\text{Imperial}}$  in the certified aerosol standard NIST SRM 2783 and in four aerosol samples (Table 5).

**Table 5.**  $\delta^{66}\text{Zn}_{\text{Imperial}} \pm 2\sigma$  for NIST SRM 2783 and Four Aerosols Samples<sup>a</sup>

samples ID	m-SSB		EENCuZn		CAIS	
	$\delta^{66}\text{Zn}_{\text{Imperial}}$	$\pm 2\sigma$	$\delta^{66}\text{Zn}_{\text{Imperial}}$	$\pm 2\sigma$	$\delta^{66}\text{Zn}_{\text{Imperial}}$	$\pm 2\sigma$
NIST SRM 2783	0.24	0.09	0.32	0.11	0.21	0.07
341C	-0.58	0.04	-0.45	0.03	-0.57	0.04
341F	-0.07	0.06	-0.07	0.02	-0.07	0.06
343C	-0.43	0.06	-0.27	0.05	-0.42	0.06
343F	-0.06	0.10	0.21	0.06	-0.05	0.10
average $\pm 2\sigma$ pamu		0.04		0.03		0.03

<sup>a</sup> Including coarse and fine fraction denoted as F and C; calculated using three different mass bias correction methods (m-SSB, EENCuZn, and CIAS, see text for details).



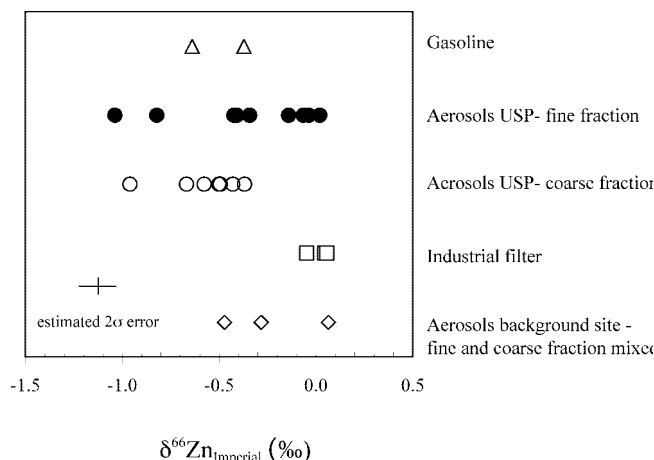
**Figure 4.** Three isotopes plot involving  $\delta^{66}\text{Zn}_{\text{Imperial}}$  and  $\delta^{68}\text{Zn}_{\text{Imperial}}$  of aerosol samples measured during this study. Also shown is the experimental mass fractionation line (solid line). Errors are at the 95% confidence interval. The dotted line is the theoretical equilibrium mass fractionation line.

We applied three mass bias correction procedures that differ in their approach to define the Cu/Zn mass bias relationship: the modified SSB (m-SSB),<sup>11</sup> the graphical external normalization procedure (EENCuZn)<sup>18</sup> and the common analyte internal standard (CAIS) method.<sup>10,13</sup> Differences in  $\delta^{66}\text{Zn}_{\text{Imperial}}$  are small and in general within the  $2\sigma$  error, suggesting that the values are accurate. The  $\delta^{66}\text{Zn}_{\text{Imperial}}$  for NIST SRM 2783 ( $0.26 \pm 0.10\%$ , mean  $\pm 2\sigma$ , calculated from the three different correction procedures) is similar to the “igneous” rock signature,<sup>2</sup> suggesting that this reference material is composed largely of “natural”, unfractionated Zn. The average precision ( $\sim \pm 0.04\%$  per atomic mass unit) was calculated from the  $2\sigma$  of each sample measurement and compares favorably with published precisions.<sup>2</sup>

Finally, the three-isotope graph shows experimental mass-dependent fractionation with a slope of  $1.903 \pm 0.091$  (95% confidence interval (CI), Figure 4), which agrees well with the theoretical equilibrium fractionation slope. The intercept is slightly off zero ( $0.12 \pm 0.04$ , 95% CI), which might suggest interferences on the  $^{68}\text{Zn}$  isotope, possibly from argides.<sup>11</sup>

#### Isotopic Variability in Aerosols and Sources in São Paulo.

The new procedure was applied to a set of aerosol samples collected during the summer of 2006 assessing air pollution in São Paulo, Brazil.<sup>26</sup> The measurements reveal significant variations in  $\delta^{66}\text{Zn}_{\text{Imperial}}$  ranging between  $-0.96$  and  $-0.37\%$  in coarse particles and between  $-1.04$  and  $0.02\%$  in fine particles (Figure 5). This variability is approximately 9 times larger than the precision achieved and allows distinguishing between different aerosol types. We measured the Zn isotopic composition in gasoline, industrial filters, and particulate matter collected at a “background site” well outside São Paulo City, representing traffic, industrial, and background emission sources, respectively. The aerosols fit largely on a mixing line between gasoline and background/industrial filter end members. Traffic has been identified as main source of particulate matter in São Paulo using Pb isotopes and receptor modeling<sup>26–28</sup> and of Zn in urban



**Figure 5.**  $\delta^{66}\text{Zn}_{\text{Imperial}}$  in aerosols from São Paulo City collected during the summer of 2006 and in important sources (gasoline, industrial filters, particulate matter from background area). The aerosols collected at USP were separated in fine and coarse fractions (see text for definition). The error of  $0.1\%$  used to estimate the precision was determined using the average of all  $2\sigma$  of the individual analyses.

particulate matter in Stockholm.<sup>29</sup> Our preliminary source assessment based on isotope system is also in line with work that linked isotopic light Zn signatures in lichens to gasoline sources.<sup>4</sup>

#### CONCLUSIONS

We developed and assessed an analytical method aimed to enable precise and accurate Zn isotope measurement in aerosols. The method uses a total of 21 mL of different HCl strength solutions and 0.6 mL of the anion resin AG MP-1. We achieve quantitative recovery of Zn and quantitative separation from Cu. The procedural blank of  $\sim 2.8$  ng is very favorable compared to previous methods.<sup>2</sup> Despite the small overall blank, the total amount of Zn needed to ensure accurate isotope ratios is  $\geq 50$  ng/mL. We note that the Cu/Zn ratio affects the quality of the mass bias correction using the external normalization. We measured Zn isotopes in aerosols from São Paulo City and found variability 9 times larger than the estimated precision of  $0.04\%$  pamu from repeated measurements of aerosols samples. Using the Zn isotope system, we suggest that the main source of Zn in aerosols is traffic emissions. Our preliminary data suggests that the Zn isotopic compositions can be a powerful tool to distinguish atmospheric sources.

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