

## Interlaboratory collaborative analysis of rainwater reference material

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**The results of an interlaboratory collaborative analysis of real-time rainwater sample obtained at the Geochemical Laboratory of National Geophysical Research Institute, Hyderabad, are presented. Estimation of eleven important toxic and trace metals (Al, V, Mn, Fe, Ni, Co, Cu, Zn, As, Cd and Pb) by inductively coupled plasma mass spectrometry (ICP-MS) is compared with reference and informative values provided by the organizer. Depending upon the Z-scores calculated, the fitness of the data for either 'pure geochemistry' or 'applied geochemistry' was assessed. An overview of Z-score results indicated that the data for Al, Mn, Ni, Co, Cu, Zn, Cd and Pb fell within the  $-2 < Z < 2$  range, which included majority of the toxic and trace metals used in several problems dealing with atmospheric deposition. These results help to further investigate the analytical discrepancies observed in the data, optimize necessary aspects and minimize the interference effects caused during analysis.**

**Keywords:** Interlaboratory testing, ICP-MS, rainwater, reference material, trace metals, Z-score.

INTERLABORATORY testing is one of the most effective ways for a geochemical laboratory to monitor its performance against its own requirements and the general level of performance of other such laboratories within and outside a country. It represents an external form of quality control and provides an opportunity to participating laboratories to decide the level of performance and take appropriate steps to improve the quality of data, instrumental techniques, interference-correction procedures, proper calibration procedures, etc.<sup>1</sup>.

In recent times, geoanalytical methods have changed considerably, resulting in improved detection limits and precision. Use of matrix matching geochemical reference samples, reagent blanks, analysis of duplicates, etc. are some of the schemes that are widely adopted to improve analytical accuracy<sup>1</sup>. In this context, it is essential to note that there is no matrix matching standard reference material currently available for rainwater analysis and, to fill this gap, the Division of Environmental Science and Engineering, National University of Singapore had organized an interlaboratory programme to analyse and certify the concentration levels of Al, V, Mn, Fe, Ni, Co, Cu, Zn, As, Cd and Pb in rainwater. National Geophysical Research Institute (NGRI), Hyderabad also participated in this inter-

national round robin analysis programme along with 15 other laboratories from different parts of the world (Table 1). Data presented here pertain to the results obtained by inductively coupled plasma mass spectrometry (ICP-MS).

Preparation of real-time rainwater standards would enhance the opportunities for quality control activities in rainwater monitoring studies. Atmospheric deposition is considered to be a major source of toxic metals such as Hg, Cd, Pb and several other trace metals to ecosystems<sup>2</sup>. Trace metals such as Fe, Mn and Cu in atmospheric droplets have been implicated in the catalysis of SO<sub>2</sub> oxidation leading to enhanced acidity of hydrometeors<sup>3</sup>. Further, trace metals emitted from particulate source types can be used to identify the origin of the precipitating air mass<sup>4</sup> and acid rain<sup>5,6</sup>.

Rainwater samples were collected in bulk by the organizers during peak monsoon periods using an automatic dry-wet precipitation collector (Model 301, Aerochem Metric Inc) consisting of HDPE bucket equipped with a sensor that activates the lid to open with the first drop of rain and close just after the event, thus preventing contamination of rainwater by dust fall<sup>7</sup>. It was filtered through 0.2 µm polycarbonate membrane filter and acidified to pH 2 using suprapure HNO<sub>3</sub> (Fluka). About 50 l of rainwater was thus collected and homogenized through circulation, and stored in HDPE tank (Nalgene®). Six sub-samples from this tank were analysed for trace elements to confirm that they were contamination-free and were then transferred to 500 ml LDPE bottles (Nalgene®). The homogeneity was found to be satisfactory by analysing randomly selected samples for trace elements by ICP-MS followed by ANOVA. Stability of trace element concentrations was also investigated over a period of 6 months. It was found that there is no significant change in trace element concentrations in rainwater samples<sup>7</sup>.

Trace metals were determined using ICP-MS (Model-ELAN DRC II, Perkin-Elmer Sciex Instrument, USA). The rainwater sample was introduced, as procured, into ICP-MS instrument by conventional pneumatic nebulization, using a peristaltic pump with a solution uptake rate of about 1 ml/min. The nebulizer gas flow, sample uptake rate, detector voltages and lens voltage were optimized for a sensitivity of about 50,000 counts/s for a 1 ng/ml solution of In. The oxide and doubly charged ion formation levels measured on CeO<sup>+</sup> and Ba<sup>++</sup> were found to be <2.5%. The instrumental and data acquisition parameters are given elsewhere<sup>8</sup>. Calibration was performed using NIST 1640 (National Institute of Standards and Technology, USA), which is a standard reference material for trace elements in natural water, to minimize matrix and other associated interference effects and to check the precision and accuracy of the analysis. The sample was analysed six times at different periods and the RSD was found to be better than 10% in most of the cases.

The results obtained by all the participating laboratories, excluding the data provided here were published by

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**Table 1.** Countries, number of laboratories that participated and analytical techniques used in the trace element analysis of rainwater<sup>7</sup>

Country	No. of laboratories	Analytical techniques*
Austria	2	Inductively coupled plasma-mass spectrometry (7)
France	1	Inductively coupled plasma-atomic emission spectrometry (2)
Germany	2	Graphite furnace atomic absorption spectrometry (3)
India	5	Total reflection X-ray fluorescence spectrometry (3)
Japan	2	Differential pulse anodic stripping voltammeter (1)
Russia	1	Ion chromatography (1)
USA	2	

\*Number of laboratories using a particular analytical technique is given in brackets.

**Table 2.** Trace metal concentration ( $\mu\text{g/l}$ ) reported by NGRI in comparison with assigned values, Z-score values and detection limits of ICP-MS

Element	Natural abundance (%)	Detection limit (ng/l)	Values obtained* (this study)	Reference values	Z-score	Performance <sup>®</sup>
<sup>55</sup> Mn	100.00	5	1.30 $\pm$ 0.35	1.21 $\pm$ 0.30	0.91	Y
<sup>58</sup> Ni	68.08	10	0.98 $\pm$ 0.04	1.10 $\pm$ 0.15	-1.56	Y
<sup>63</sup> Cu	69.17	5	4.27 $\pm$ 0.23	4.44 $\pm$ 0.42	-0.61	Y
<sup>64</sup> Zn	48.60	40	15.98 $\pm$ 0.48	15.50 $\pm$ 2.30	0.57	Y
<sup>208</sup> Pb	52.40	1.2	2.10 $\pm$ 0.22	2.23 $\pm$ 0.410	-0.87	Y

\*Average of six values  $\pm$  SD; <sup>®</sup>Category no. 1 (pure geochemistry); Y, Fell within acceptable range.

Karthikeyan and Balasubramanian<sup>7</sup>. The trace metal data of the rainwater obtained at NGRI using ICP-MS are given in Tables 2 and 3 in comparison with the 'assigned' values, and Z-score values calculated for each element. The appropriate Z-score allows a contributing laboratory to assess the accuracy of its results in comparison with assigned values. The assigned values for individual elements (being the best estimate of the true compositions of the sample) were calculated from the mean of the submitted dataset using robust statistical procedures for 11 trace elements (Cu, Pb, Mn, Ni, Zn, Fe, Cd, Co, V, As and Al). These results were tested for outliers using Grubbs test, and then the grand means were calculated for each element. In general, the concentrations of trace elements are quite similar after eliminating the outliers, and at least more than 80% of the results was consistent for all the 11 elements. It was observed by the organizer that several participants reported concentrations of one or two trace elements with a significant bias, which was presumably due to contamination or blank contribution.

Based on the analytical results obtained from the inter-comparison study using different analytical techniques (Table 1), reference values were assigned for each element following IAEA guidelines on certified reference materials preparation<sup>9</sup>. Two main criteria were used for assigning a reference value, i.e. overall mean obtained from the analytical data of more than ten laboratories (mean values) and trace element concentrations obtained by at least two different analytical techniques. The results for those elements that did not fit these two conditions were separately calculated as informative values. For at least five elements, viz. Cu, Pb, Mn, Ni and Zn, 'reference values' could be assigned (Table 2) and for the other six elements,

viz. Fe, Cd, Co, V, As and Al, 'informative values' are only provided (Table 3). In the overall data analysis, data from the laboratory organizing the intercomparison study were not considered. Therefore, it can be concluded that the intercomparison study undertaken in cooperation with participating laboratories from different parts of the world provided reliable analytical data for certification of the rainwater reference material for 11 trace elements.

Results ( $x$ ) from the individual laboratories were converted into Z-score using the function  $Z = (x - X_a)/\sigma$ , where  $X_a$  is the assigned value (both reference value/informative value) calculated based on the best estimate of the true value obtained from different laboratories and  $\sigma$  is the 'target value for standard deviation' and is derived from a fitness-for-purpose criterion<sup>10</sup>. Z-scores in the range  $\pm 2$  are regarded as satisfactory. Scores outside this range are unsatisfactory and suggest that the participating laboratory should investigate analytical discrepancies and correct its procedures. The  $\sigma$  value for each element in the higher precision 'pure geochemistry' type of analysis (category 1, Table 4) was calculated as  $\sigma = 0.01 c^{0.8495}$ , where  $\sigma$  and  $c$  (the element concentration) are expressed as fractions. For the lower precision 'applied geochemistry' type of analysis (category 2, Table 4),  $\sigma$  value was double. If the uncertainty of the assigned value is greater than about  $0.5\sigma$ , the value of the proficiency test is weakened for that element. This happens when the dispersion of results is unusually high or there are only a few results<sup>10</sup>.

Table 2 shows that the data obtained for Mn, Ni, Cu, Zn and Pb are well within the acceptable range, i.e. with Z-score values better than  $\pm 2$  and are most suitable for pure geochemical studies. Among informative values

**Table 3.** Trace metal concentration ( $\mu\text{g/l}$ ) reported by NGRI in comparison with informative values, Z-score values and detection limits of ICP-MS

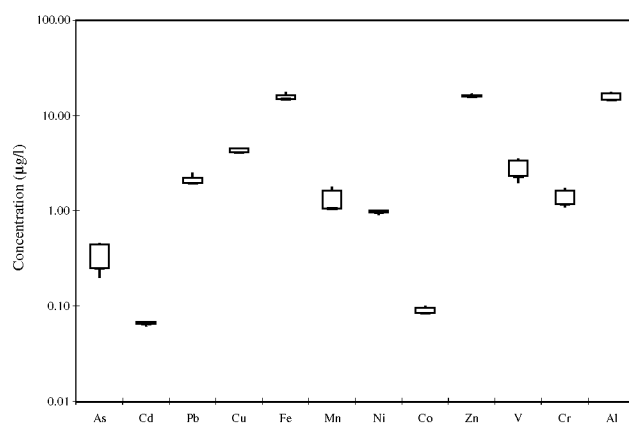
Element	Natural abundance (%)	Detection limit (ng/l)	Values obtained* (this study)	Informative values <sup>†</sup>	Z-score	Performance <sup>®</sup>
<sup>27</sup> Al	100.00	10	15.65 $\pm$ 1.45	14.50 $\pm$ 1.7	1.39	Y
<sup>51</sup> V	99.75	10	2.88 $\pm$ 0.72	1.62 $\pm$ 0.31	6.42	N
<sup>52</sup> Cr	83.79	5	1.37 $\pm$ 0.27	NA	NA	NA
<sup>57</sup> Fe	2.20	500	15.57 $\pm$ 1.09	18.50 $\pm$ 2.8	-3.56	N
<sup>59</sup> Co	100.00	10	0.09 $\pm$ 0.01	0.084 $\pm$ 0.024	0.55	Y
<sup>75</sup> As	100.00	5	0.35 $\pm$ 0.12	0.14 $\pm$ 0.03	6.43	N
<sup>114</sup> Cd	28.73	5	0.07 $\pm$ 0.01	0.066 $\pm$ 0.023	-0.04	Y

\*Average of six values  $\pm$  SD; <sup>†</sup>At 95% confidence level; NA, Not available; <sup>®</sup>Category no. 1 (pure geochemistry); Y, Fell within acceptable range; N, Fell outside the range.

**Table 4.** Precisions (% RSD) required for trace elements for different applications in earth sciences<sup>9</sup>

Concentration of the analyte	Category 1 RSD %	Category 2 RSD %
100%	1.0	2.0
10%	1.4	2.8
1%	2.0	4.0
1000 ppm	2.8	5.6
100 ppm	4.0	8.0
10 ppm	5.7	11.4
1 ppm	8.0	16.0
0.1 ppm	11.3	22.6
0.01 ppm	15.0	30.0

RSD = 100  $\sigma/c$  = relative standard deviation, calculated from  $\sigma = 0.1c^{0.8495}$  (Category 1 data) or  $\sigma = 0.2c^{0.8495}$  (Category 2 data).

**Figure 1.** Box plot showing the distribution of trace metals in rainwater. The box represents the interquartile range and either end of the line indicates minimum and maximum values.

(Table 3), data for Al, Co and Cd are well within the acceptable range, while data for V, Fe and As do not match with the indicated value. Often, this level of accuracy may be sufficient for detection of high contrast anomalies and for discerning subtle geochemical variations. Since assigned value for Cr has not been reported, Z-score was not calculated. However, the Cr value (1.369  $\mu\text{g/l}$ ) obtained from this study is reported here (Table 2).

Possible causes for errors in the data arising out of inhomogeneity of the sample are ruled out, as the samples distributed to the participating laboratories are of established homogeneity<sup>7</sup>. It is also appropriate to mention here that this particular sample was analysed using routine procedures established in our laboratory<sup>11</sup>. The standard deviation, 1st and 3rd quartiles of the data are shown in Figure 1 and are found to be within permissible errors for many of the trace metals. The higher value obtained in the case of V may be because of direct overlap of interfering polyatomic species generated in the plasma<sup>12</sup>. In general, ICP-MS suffers from spectroscopic and matrix interferences. For example, <sup>51</sup>V<sup>+</sup> has a direct overlapping interference from <sup>51</sup>ClO<sup>+</sup> due to the formation of ClO<sup>+</sup> polyatomic molecular species in the plasma<sup>13,14</sup> when the sample contains Cl<sup>-</sup> ions. As a result, a positive error is expected in V values. However, the magnitude of error depends upon the formation levels of ClO<sup>+</sup> molecule and concentration of chloride present in the sample. The concentration of Fe was measured at  $m = 57$  (abundance = 2.2%) instead of Fe at  $m = 56$  (abundance = 91.72%)<sup>15</sup>, because of the well-known isobaric interferences caused by <sup>40</sup>Ca<sup>16</sup>O<sup>+</sup>, <sup>40</sup>Ar<sup>15</sup>N<sup>1</sup>H<sup>+</sup>, <sup>36</sup>Ar<sup>18</sup>O<sup>+</sup>, <sup>38</sup>Ar<sup>17</sup>O<sup>1</sup>H<sup>+</sup>, <sup>37</sup>Cl<sup>18</sup>O<sup>1</sup>H<sup>+</sup> in the plasma from the most abundant Ar and Cl isotopes<sup>16</sup>. This may be one of the reasons for the low value of Fe obtained in this study (Table 3), but meagre data are available to document these types of problems, particularly when the analyte is at ppt concentrations<sup>17</sup>. Interference of the As signal (at  $m = 75$ ) with <sup>40</sup>Ar<sup>35</sup>Cl is generally known and prohibits ICP-MS determination of As in water samples<sup>18</sup>.

The problem can be solved by mathematical correction if necessary, using matrix/trace element separation. Use of Dynamic Reaction Cell (DRC) can help minimize the above described interferences. In DRC, the reaction gas (like NH<sub>3</sub>, CH<sub>4</sub> or CO<sub>2</sub>) is made to react with the interfering species, thereby totally eliminating or minimizing interferences encountered for certain elements. Thus, chemical resolution in DRC can be used to overcome traditional spectral overlaps<sup>19,20</sup> like <sup>40</sup>Ca<sup>+</sup>/<sup>40</sup>Ar<sup>+</sup>, <sup>56</sup>Fe<sup>+</sup>/<sup>40</sup>Ar<sup>16</sup>O, <sup>75</sup>As<sup>+</sup>/<sup>40</sup>Ar<sup>35</sup>Cl<sup>+</sup> and resolve the signals of isobaric isotopes<sup>21</sup>.

Interlaboratory and collaborative studies provide an ideal means to certify standard reference material (SRM).

## RESEARCH COMMUNICATIONS

This study has helped to fill the gap that exists in the availability of rainwater SRM. This exercise and the follow-up interactions provided the individual laboratories an opportunity to assess their analytical capabilities, and enabled them to appropriately address the issues related to water analysis. ICP-MS with detection limits in the range of 0.01 to 0.10 ng/ml, is capable of determining several trace metals in real-time rainwater samples at their natural abundance levels with precisions and accuracies required for such certification programmes. About 80% of the data provided by this study is within the acceptable range of the assigned values for rainwater reference materials.

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