

# A trial proficiency test of eight NAA laboratories in Asia using stream sediments

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**Abstract** Eight neutron activation analysis research groups from seven countries have participated in a trial proficiency test under the auspices of the Forum for Nuclear Cooperation in Asia. Three stream sediment reference materials were used in the test. A high degree of proficiency was found in the quantification of Co and Sc and more than 20 elements were well quantified by the majority of laboratories. The results support the use of neutron activation analysis, as practised by the participants, for geochemical mapping. The data produced in this study may provide an opportunity to improve the characterisation of the three reference materials.

**Keywords** Proficiency test · NAA ·  $k_0$ -NAA · Geochemical mapping · JSd-1 · JSd-2 · JSd-3

## Introduction

The Forum for Nuclear Cooperation in Asia (FNCA) is an organisation that provides a cooperative framework for the peaceful use of nuclear technology in the Asian region. One of the current aims of the FNCA is to demonstrate the socio-economic benefits that may be gained through the use of research reactors for neutron activation analysis (NAA). A key objective of the NAA Project is to promote engagement between NAA laboratories and end-users in government, universities and industry. NAA has been used extensively in the field of geochemical mapping (for example, Minami et al. [1]), with potential applications in mineral exploration and environmental management.

In the first phase of a demonstration geochemical mapping sub-project, eight NAA research groups from seven FNCA member countries participated in a trial proficiency test using stream sediments. The participating

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countries were Japan (two university groups), China, Vietnam, Indonesia, Australia, Bangladesh (using the facilities of the Atomic Institute in Vienna) and Malaysia. The eight laboratories have been randomly assigned identifying letters A to H.

The work described in this paper had two objectives. The first was to quantify the proficiency of the participating NAA laboratories and the second objective was to determine whether the data obtained might be used to improve the characterisation of the stream sediment reference materials.

## Experimental

### Materials

Three reference materials from the ‘sedimentary rock series’ issued by the Geological Survey of Japan (GSJ) were used in the trial proficiency test. The stream sediment reference materials were chosen because they have been used extensively as comparators in relative NAA used for geochemical mapping (for example, Minami et al. [1]).

Stream sediments JSd-1, JSd-2 and JSd-3 were produced by the GSJ between 1987 and 1989, using the GSJ standard operating procedure for homogeneity and stability testing of geochemical reference material. This procedure was very close to that described recently by Terashima et al. [2]. During preparation the reference materials were ground using an agate mortar and sieved to 100 mesh. To preserve homogeneity the GSJ split the materials into bottles that were numbered to ensure traceability. Reference material JSd-1 used in this study was taken from the bottle labelled ‘Split 6, Position 5’; material JSd-2 was from bottle ‘Split 3, Position 13’; and material JSd-3 was from bottle ‘Split 6, Position 13’. The materials for distribution to the participants in this study were prepared at Nagoya University by spooning into vials, with each vial containing approximately 5 g. One vial of each of the three stream sediments was sent to each participating laboratory, without revealing the identity of the samples.

### Proficiency test protocol

Participants were requested to determine the concentration of as many elements as possible, using the NAA measurement protocols that would normally be employed in that laboratory for stream sediment samples.

At the time of bottling, the samples contained less than 1% adsorbed moisture so there was no requirement for

participants to dry the samples or determine the moisture content prior to measurement.

Participants were instructed to measure four aliquots of each sample, with each aliquot to weigh at least 30 mg. The aliquots, and any certified reference materials that may have been used as comparators in relative NAA, were to be measured within a short period of time, preferably on the same day.

### Measurements

Sample irradiations were performed in a variety of research reactor types, with power ranging from 250 kW to 20 MW and neutron flux ranging from  $3 \times 10^{12}$  to  $5 \times 10^{13}$   $\text{cm}^{-2} \text{s}^{-1}$ . Of the eight participating laboratories, two used the  $k_0$ -method of standardisation for NAA (laboratories A and F), five used the relative method (B, D, E, G and H) and one laboratory used a combination of the two (C).

### Statistical evaluation

An assigned value is defined as the ‘value attributed to a particular quantity and accepted, sometimes by convention, as having an uncertainty appropriate for a given purpose’ [3] and must be the best available estimate of the true concentration of an analyte. For this study the assigned values and expanded uncertainty (coverage  $k = 2$ ) for the elements comprising the stream sediment reference materials JSd-1, JSd-2 and JSd-3 have been taken from Imai et al. [4] and are provided in Tables 1, 2 and 3. These values were the consensus of at least four reported results and were calculated as the average for each element after the removal of outliers. It is important to note that the uncertainty on the consensus values reflects the number of reported values contributing to each average value and in some cases may be relatively large. For example, only 5 reported values were used to determine the concentration of Gd in JSd-1, leading to a standard deviation of 25%.

All but one of the laboratories provided the multiple measurements of each element in each aliquot as a concentration and a standard deviation. These multiple measurements were combined to produce a single weighted mean and standard deviation of the weighted mean. Laboratory B measured only three aliquots of each material and estimated the uncertainty on the mean as the standard deviation of the three determinations of each element. The uncertainty-based evaluation of the data were in keeping with the conclusions of Hasselbarth et al. [5].

The consensus of participant laboratories in this study was calculated as the robust average of the reported results.

**Table 1** Laboratory performance for stream sediment JSd-1

| Element                                   | Assigned value | Laboratory z-score |             |             |             |                         |             |              |             | Robust average <sup>a</sup> |
|---|----------------|--------------------|-------------|-------------|-------------|-------------------------|-------------|--------------|-------------|-----------------------------|
|   |                | A                  | B           | C           | D           | E                       | F           | G            | H           |                             |
| Al (%)                                    | 7.75 ± 0.10    | 0.3                | 0.1         | x           | x           | <u>0.8</u> <sup>b</sup> | <u>-3.9</u> | -0.1         | x           | 7.78 ± 0.15                 |
| As  | 2.4 ± 1.0      | -0.5               | -1.4        | 0.0         | -2.4        | -0.6                    | x           | -4.3         | x           | 2.20 ± 0.20                 |
| Ba  | 520 ± 30       | -0.2               | 0.2         | <u>-2.1</u> | -0.4        | -0.7                    | 0.3         | -0.3         | <u>1.3</u>  | 513 ± 24                    |
| Ca (%)                                    | 2.17 ± 0.07    | 0.7                | <u>2.1</u>  | 0.4         | x           | <u>1.5</u>              | x           | <u>-24.2</u> | x           | 2.23 ± 0.13                 |
| Ce  | 34 ± 5         | 0.1                | -0.5        | -1.1        | -0.7        | <u>-4.3</u>             | 1.5         | -0.1         | -1.8        | 32.7 ± 2.2                  |
| Co  | 11.2 ± 2.8     | -0.1               | -0.6        | 0.6         | -0.1        | 0.7                     | 0.5         | -0.8         | -0.5        | 11.2 ± 0.4                  |
| Cr  | 22 ± 4         | -0.7               | 2.7         | -0.1        | -0.7        | 0.8                     | 0.9         | <u>-3.8</u>  | <u>9.5</u>  | 22.1 ± 2.4                  |
| Cs  | 1.9 ± 0.8      | 0.4                | 1.4         | 1.7         | 4.1         | 1.9                     | 1.5         | 0.7          | -2.5        | 2.08 ± 0.11                 |
| Dy  | 2.2 ± 0.8      | 3.1                | x           | x           | x           | x                       | x           | x            | x           | -                           |
| Eu  | 0.9 ± 0.2      | -0.4               | x           | 1.3         | 0.9         | 2.8                     | 0.5         | 1.7          | 0.0         | 0.96 ± 0.07                 |
| Fe (%)                                    | 3.54 ± 0.14    | -0.6               | 0.9         | 0.0         | 0.0         | 0.7                     | 0.2         | -1.4         | 0.1         | 3.54 ± 0.14                 |
| Ga  | 17 ± 4         | x                  | x           | x           | x           | -0.2                    | x           | -0.1         | x           | -                           |
| Gd  | 2.7 ± 1.4      | 4.3                | x           | x           | x           | x                       | x           | x            | x           | -                           |
| Hf  | 3.6 ± 0.6      | 0.5                | x           | -0.1        | -1.1        | 0.8                     | 0.7         | -1.3         | -0.4        | 3.57 ± 0.23                 |
| K (%)                                     | 1.81 ± 0.06    | -0.6               | 1.1         | 0.9         | x           | <u>2.5</u>              | <u>2.9</u>  | 1.1          | 0.0         | 1.89 ± 0.10                 |
| La  | 18.1 ± 2.6     | -1.0               | 0.0         | <u>4.1</u>  | -1.1        | -0.1                    | 0.9         | -0.4         | -2.0        | 17.8 ± 1.5                  |
| Mg (%)                                    | 1.09 ± 0.06    | 1.6                | x           | x           | x           | 0.8                     | x           | <u>-2.4</u>  | x           | -                           |
| Mn  | 720 ± 90       | 0.2                | <u>-3.6</u> | x           | x           | 1.0                     | 0.0         | -0.3         | x           | 715 ± 27                    |
| Na (%)                                    | 2.02 ± 0.08    | 0.9                | x           | 0.0         | 0.0         | <u>3.7</u>              | -0.4        | -0.8         | <u>1.5</u>  | 2.06 ± 0.08                 |
| Nd  | 17.6 ± 1.4     | 2.4                | x           | 5.1         | 1.2         | x                       | x           | <u>-1.2</u>  | <u>-3.3</u> | -                           |
| Rb  | 67 ± 6         | 1.2                | x           | 0.4         | -0.3        | <u>-2.5</u>             | 0.1         | <u>-1.8</u>  | -0.2        | 66 ± 4                      |
| Sc  | 10.9 ± 1.2     | 0.1                | -0.4        | 0.5         | -0.2        | 0.5                     | 0.2         | -0.5         | -0.4        | 10.9 ± 0.3                  |
| Sm  | 3.5 ± 0.4      | -1.0               | 1.7         | 0.8         | 0.4         | -1.1                    | 1.1         | 1.8          | -0.5        | 3.59 ± 0.28                 |
| Sr  | 340 ± 23       | 0.4                | x           | x           | <u>-3.4</u> | x                       | x           | -0.6         | <u>2.1</u>  | -                           |
| Ta  | 0.9 ± 0.2      | <u>-3.4</u>        | x           | -2.6        | -0.1        | -1.2                    | x           | -3.3         | <u>6.7</u>  | -                           |
| Tb  | 0.4 ± 0.2      | 1.8                | x           | 4.8         | 2.3         | x                       | x           | 2.7          | 1.1         | -                           |
| Th  | 4.4 ± 0.8      | 0.0                | 0.1         | 0.5         | -0.4        | -1.5                    | 1.1         | 2.2          | 0.2         | 4.47 ± 0.21                 |
| Ti  | 3,860 ± 170    | -0.6               | 1.1         | x           | x           | <u>1.7</u>              | x           | -1.2         | x           | 3,890 ± 300                 |
| U   | 1.0 ± 0.2      | x                  | -1.1        | -0.1        | x           | x                       | x           | <u>-11.5</u> | x           | -                           |
| V   | 76 ± 17        | 0.8                | 1.0         | x           | x           | 2.8                     | -1.2        | 0.7          | x           | 80.5 ± 2.2                  |
| Yb  | 1.2 ± 0.4      | -1.1               | x           | 2.6         | 1.5         | x                       | 1.0         | 2.9          | 2.4         | -                           |
| Zn  | 97 ± 19        | 1.9                | 1.8         | 2.2         | -2.5        | 1.2                     | <u>5.7</u>  | -1.9         | -1.0        | 103 ± 16                    |
| Zr  | 132 ± 14       | 5.7                | x           | x           | -2.6        | x                       | x           | x            | x           | -                           |
| Total elements reported                   |                | 31                 | 19          | 23          | 23          | 25                      | 20          | 30           | 21          |                             |
| Percentage of  z-score  ≤ 2               |                | 84                 | 84          | 70          | 74          | 76                      | 85          | 70           | 71          |                             |
| Percentage of  E <sub>n</sub> -score  ≤ 1 |                | 90                 | 90          | 87          | 96          | 72                      | 85          | 80           | 71          |                             |

Concentration and uncertainty (coverage  $k = 2$ ) are in mg kg<sup>-1</sup> or mass fraction percent (%)

<sup>a</sup> Calculated only if at least four laboratories reported a satisfactory z-score ( $|z\text{-score}| \leq 2$ )

<sup>b</sup> Underlined z-scores have a corresponding |E<sub>n</sub>-score| > 1

The robust averages and associated expanded measurement uncertainties were determined using the procedure described in ISO 13258:2005 (E) [3]. The evaluation was based on the protocol described in the IUPAC international harmonised protocol for the proficiency testing of analytical chemistry laboratories [6].

Participants' results in this study were evaluated using calculated z-scores and E<sub>n</sub>-scores [3]. The z-scores were calculated according to Eq. 1 below:

$$z = \frac{(\chi - X)}{\sigma} \quad (1)$$

**Table 2** Laboratory performance for stream sediment JSd-2

| Element                                   | Assigned value | Laboratory z-score      |             |             |             |             |             |              |            | Robust average <sup>a</sup> |
|---|----------------|-------------------------|-------------|-------------|-------------|-------------|-------------|--------------|------------|-----------------------------|
|   |                | A                       | B           | C           | D           | E           | F           | G            | H          |                             |
| Al (%)                                    | 6.52 ± 0.17    | <u>0.9</u> <sup>b</sup> | −0.0        | x           | x           | <u>1.6</u>  | 0.7         | −0.4         | x          | 6.67 ± 0.26                 |
| As  | 39 ± 6         | 1.5                     | 1.7         | 0.5         | −0.8        | 0.6         | −0.4        | <u>−3.4</u>  | x          | 39 ± 4                      |
| Ba  | 1,200 ± 110    | 0.8                     | 0.8         | <u>−2.0</u> | −0.2        | −0.2        | 1.4         | −0.4         | 0.1        | 1,210 ± 70                  |
| Ca (%)                                    | 2.61 ± 0.08    | <u>1.4</u>              | 0.7         | <u>3.0</u>  | x           | <u>3.0</u>  | x           | <u>−24.1</u> | x          | 2.74 ± 0.28                 |
| Ce  | 23 ± 4         | 0.9                     | 0.1         | −0.9        | −0.6        | x           | 0.9         | −0.6         | −0.5       | 23.0 ± 1.0                  |
| Co  | 48 ± 5         | 1.6                     | 0.0         | 1.0         | 0.3         | <u>1.7</u>  | 0.5         | −0.3         | −0.1       | 50.3 ± 2.5                  |
| Cr  | 108 ± 9        | 1.4                     | 1.1         | 1.0         | −0.7        | <u>−0.6</u> | 0.5         | <u>−2.8</u>  | <u>3.6</u> | 112 ± 11                    |
| Cs  | 1.1 ± 0.5      | −0.7                    | −0.8        | −0.9        | 0.1         | 1.7         | 0.4         | −0.1         | −3.5       | 1.04 ± 0.06                 |
| Cu  | 1,120 ± 150    | 1.0                     | x           | x           | x           | x           | x           | x            | x          | –                           |
| Dy  | 2.9 ± 0.7      | 1.0                     | x           | x           | x           | x           | x           | x            | x          | –                           |
| Eu  | 0.81 ± 0.10    | 1.8                     | x           | 0.7         | 0.9         | <u>2.1</u>  | 1.1         | <u>2.8</u>   | −1.4       | 0.88 ± 0.06                 |
| Fe (%)                                    | 8.15 ± 0.5     | −0.6                    | 0.7         | 0.2         | −0.2        | 1.7         | −0.4        | −0.8         | −0.3       | 8.12 ± 0.18                 |
| Ga  | 15 ± 6         | x                       | x           | x           | x           | 0.22        | x           | −0.78        | x          | –                           |
| Hf  | 2.7 ± 0.4      | 3.5                     | x           | 1.6         | 1.6         | <u>4.4</u>  | 1.0         | −0.1         | −1.2       | 3.0 ± 0.4                   |
| K (%)                                     | 0.95 ± 0.05    | −1.0                    | −2.1        | −0.3        | 0.6         | <u>1.9</u>  | <u>6.5</u>  | −0.2         | −1.6       | 0.95 ± 0.06                 |
| La  | 11.3 ± 1.8     | 0.3                     | 1.5         | <u>5.2</u>  | −0.4        | 0.7         | 1.1         | 0.7          | −2.0       | 11.8 ± 0.7                  |
| Lu  | 0.25 ± 0.11    | x                       | x           | 3.3         | 3.9         | −2.4        | x           | 2.0          | x          | –                           |
| Mg (%)                                    | 1.65 ± 0.09    | 0.1                     | x           | x           | x           | 2.0         | x           | −0.6         | x          | –                           |
| Mn  | 930 ± 130      | 0.3                     | <u>−2.4</u> | x           | x           | 1.0         | 0.2         | −0.5         | x          | 930 ± 70                    |
| Na (%)                                    | 1.81 ± 0.12    | 1.1                     | x           | 0.1         | −0.1        | <u>3.0</u>  | 0.5         | −1.5         | 0.1        | 1.83 ± 0.05                 |
| Nd  | 13 ± 6         | 2.6                     | x           | 4.4         | 1.8         | x           | x           | x            | 1.7        | –                           |
| Rb  | 26.9 ± 2.9     | 3.8                     | x           | −0.5        | 1.6         | <u>5.1</u>  | <u>−2.0</u> | x            | −0.8       | 29 ± 6                      |
| Sc  | 17.5 ± 1.9     | 0.8                     | −0.1        | 1.0         | 0.3         | 1.6         | 0.6         | 0.0          | 0.6        | 18.2 ± 0.6                  |
| Se  | 18.8 ± 1.5     | 2.7                     | x           | x           | 0.1         | x           | 0.3         | x            | x          | –                           |
| Sm  | 2.7 ± 0.4      | 0.4                     | <u>3.2</u>  | 1.4         | 0.9         | 1.4         | 1.5         | 1.1          | 0.1        | 2.90 ± 0.09                 |
| Ta  | 0.5 ± 0.3      | −4.3                    | x           | −4.0        | −2.4        | −2.9        | x           | −5.0         | 0.2        | 0.40 ± 0.06                 |
| Tb  | 0.44 ± 0.07    | 2.6                     | x           | 2.6         | 1.3         | <u>7.1</u>  | x           | 2.7          | −1.7       | 0.51 ± 0.04                 |
| Th  | 2.3 ± 0.3      | 2.1                     | 1.1         | <u>4.1</u>  | 0.7         | <u>6.4</u>  | 0.4         | −0.2         | 2.0        | 2.61 ± 0.25                 |
| Ti  | 3,700 ± 600    | −1.4                    | −0.6        | x           | x           | 2.7         | x           | 0.4          | x          | 3,690 ± 290                 |
| U   | 1.10 ± 0.13    | <u>159</u>              | 0.5         | 0.1         | x           | 3.3         | x           | <u>−12.0</u> | x          | –                           |
| V   | 125 ± 8        | 1.6                     | 0.9         | x           | x           | <u>3.5</u>  | <u>2.7</u>  | 0.8          | x          | 141 ± 12                    |
| Yb  | 1.7 ± 0.6      | 2.6                     | x           | 2.1         | 2.2         | x           | 1.5         | 3.3          | 2.9        | 1.95 ± 0.08                 |
| Zn  | 2,100 ± 400    | 1.8                     | 1.0         | −0.2        | <u>−3.7</u> | 0.1         | −1.8        | <u>−5.2</u>  | −2.0       | 1,900 ± 300                 |
| Zr  | 110 ± 40       | x                       | x           | x           | 2.5         | x           | x           | x            | x          | –                           |
| Total elements reported                   |                | 31                      | 19          | 24          | 24          | 27          | 22          | 28           | 20         |                             |
| Percentage of  z-score  ≤ 2               |                | 71                      | 84          | 67          | 79          | 56          | 91          | 68           | 85         |                             |
| Percentage of  E <sub>n</sub> -score  ≤ 1 |                | 84                      | 90          | 83          | 96          | 59          | 86          | 79           | 95         |                             |

Concentration and uncertainty (coverage  $k = 2$ ) are in mg kg<sup>−1</sup> or mass fraction percent (%)

<sup>a</sup> Calculated only if at least four laboratories reported a satisfactory z-score ( $|z\text{-score}| \leq 2$ )

<sup>b</sup> Underlined z-scores have a corresponding |E<sub>n</sub>-score| > 1

where  $z$  is the z-score,  $\chi$  is a participant's result,  $X$  is the study assigned value and  $\sigma$  is the target standard deviation.

The target standard deviation ( $\sigma$ ) is the product of the assigned value and the predicted between-laboratory coefficient of variation (CV).

CV is a measure of the between-laboratory variation that would be expected from participants, given the analyte concentration, and is usually set by the study coordinator. Based on practical experience and published data [7] the CV for this study was chosen to be 4% for the seven analytes greater than 1 g kg<sup>−1</sup> and 7% for all others.

**Table 3** Laboratory performance for stream sediment JSd-3

| Element                                   | Assigned value | Laboratory z-score |      |             |             |            |                         |              |             | Robust average <sup>a</sup> |
|---|----------------|--------------------|------|-------------|-------------|------------|-------------------------|--------------|-------------|-----------------------------|
|   |                | A                  | B    | C           | D           | E          | F                       | G            | H           |                             |
| Ag  | 3.4 ± 1.0      | 0.8                | x    | x           | x           | x          | x                       | x            | x           | –                           |
| Al (%)                                    | 5.24 ± 0.24    | 0.5                | 0.2  | x           | x           | 0.7        | <u>4.4</u> <sup>b</sup> | 0.0          | x           | 5.35 ± 0.13                 |
| As  | 252 ± 33       | 0.7                | 0.8  | 0.4         | –0.2        | 1.3        | 0.8                     | <u>–2.8</u>  | x           | 261 ± 9                     |
| Ba  | 462 ± 50       | –1.5               | –0.3 | <u>–2.8</u> | –1.2        | –1.7       | –0.4                    | 0.0          | <u>–4.5</u> | 420 ± 40                    |
| Ca  | 4,000 ± 600    | –0.9               | –0.8 | 0.9         | x           | x          | x                       | 2.7          | x           | –                           |
| Ce  | 42 ± 7         | 0.6                | –0.1 | 0.1         | –0.3        | 0.2        | 1.4                     | 1.1          | <u>–6.0</u> | 42.6 ± 1.9                  |
| Co  | 12.7 ± 1.7     | –0.2               | –1.0 | 0.7         | –0.7        | 1.4        | –0.2                    | –0.2         | –1.7        | 12.5 ± 0.8                  |
| Cr  | 35 ± 5         | –0.3               | 2.2  | 0.5         | –1.3        | –0.6       | 0.1                     | <u>–2.8</u>  | <u>–2.2</u> | 34 ± 3                      |
| Cs  | 30.6 ± 2.2     | –0.8               | 0.0  | 0.3         | <u>2.5</u>  | 0.8        | –0.4                    | –0.1         | <u>–3.5</u> | 30.5 ± 1.8                  |
| Cu  | 426 ± 21       | 0.9                | x    | x           | x           | x          | x                       | x            | x           | –                           |
| Eu  | 0.69 ± 0.05    | –0.5               | x    | <u>1.8</u>  | 0.9         | <u>1.5</u> | 0.7                     | <u>1.4</u>   | –0.9        | 0.72 ± 0.05                 |
| Fe (%)                                    | 3.06 ± 0.26    | –0.5               | –0.5 | 0.0         | –0.9        | 0.0        | –0.8                    | –0.1         | <u>–3.4</u> | 3.00 ± 0.06                 |
| Ga  | 13.5 ± 1.0     | 0.4                | x    | x           | x           | –0.9       | x                       | <u>4.6</u>   | x           | –                           |
| Hf  | 3.2 ± 0.4      | <u>3.2</u>         | x    | 0.5         | <u>8.1</u>  | <u>2.8</u> | 1.4                     | 0.1          | <u>–2.7</u> | 3.6 ± 0.5                   |
| K (%)                                     | 1.64 ± 0.10    | –0.3               | –0.6 | 1.6         | 0.6         | –0.7       | <u>3.3</u>              | <u>4.4</u>   | <u>–6.6</u> | 1.66 ± 0.12                 |
| La  | 19.8 ± 3.6     | –0.2               | 0.1  | 5.8         | 0.0         | 1.1        | 1.5                     | 0.3          | <u>–4.6</u> | 20.4 ± 1.3                  |
| Lu  | 0.20 ± 0.10    | x                  | x    | 3.9         | 4.7         | 3.2        | x                       | 0.2          | x           | –                           |
| Mg  | 7,100 ± 400    | 0.1                | x    | x           | x           | <u>4.8</u> | x                       | <u>–5.3</u>  | x           | –                           |
| Mn  | 1,150 ± 150    | –0.3               | –1.8 | x           | x           | 0.2        | –0.4                    | –0.9         | x           | 1,100 ± 70                  |
| Na  | 3,000 ± 700    | 1.1                | x    | 2.5         | –0.3        | 0.6        | 1.0                     | 2.0          | <u>–7.0</u> | 3,150 ± 170                 |
| Nd  | 15.7 ± 1.5     | <u>4.4</u>         | x    | 7.3         | 0.2         | x          | x                       | –2.8         | x           | –                           |
| Rb  | 285 ± 18       | 0.4                | x    | 0.3         | –0.9        | –0.3       | –0.5                    | <u>1.5</u>   | <u>–4.3</u> | 280 ± 20                    |
| Sc  | 10.5 ± 1.4     | –0.7               | –0.5 | 1.2         | 0.3         | 1.0        | 0.6                     | 1.1          | –0.9        | 10.7 ± 0.6                  |
| Se  | 1.3 ± 1.2      | 2.8                | x    | x           | 10.7        | x          | x                       | x            | x           | –                           |
| Sm  | 3.3 ± 0.4      | –0.2               | 1.4  | 0.5         | 0.1         | <u>2.7</u> | 1.6                     | 0.6          | <u>–2.3</u> | 3.40 ± 0.25                 |
| Ta  | 0.7 ± 0.4      | –3.7               | x    | –4.9        | –2.0        | –0.6       | x                       | –1.7         | x           | –                           |
| Tb  | 0.37 ± 0.09    | <u>4.4</u>         | x    | <u>6.3</u>  | 2.8         | 3.2        | x                       | 3.4          | –1.6        | –                           |
| Th  | 7.8 ± 4.3      | –1.3               | –1.3 | –0.3        | –1.5        | –2.2       | –1.2                    | –1.2         | –1.7        | 7.06 ± 0.13                 |
| Ti  | 2,400 ± 400    | 0.7                | 1.6  | x           | x           | 0.5        | x                       | 0.2          | x           | 2,480 ± 50                  |
| U   | 1.7 ± 0.3      | x                  | –1.4 | –0.7        | x           | <u>4.0</u> | x                       | <u>–11.4</u> | x           | 1.5 ± 0.8                   |
| V   | 70 ± 7         | 1.5                | 1.4  | x           | x           | <u>2.7</u> | <u>1.7</u>              | 0.8          | x           | 77.8 ± 2.9                  |
| W   | 180 ± 60       | 3.3                | x    | 1.6         | x           | x          | 1.0                     | <u>–13.7</u> | x           | –                           |
| Yb  | 1.4 ± 0.4      | 1.1                | x    | 1.4         | 1.7         | x          | <u>12.7</u>             | <u>4.2</u>   | –1.2        | 1.60 ± 0.26                 |
| Zn  | 136 ± 7        | <u>1.1</u>         | 0.6  | 0.9         | <u>–3.0</u> | <u>1.2</u> | 0.0                     | <u>–2.7</u>  | <u>–5.7</u> | 135 ± 12                    |
| Zr  | 124 ± 16       | <u>9.0</u>         | x    | x           | –2.0        | x          | x                       | x            | x           | –                           |
| Total elements reported                   |                | 33                 | 19   | 45          | 24          | 27         | 22                      | 31           | 18          |                             |
| Percentage of  z-score  ≤ 2               |                | 79                 | 95   | 84          | 75          | 70         | 86                      | 61           | 33          |                             |
| Percentage of  E <sub>n</sub> -score  ≤ 1 |                | 85                 | 100  | 89          | 88          | 74         | 82                      | 68           | 33          |                             |

Concentration and uncertainty (coverage  $k = 2$ ) are in mg kg<sup>–1</sup> or mass fraction percent (%)

<sup>a</sup> Calculated only if at least four laboratories reported a satisfactory z-score ( $|z\text{-score}| \leq 2$ )

<sup>b</sup> Underlined z-scores have a corresponding |E<sub>n</sub>-score| > 1

A z-score with absolute value:

- $|z| \leq 2$  is satisfactory;
- $2 < |z| \leq 3$  is questionable; and
- $|z| > 3$  is unsatisfactory.

The E<sub>n</sub>-score is complementary to the z-score in assessing laboratory performance. The E<sub>n</sub>-score includes measurement uncertainty and is calculated according to Eq. 2 below:

$$E_n = \frac{(\chi - X)}{\sqrt{U_\chi^2 + U_X^2}} \quad (2)$$

where  $E_n$  is the  $E_n$ -score,  $\chi$  is a participant's result,  $X$  is the assigned value,  $U_\chi$  is the expanded uncertainty of the participant's result and  $U_X$  is the expanded uncertainty of the assigned value.

An  $E_n$ -score with absolute value:

- $|E_n| \leq 1$  is satisfactory; and
- $|E_n| > 1$  is unsatisfactory.

## Results

The assigned values for each test sample together with participants z-scores are listed in Tables 1, 2 and 3. An 'x' is entered where a laboratory did not report that element. If the corresponding absolute  $E_n$ -score was greater than 1, indicating an unsatisfactory result, then the z-score has been underlined; otherwise the  $E_n$ -scores were satisfactory.

The column at the right of the tables provides the robust average and expanded uncertainty (coverage  $k = 2$ ) of the measured values for each element. The robust average for an element can be taken as a consensus value and has only been entered if at least four laboratories reported a result for which the laboratory z-score was satisfactory.

The three rows at the bottom of the tables provide a tally for each laboratory of the total number of elements

reported, the percentage of the reported z-scores that were satisfactory ( $|z| \leq 2$ ) and the percentage of the reported  $E_n$ -scores that were satisfactory ( $|E_n| \leq 1$ ).

## Discussion

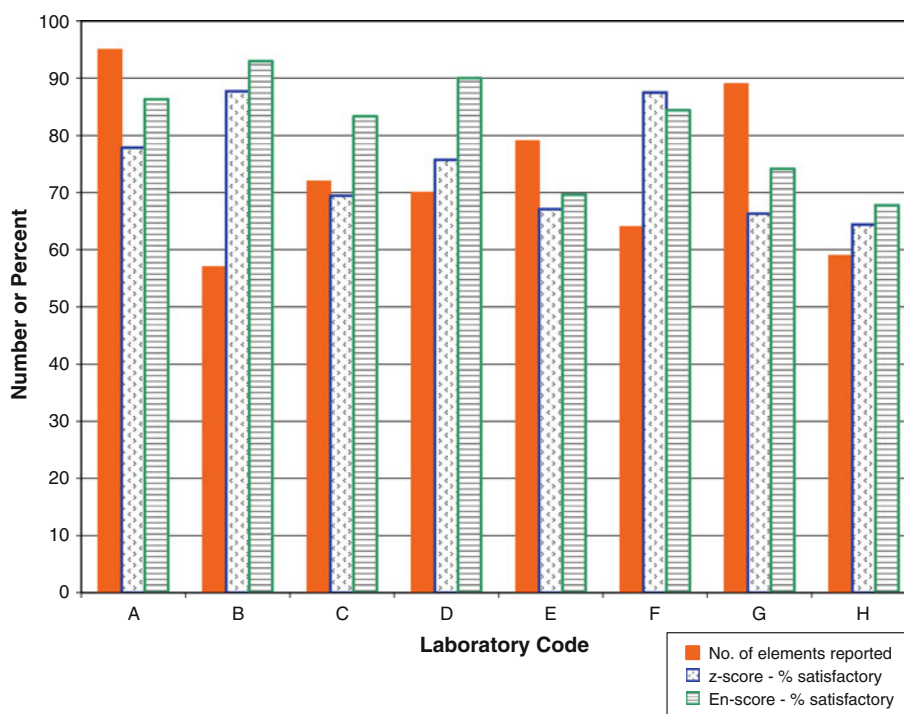
### Laboratory performance

Of 585 results, 433 (74%) returned a satisfactory z-score and 473 (81%) returned a satisfactory  $E_n$ -score. Part of the reason for the somewhat higher performance measured by the  $E_n$ -score may be due to the inclusion of elements such as Gd in JSd-1 and Nd in JSd-2, for which the assigned values themselves have high uncertainties, as explained above. Where a result has a satisfactory z-score but an unsatisfactory  $E_n$ -score, it is likely that the expanded measurement uncertainty has been underestimated.

No laboratory reported results for all elements in all samples and none of the laboratories returned satisfactory z-scores for all results that they reported.

Figure 1 presents the total number of elements reported by each laboratory, summed over the three stream sediments, the percentage of those results that returned a satisfactory z-score and the percentage that returned a satisfactory  $E_n$ -score. Note that three laboratories (C, D and H) did not report results for elements that are measured by activated nuclides that have a half-life less than about 12 h.

**Fig. 1** Overall performance of the participants in the trial proficiency test, combining the results from all three test materials



Complete information has been shared among the participants in the study in order to maximise learning opportunities. It is expected that laboratories will seek to understand the reasons for discrepancies in their results from the assigned or consensus values, paying attention to the overall uncertainty budget of reported values. A desirable outcome would be an improvement in the overall quality and uniformity of NAA performance in the Asian region. Such an improvement could be quantified by running a second proficiency test in the future.

#### Commentary on elements

Co and Sc were reported by all eight laboratories in all three samples, and all of these results returned satisfactory z-scores. Satisfactory z-scores and  $E_n$ -scores were returned for a high percentage of the measurements of Ce, Fe, Mn and Sm. Overall, robust average values could be determined for 70% of the elements listed in the tables.

It can be seen from the tables of results that there is generally good agreement between the assigned values and the robust averages of the measurements. It can also be seen that the expanded uncertainty on the robust average of participants' results was less than half of that for the corresponding assigned value in 34 instances and was the case for Ce, Co, Mn and Sc in all three reference materials. This observation suggests that the characterization of the three stream sediment reference materials used in the study could be improved.

#### Geochemical mapping

Where a geochemical mapping program requires the analysis of sediment-like samples, this study has confirmed that NAA, as practised at laboratories in the Asian region, is a suitable technique for more than 20 elements.

#### Conclusion

The combined results of all participating laboratories found that 74% of the measurements returned a satisfactory

z-score and 81% returned a satisfactory  $E_n$ -score. Sharing of the detailed proficiency test information among the participants, as one aspect of laboratory quality assurance, is expected to lead to an improvement in the quality and uniformity of NAA performance in the Asian region.

A high degree of proficiency was found in the determination of the concentration of Co and Sc in the three stream sediments. Overall, robust average values could be determined for 70% of the elements listed in the tables. The results of the study support the use of NAA, as practised by the participants, for geochemical mapping.

Given the large number of determinations reported by the participants and the general agreement between the reported values and the assigned values, the data produced in this study may provide an opportunity to improve the characterisation of the three stream sediment reference materials, JSd-1, JSd-2 and JSd-3. This may particularly be the case where the uncertainty on the consensus value was significantly less than the uncertainty on the assigned value.

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