Results of proficiency testing with regard to sediment analysis by FAAS, ICP-MS and TXRF

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Three different techniques of instrumental analysis applied at ISAS were evaluated within a proficiency test, organised by IRMM in Geel. The 3 techniques, in particular flame atomic absorption spectrometry (FAAS), inductively coupled plasma mass spectrometry (ICP-MS) and total-reflection X-ray fluorescence (TXRF) were used for multielement trace analysis of a sediment sample after digestion. The reported results of up to 9 elements were evaluated with respect to the reference values after the disclosure of the latter. The relative deviations, mostly $<4\%$, demonstrate the high accuracy of the 3 techniques. In addition, the uncertainty bars of report and reference show a high degree of overlapping, which gives evidence that the mean values are not significantly different. The high ranking of ISAS results among all 239 participants of the test confirms these findings. With regard to accuracy, ICP-MS and TXRF are somewhat inferior to conventional FAAS but in their favour they are labour- and time-saving and have a good detection power.

Introduction

Interlaboratory comparisons, also called round-robin tests, can have three different aims: the validation of an analytical method applied to a certain analytical problem, the certification of a certain sample or material regarding the elements content and the evaluation of an analytical laboratory with respect to its performance for a certain analytical task. The latter is also called proficiency testing.

A special interlaboratory comparison was carried out within an international measurement programme (IMEP), coordinated by the Institute for Reference Materials and Measurements (IRMM) in Geel, Belgium. This test, called IMEP-14, was related to the determination of trace elements in a sediment material, mainly on the mmol kg^{-1} level. The sediment sampled from a channel was treated until it was a fine powder. This powder was analysed by seven experienced reference laboratories (RL) in a certification campaign, mainly using isotope dilution mass spectrometry (IDMS) as a primary method of measurement (PMM). So-called reference values were determined but first of all, these values were undisclosed. Aliquots of about 40 g, bottled in glass containers, were forwarded to interested laboratories on payment of a charge (300 Euro). Participants of the test were asked to measure the content of up to 12 elements in certified test samples (CTS) of the sediment.

The CTS were distributed in July 1999 and the deadline for delivery of the results was November 1999 (extended to January 2000). In February 2000, the reference values were reported to the participants and in October 2000, the final report[1] on IMEP-14 was sent to the participants by IRMM. In total, 239 laboratories took part in the proficiency test, coming from 43 countries—mainly Germany (35), Hungary (25), Austria (23), Japan (17) and Sweden (16). More than 13 different analytical techniques were applied, mostly ICP-AES (inductively coupled plasma atomic emission spectrometry; 32%), ICP-MS (ICP mass spectrometry; 18%), FAAS (flame atomic absorption spectrometry; 21%), ETAAS (electrothermal AAS; 9%) and XRF (X-ray fluorescence; 5%). Only half of the participants were certified or accredited, but all had experience in the analysis of similar types of samples.

The ISAS (Institute of Spectrochemistry and Applied Spectroscopy, Dortmund, Germany) participated in the test with three different techniques, these being FAAS, ICP-MS and TXRF (total-reflection XRF) as a special variant of XRF. General information about ICP-MS and TXRF can be found in the literature.[2,3] The test was carried out with the aim of a proficiency test of our non-commercial laboratory but also a validation of the three techniques. Our main intention was to question the reliability of the three techniques, especially the accuracy of the younger modes of ICP-MS and TXRF in comparison with that of the established technique of FAAS. The corresponding results will be given in this Technical Note.

Experimental

Aliquots of the sediment powder delivered by IRMM were digested and analysed by FAAS, ICP-MS and TXRF.

Sample material

The sediment had previously been analysed by seven reference laboratories from different parts of the world in an independent certification campaign.[4] The main technique employed in this campaign was IDMS but also NAA (neutron activation analysis) and Z-AAS (Zeeman atomic absorption spectroscopy) were applied. The values were characterised as certified when (i) only one RL delivered a result and the technique applied was a PMM or when (ii) more than one RL gave a result and the RSD of the different results is $<2\%$. In all other cases, the values were characterised as assigned.

Reference values for 10 elements were established and reported to participants *after* they had reported their results. These elements are: As, Cd, Cr, Cu, Fe, Pb, Hg, Ni, U and Zn. The elements B and Se were excluded since no reliable measurement data could be provided by the organizers. Table 1 gives the reference values in the SI unit mol kg^{-1} and the respective uncertainties with $k=2$. Half of the values are called certified, half of them are called assigned. The reference values are in the range from 3.5 μmol kg^{-1} (mercury) up to 0.45 mol kg^{-1} (iron). The relative uncertainty is about 3% for the certified values and is some 10% for the assigned values.

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Table 1 Reference values for 10 elements in the sediment sample given in mol kg^{-1} (IMEP-14, trace elements in sediment, reported[1] by IRMM, Geel, Belgium). a: Assigned; c: certified

Element	Reference value/ mol kg^{-1}	Uncertainty $k=2$/ mol kg^{-1}	Character
As	279×10^{-6}	28×10^{-6}	a
Cd	23.20×10^{-6}	0.78×10^{-6}	c
Cr	1103×10^{-6}	31×10^{-6}	c
Cu	743×10^{-6}	74×10^{-6}	a
Fe	454×10^{-3}	45×10^{-3}	a
Pb	421.1×10^{-6}	8.4×10^{-6}	c
Hg	3.48×10^{-6}	0.56×10^{-6}	a
Ni	444×10^{-6}	12×10^{-6}	c
U	6.73×10^{-6}	0.32×10^{-6}	c
Zn	4.95×10^{-3}	0.49×10^{-3}	a

Some 40 g of the sediment powder was available for analysis. In ISAS the powder was digested by two independent techniques: high pressure ashing and microwave digestion. The microwave technique, being a very fast method, was applied in addition to the well established but time consuming ashing technique.

Sample preparation

High pressure ashing. For this decomposition, 400–500 mg of the sediment sample was weighed in a 70 ml quartz vessel. 4 ml of nitric acid (65%, subboiled, Merck, Darmstadt, Germany) and 0.5 ml hydrochloric acid (30%, Suprapure, Merck) was added. This mixture was treated in a high pressure asher (HPA®, Kürner, Rosenheim, Germany) at the following temperatures and a maximum pressure of 13 MPa: step 1, 20 °C up to 320 °C for 50 min; step 2, 320 °C for 50 min; step 3, cooling down to <40 °C. The resulting solution and the insoluble residue of the sample was transferred quantitatively into a PTFE vessel. A treatment with 2 ml of hydrofluoric acid (40%, Suprapure, Merck) on a hot-plate followed in order to dissolve siliceous components of the sample. The excess hydrofluoric acid was then removed by addition of 2 ml of nitric acid (65%) and evaporation almost to dryness. The resulting decomposition residue then was transferred with de-ionised water quantitatively into a volumetric flask and filled up to exactly 10 ml. These solutions were prepared for the analysis by TXRF and FAAS. A proper dilution could be carried out if necessary. In total, 4 acid blanks and 10 different sediment samples (IMEP-14) were decomposed separately.

Microwave digestion. About 100 mg of sediment powder was placed in a modified polytetrafluoroethylene vessel. 4 ml of HNO$_3$ (subboiled, p.a. quality, Merck) and 1 ml of HF (48%, Ultrapure, Merck) were added. The loaded vessels were inserted in a Multiwave (PerkinElmer–Paar, Überlingen, Germany) for microwave assisted digestions. For a total decomposition, the microwave power was increased from 300 to 1000 W in 5 min and then was kept constant for 25 min as long as a maximal pressure of 3 MPa was not reached. The mean temperature was about 183 °C. After a cooling period of 20 min, the clear sample solutions were filled in 50 ml PP-measuring flasks. 2.5 ml of these solutions were transferred to 25 ml PFA-measuring flasks. Rh and Re (Merck) were added as internal standards with a concentration of 40 ng ml^{-1}. Altogether, 6 different samples and 6 different blanks were digested separately and analyzed by ICP-MS. In addition, 6 test samples (Canadian Stream Sediment Reference Material STSD-4) were subjected to this digestion method and analysed by ICP-MS in order to check its accuracy. The deviation from the reference value of the certificate was better than ±10% for all elements investigated.

Instrumentation

FAAS. A Hitachi Z8000 spectrometer (Hitachi Ltd., Tokyo, Japan) with Zeeman background correction was used for all measurements operating at standard conditions. For sample introduction, 100 µl of each sample was injected into the air–acetylene flame.

ICP-MS. Analysis was carried out with a PQ II Turbo Plus (VG Elemental, Winsford, Cheshire, UK). A HF-resistant V-groove nebuliser with a Scott-type spray chamber made of quartz and cooled to 5 °C was used with a sample delivery rate of 0.6 ml min^{-1} supplied by a peristaltic pump (Gilson Minipuls 3). Tuning of the ICP-MS instrument was performed using ^{140}Ce. Optimisation was performed with respect to a high signal intensity, to a low oxide and a low doubly charged ion ratio. Conventional Ni cones were applied. For data acquisition (60 s per run, 5 runs per sample) analogue as well as pulse counting detection was chosen. A forward power of 1400 W (P_{refl}: 3 W) was used. The flow rates of argon were chosen as follows: cooling gas 15 l min^{-1}, auxiliary gas 1.7 l min^{-1}, nebuliser gas 1.07 l min^{-1}.

TXRF. The spectrometer Extra II (Rich. Seifert & Co., Ahrensburg, Germany) with a QX 2000 analyser (Link Systems, Oxford Instruments, High Wycombe, Buckinghamshire, UK) was used for TXRF analysis. Two line-focus X-ray tubes with a Mo- and with a W-anode were chosen sequentially and both were operated at 50 kV and 38 mA. For each sample, a spectrum was recorded in the energy-dispersive mode: a first spectrum with the Mo, a second spectrum with the W-anode. The acquisition time for each spectrum was set to 300 s.

Results and discussion

Analytical performance

FAAS. Calibration was carried out using 5 external aqueous standard solutions for each single element, which were adjusted properly to the high Ca concentration in the sample material. The accuracy and reproducibility of this calibration technique were previously checked by applying the method of standard additions. No significant differences were found.

100 µl of sample and standard solutions were sequentially injected into the spray chamber of the spectrometer. Each sample was measured twice. The calibration graph and the mean value for each determination were calculated using the spectrometer program. In total, 10 different samples (decompositions) were analysed, blanks were taken into account and 7 elements (Cd, Cr, Cu, Fe, Ni, Pb and Zn) could be determined quantitatively. The remaining elements As, Hg and U could not be determined by conventional FAAS.

ICP-MS. The 6 sediment samples decomposed by microwave digestion were analysed by ICP-MS. An external calibration with 5 standard samples was carried out using a multielement standard solution (Merck VI). For each standard and each sample 5 runs were applied. Altogether, 9 elements could be determined quantitatively *via* the following isotopes: ^{52}Cr, ^{57}Fe, ^{60}Ni, ^{63}Cu, ^{66}Zn, ^{75}As, ^{111}Cd, ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{238}U. Only Hg was not determined.

The intensity values were corrected by subtraction of the respective blank. The nickel value was corrected due to the well known CaO–CaOH interference. The values for iron were extrapolated, the values of all the other elements were interpolated.

TXRF. The very simple method of internal quantification was applied. Aliquots of 1 mL of the solutions derived from high pressure ashing were taken, diluted 1:10 and each spiked

with a standard solution (Johnson Matthey, Karlsruhe, Germany) containing Se. The concentration of this element was adjusted to 5 μg ml^{-1}. A droplet of 10 μl of each solution was pipetted onto siliconized quartz-glass carriers and dried by use of IR light. The dry residues of the solutions (some μg) were analysed.

Selenium added to the solutions and found in the dry residues served as the internal standard element with a known mass (50 ng). The masses of all other elements found in the residues were determined *via* sensitivity values. The sensitivity values of these elements in relation to that of Se had been determined by aqueous standard solutions sometime beforehand. Finally, the content of the detected elements in the sediment sample was calculated in relation to the dilution factor. Altogether 6 sediment samples were analysed and 6 elements could be determined quantitatively (Cr, Cu, Fe, Pb, Ni and Zn). The remaining 4 elements could not be determined.

Detection limits

The content of an element to be determined quantitatively should be significantly above the detection limit. This limit was determined according to the IUPAC definition[5]

$$DL = 3 c_{BEC} s_{rel}$$

where c_{BEC} is the background equivalent concentration and s_{rel} is the relative s of the blank measurements. Both quantities were determined from measurements. The latter has to be relevant for the whole procedure (including digestion and analysis), not only for the spectral background (repetitive measurements).

Detection limits are listed in Table 2. For most elements, the contents of the sediment sample (Table 1) are distinctly above these limits. For quantitative determinations, a factor >3 is recommended and this condition is fulfilled for the elements determined by TXRF, FAAS and ICP-MS.
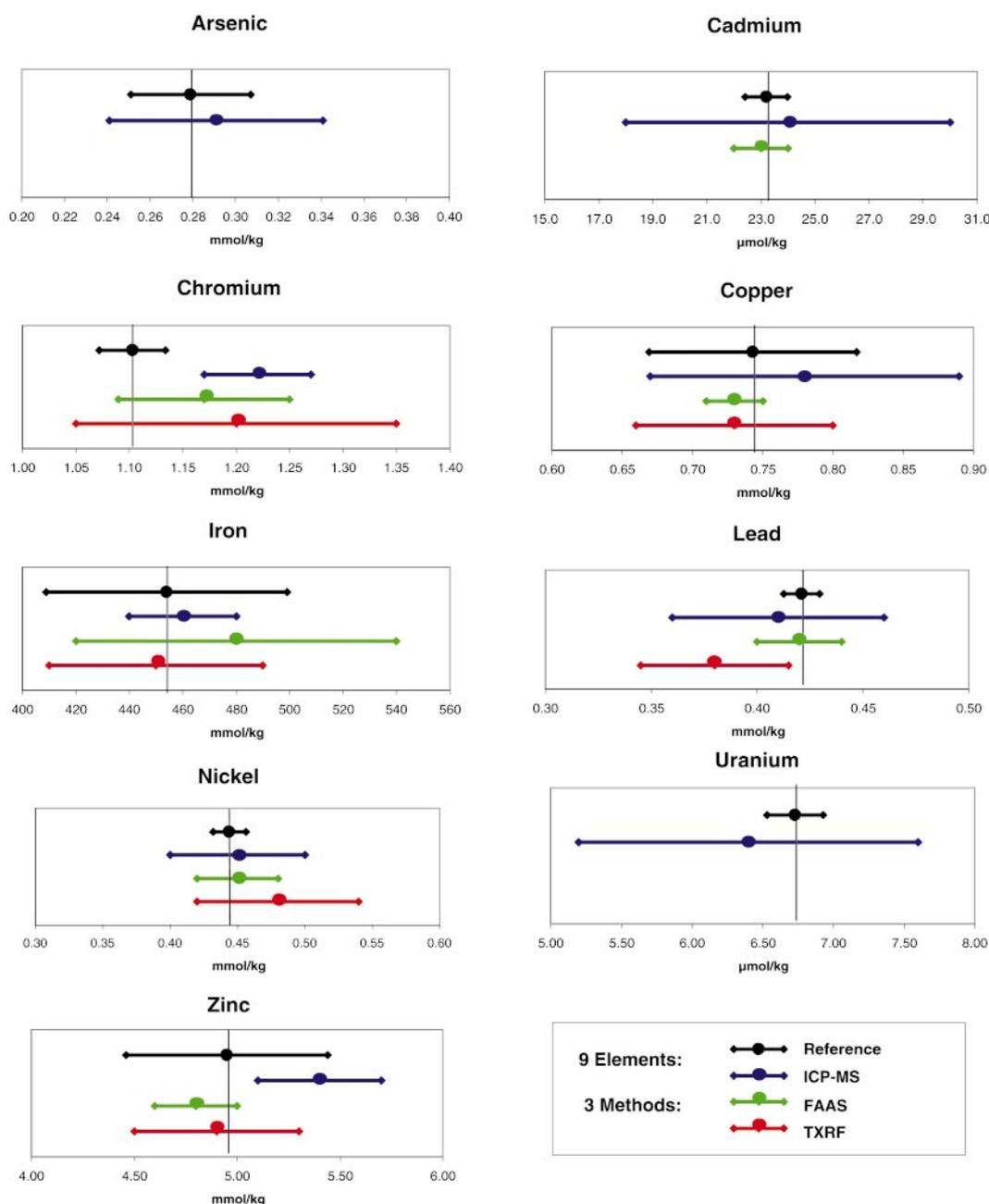

Fig. 1 Results found for the different elements in the sediment sample with mean value and uncertainty interval. Green: FAAS, blue: ICP-MS, red: TXRF; black: reference.[1]

Table 2 Detection limits for different elements in sediment, determined by three techniques: FAAS, ICP-MS and TXRF. All values are given in µmol kg^{-1}

Element	Detection limit		
	FAAS	ICP-MS	TXRF
As	—	6	—
Cd	2	1	—
Cr	45	8	250
Cu	10	8	50
Fe	40	400	400
Pb	10	4	20
Ni	30	5	90
U	—	0.1	—
Zn	5	40	50

Comparison with reference values

For each analytical technique—FAAS, ICP-MS and TXRF—6 or even 10 individual values were determined for the content of the above mentioned elements. These values were given in the SI unit mol kg^{-1} as recommended by the organizer IRMM. Accordingly, the mean values were calculated and the expanded uncertainties with a coverage factor $k = 2$ were estimated. This range, claiming to contain the true value, was determined according to the guides issued by ISO.[6] It is distinctly broader than the doubled s range (standard deviation of individual values) since all possible errors are taken into consideration.

All results of the ISAS laboratory are demonstrated as a bar chart in Fig. 1. Coloured bars plotted for the 3 techniques applied can be compared with the bars of the reference values (black; from Table 1). 7 elements are represented by FAAS (green), 9 elements by ICP-MS (blue) and 6 elements by TXRF (red). The remaining elements could not be determined accurately because of a very low content. Hg with a content <4 µmol kg^{-1} could be determined by none of the 3 techniques.

At first, the relative deviations between measured or reported values and reference values were calculated and listed in Table 3. These deviations range from about -10% to about $+11\%$. Their arithmetic mean allows a first ranking: TXRF $+0.6\%$, FAAS $+1.0\%$ and ICP-MS $+3.0\%$. This mean, however, is not relevant. It only shows that ICP-MS has a certain positive offset for all elements. The ''root mean square'' of the deviations (square root of the mean of the squared deviations) gives a more relevant valuation: FAAS 3.5%, ICP-MS 5.6% and TXRF 6.4%. To complete this picture, the degree of overlapping of the uncertainty intervals was considered.

The different coloured bars in Fig. 1 more or less overlap with the reference bars in black. In order to evaluate the 3

Table 3 Relative deviations between reported results and reference values for different trace elements in the sediment sample, determined by 3 techniques

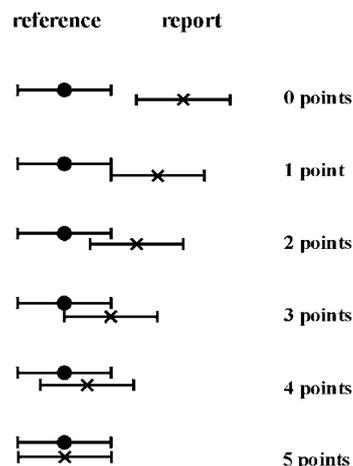| Element	Relative deviation		
	FAAS(%)	ICP-MS(%)	TXRF(%)
As		+3.9	
Cd	−0.9	+3.5	
Cr	+6.1	+10.6	+8.8
Cu	−1.8	+5.0	−1.8
Fe	+5.7	+1.3	−0.9
Pb	−0.3	−2.6	−9.8
Ni	+1.3	+1.4	+8.1
U		−4.9	
Zn	−3.0	+9.1	−1.0
Arithmetic mean	+1.0	+3.0	+0.6
Root mean square	3.5	5.6	6.4

Fig. 2 Different overlappings of the uncertainty intervals of reported and reference values. The degree of overlapping was expressed by a figure of merit (between 0 and 5 points).

Table 4 Degree of overlapping between report and reference, determined for 3 techniques with respect to different trace elements in sediment

Element	Degree of overlapping		
	FAAS	ICP-MS	TXRF
As	—	4.5	—
Cd	4.5	4.7	—
Cr	2.5	(0.0)	3.4
Cu	4.4	4.3	4.6
Fe	3.9	4.6	4.8
Pb	4.8	4.5	2.2
Ni	4.4	4.7	3.5
U	—	4.3	—
Zn	4.0	2.6	4.8
Mean	4.1	3.8 (4.3)	3.9

techniques with regard to their accuracy, a figure of merit was defined as a measure for the degree of overlapping. This quantity of course should contain the distance of a reported mean value and the corresponding reference value in relation to the length of the corresponding bars. It should lead to a certain figure of merit expressed by a number of points as is demonstrated in Fig. 2 with 0–5 points. This figure of merit m can be calculated by the equation:

$$m = 5 - \left| c_{\mathrm{rep}} - c_{\mathrm{ref}} \right| / u_{\mathrm{pool}} \quad (1)$$

where c_{rep} is the mean reported content, c_{ref} is the reference value and u_{pool} is defined by

$$u_{\mathrm{pool}} = \sqrt{\left(u_{\mathrm{rep}}^2 / n_{\mathrm{rep}} + u_{\mathrm{ref}}^2 / n_{\mathrm{ref}} \right)} \quad (2)$$

with $u_{\mathrm{rep}} = $ uncertainty of the reported value, $u_{\mathrm{ref}} = $ uncertainty of the reference value and n_{rep} or $n_{\mathrm{ref}} = $ number of corresponding determinations. It was assumed that >10 determinations were carried out for the reference values.

Eqn. (1) can be related to the statistical t-test applied to the comparison of two mean values with different s values (a modified t-test[7]). In this regard $m \leqslant 3.9$ means that there is a significant difference between the two values at the level of 5%; $m > 3.9$, however, means that there is no evidence that both values are significantly different, *i.e.*, there is no evidence of a systematic error (confidence interval 95%).

The figure of merit m was calculated and listed in Table 4. In most cases, values are >4.4, just demonstrating a high
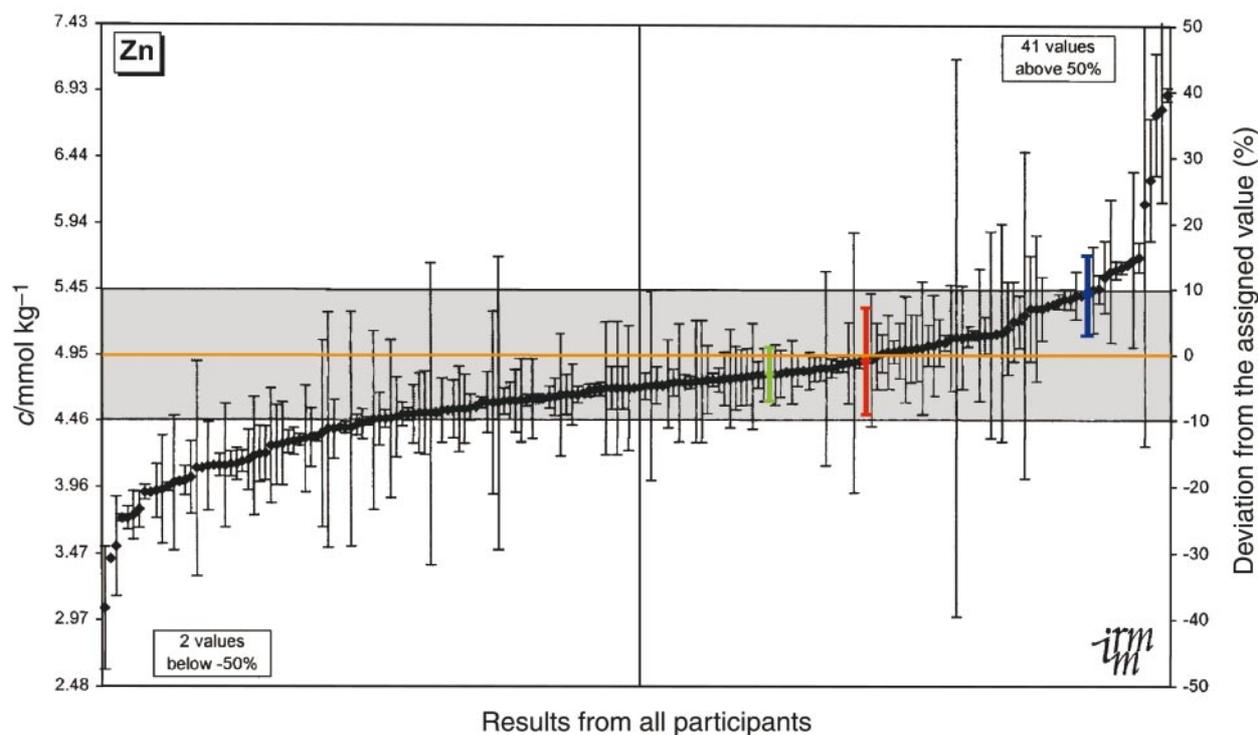
Fig. 3 Results from all participants of IMEP-14, related to the content of Zn in the sediment sample.[1] The shaded band gives the reference value and the uncertainty interval. Green: FAAS, blue: ICP-MS and red: TXRF at ISAS, Dortmund.

accuracy of the 3 techniques. One outlier with $m = 0$ was found for Cr by ICP-MS. Fig. 1 confirms that this is the only case where no overlapping exists between report and reference bars. It is due to the fact that the uncertainty was estimated in accord with the test result of the standard STSD-4 which was highly accurate for this element. The mean values are 4.1 for FAAS, 3.9 for ICP-MS and 3.9 for TXRF. These values give a rather equal ranking of the 3 techniques. Obviously, the degree of overlapping could not confirm the ranking by the relative deviations. The degree of overlapping, however, gives a more relevant valuation since it includes the total uncertainty intervals and not only the mean values.

Comparison with results of all participants

Eight months after the report of the reference values, the final report[1] was given by the organizer, IRMM. It especially represents an overview of the results of all participants without disclosing the individual origin. For any element, the results were ordered after increasing values in a graphical presentation. Fig. 3 gives a typical example for the element Cu. All elements show the typical curve for the distribution of the individual values.

The results of the 3 techniques performed in ISAS laboratory

Table 5 Ranking of the 3 techniques among 100 participants of the interlaboratory test IMEP-14 (trace elements in sediment)

Element	Rank among 100 participants		
	FAAS	ICP-MS	TXRF
As	—	84	—
Cd	98	85	—
Cr	83	77	80
Cu	96	74	94
Fe	59	84	92
Pb	97	89	59
Ni	96	95	71
U	—	97	—
Zn	85	50	97
Average	88	82	82

were coloured again as beforehand and a further ranking could be derived. For that, the number of laboratories which had a better result than ISAS was determined, *i.e.*, which had a smaller deviation from the reference. This number was related to the number of all participants, was multiplied by 100 and subtracted from 100. The calculated figure is the rank number among 100 participants. These values, mostly above 85 up to 98, are listed in Table 5. The average values give a ranking FAAS 88, ICP-MS 82 and TXRF 82, which corresponds to the previous ranking of overlapping. The high values demonstrate that the 3 techniques are among the most accurate ones performed in this proficiency test.

Conclusions

In general, it can be concluded from the results that all three different techniques applied at ISAS (FAAS, ICP-MS and TXRF) are well suited for the analysis of sediment samples after ashing or digestion. Far above detection limit, 9 of the 10 elements of interest can be analysed by ICP-MS, 7 of 10 by FAAS and 6 of 10 by TXRF, demonstrating the multielement capabilities even in a very complex matrix, where the techniques usually are hampered by spectral interferences. For ICP-MS the best detection limits have been realized, but a significant difference with respect to the accuracy of the results has not been found. The ranking in comparison to other participants of the proficiency testing demonstrates that all three techniques are among the most accurate. FAAS has been slightly superior to ICP-MS and TXRF, which demonstrates that this conventional technique still plays an important role in trace determinations even in complex materials, although FAAS is more laborious and time consuming. The simplest and most rapid technique is TXRF which, however, shows poorer detection limits because of its microanalytical character.

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