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SLRS-5 Elemental Concentrations of Thirty-Three Uncertified Elements Deduced from SLRS-5/SLRS-4 Ratios

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The fifth version of natural river water certified reference material, SLRS-5 (National Research Council – Conseil National de Recherches Canada), is commonly used to control the quality of major and trace element measurements. Concentrations of silicon and thirty-one uncertified trace elements have been reported for the certified reference material SLRS-4, but they are not yet available for SLRS-5. Here, SLRS-5/SLRS-4 ratios were deduced from SLRS-5 and SLRS-4 measurements by inductively coupled plasma-atomic emission spectrometry and high-resolution inductively coupled plasma-mass spectrometry for certified elements and thirty-five uncertified elements (rare earth elements, B, Bi, Br, Cs, Ga, Ge, Hf, Li, Nb, P, Pd, Rb, Rh, S, Sc, Si, Sn, Th, Ti, Tl, Y). Both reference materials were measured directly one after the other, so that calculated elemental ratios would not be notably influenced either by calibration uncertainties or by eventual long-term instrumental drift. The computed ratios are in good agreement with those deduced from the certified values. We also report concentrations for thirty-three uncertified elements in SLRS-5 by combining the measured SLRS-5/SLRS-4 ratios and the published SLRS-4 values. The resulting new data set provides target SLRS-5 values, which will be useful in quality control procedures.

Keywords: river water reference material, SLRS-5/SLRS-4 ratios, SLRS-5 concentrations, compilation, trace elements.

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Le materiel de référence d'eau de rivière SLRS-5 (NRC-CNRC) est couramment utilisé pour contrôler la qualité des mesures d'éléments majeurs et d'éléments traces. Les concentrations de silicium et de trente-et-un éléments traces non certifiés ont été publiés pour le matériel de référence SLRS-4, mais pas encore pour le SLRS-5. Dans cette étude, des rapports SLRS-5/SLRS-4 ont été calculés à partir de mesures de SLRS-5 et de SLRS-4, effectuées par ICP-AES et HR-ICP-MS pour les éléments certifiés et pour trente-cinq éléments non certifiés (terres rares, B, Bi, Br, Cs, Ga, Ge, Hf, Li, Nb, P, Pd, Rb, Rh, S, Sc, Si, Sn, Th, Ti, Tl, Y). Les deux materiaux de référence ont été mesurés immédiatement l'un après l'autre, de sorte que les rapports élémentaires calculés ne soient pas influencés de façon notable par les incertitudes d'étalonnage ou par une éventuelle dérive instrumentale sur le long terme. Ces rapports s'avèrent être en adéquation avec ceux déduits des valeurs certifiées. Nous proposons également les concentrations de trente-trois éléments non certifiés pour le SLRS-5, calculées en combinant les rapports SLRS-5/SLRS-4 et les concentrations de SLRS-4 publiées. Ces données permettent de fournir des valeurs cibles pour le SLRS-5, qui pourront être utiles lors de procédures de contrôle de qualité.

Mots-clés : Matériel de référence d'eau de rivière, rapports SLRS-5/SLRS-4, concentrations du SLRS-5, compilation, éléments traces.

Natural river water certified reference material (CRM) SLRS-4 (Saint-Laurent River Surface) was formerly distributed by the National Research Council – Conseil National de Recherches Canada (NRC-CNRC). It was routinely used by geochemists to control the accuracy of major and trace element analyses in water samples, for example, in river water

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(Katarina *et al.* 2009), seawater (Lawrence *et al.* 2006, Bayon *et al.* 2010), snow (Soyol-Erdene *et al.* 2011) or ice samples (Krachler *et al.* 2005). Because of its large distribution in the past, the SLRS-4 composition was widely measured for certified elements and also often for uncertified elements. Inter-comparison results for uncertified elements provided by six laboratories have been compiled in Yeghicheyan *et al.* (2001). SLRS-4 is no longer available, so previous studies reporting its chemical composition will become obsolete once the remaining bottles have been used up. A new CRM called SLRS-5 is now sold to replace SLRS-4, with the same set of certified elements (Al, Sb, As, Ba, Be, Cd, Cr, Co, Cu, Fe, Pb, Mn, Mo, Ni, Sr, U, V, Zn, Ca, Mg, K, Na). Providing compositional values for uncertified elements in SLRS-5, as was done previously for SLRS-4, would therefore be useful. Absolute determination of these additional concentrations, which necessarily involves several independent laboratories, would require a considerable amount of work and has not yet been performed for SLRS-5. Assuming that the data reported in Yeghicheyan *et al.* (2001), and supplemented by Rodushkin *et al.* (2005) and Lawrence *et al.* (2006), are accurate, an alternative method consists in measuring both SLRS-5 and SLRS-4, calculating elemental ratios and deducing the uncertified SLRS-5 concentrations. If both reference materials are measured one after the other, the elemental ratios should not be notably influenced either by external uncertainties of calibration or by instrumental drift. Because the matrices and chemical compositions of both reference materials are quite similar, problems related to potential physical and chemical interferences should be limited by using a ratio calculation process. We therefore present calculated SLRS-5/SLRS-4 ratios for an extended set of elements measured using inductively coupled plasma-atomic emission spectrometry (ICP-AES) and/or high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS). SLRS-5 deduced concentrations can be used for future studies as guidelines values, as was previously the case for SLRS-4.

Materials and methods

Cleaning procedure

All solutions were transferred into polypropylene vials which had been thoroughly washed using the following protocol: (a) washing with common dish detergent in a laboratory room; (b) soaking for 24 hr in a bath of 2% Decon® (Decon Laboratories Limited, Hove, UK) detergent diluted with reverse osmosis water; (c) soaking from 24 hr to 2 weeks in 2% v/v Normapur® (Prolabo, Fontenay-sous-bois, France) analytic grade HCl (intense rinsing with reverse osmosis water was performed between each of these three-first steps); (d) rinsing with ultrapure water (Milli-Q or Elgapure systems made by Millipore, Billerica, USA and ELGA Labwater, Marlow, UK respectively) in an ISO 5 clean room; (e) soaking from 1 week to 3 months in a 5% v/v Merck™ Suprapur® HCl (Merck KGaA, Darmstadt, Germany); (f) rinsing six times with ultrapure water under an ISO 1 laminar flow hood; (g) drying.

Instrumentation and settings

Elemental concentrations in SLRS-4 and SLRS-5 were determined using a ThermoFisher Scientific Element 2 (Thermofisher Scientific, Bremen, Germany) HR-ICP-MS and/or a Spectro *ARCOS* ICP-AES, both installed in a clean room (ISO 5), equipped with autosamplers placed under laminar flow hoods (ISO 1). The temperature of the clean room was regulated at 20.0 ± 0.5 °C. For the HR-ICP-MS, solutions were introduced into the plasma (a) via a concentric nebuliser (600 µl min^{-1}) and a Scott spray chamber cooled with a Peltier effect at 4 °C or (b) via an APEX HF desolvation system using a PFA ST micro-nebuliser with self-aspiration allowing oxide formation to be divided by approximately a factor of two (Table 1). For the APEX (used for measurements of the rare earth elements, REE), the nebulised solutions were transferred through a 150 °C heated cyclonic PFA spray chamber and then into a 2 °C Peltier-cooled PFA condenser. Both sampler and skimmer cones were made from nickel. ICP-AES analyses were performed using either (a) a cross-flow pneumatic nebuliser mounted in combination with a Scott spray chamber or (b) a CETAC AT ultrasonic nebuliser (USN) followed by a furnace/cooler desolvation system. The USN allowed the signal intensity to be increased by a factor of 10. Detection limits (DLs) are at least six times better than when using a pneumatic nebuliser (Desboeufs *et al.* 2003, Asfaw and Beauchemin 2010). The USN evaporation and condensation temperatures were set at 120 and 10 °C, respectively. The HR-ICP-MS and ICP-AES operating parameters were optimised daily to obtain signals that were as sensitive and stable as possible (Table 1).

The elements were determined (a) using ICP-AES only, for the most concentrated (Na, Ca, Mg, S, Si and K), (b)

Table 1.
Instrument operating conditions

	HR-ICP-MS Scott/APEX	ICP-AES
RF power (W)	1250	1350–1400
Plasma argon flow (l min^{-1})	16	12
Auxiliary argon flow (l min^{-1})	0.9/1.1	1
Nebuliser argon flow 2(l min^{-1})	0.945/1.050	0.80–0.90
Sample flow (ml min^{-1})	0.6/free (~ 0.3)	0.5–2.0
Number of replicates	3	3–4

using HR-ICP-MS equipped with one of its introduction systems (Table 1) for the elements with concentrations under the analytical DLs of ICP-AES or (c) using both methods (Table 2). Except for the REE, isotope and resolution settings for the HR-ICP-MS were those recommended by the supplier (Table 2). Diverse types of interferences, including isobaric, oxide, hydroxide, hydride, nitride and Ar-related interferences, were systematically envisaged. Their influence was maintained at a negligible level by running the mass spectrometer in 'medium-' or 'high'-resolution mode (resolution $\approx$ 4000 and 10000 respectively) when needed, as there was neither isobaric interference nor oxide formation for the m/z at which the targeted elements were measured. In particular, REE were determined using high-resolution mode where oxide interferences were well separated. Wavelength values for ICP-AES measurements were selected according to the signal-to-noise ratios and potential interferences (Table 2). They also mostly corresponded to those recommended by the supplier.

Measurements

External calibration was performed for the elements shown in Table 2, except for Br, Cs, Ga, Ge, Pd and Rh, which were measured by HR-ICP-MS only but not calibrated. For the latter, only the SLRS-5/SLRS-4 ratios in terms of ion fluxes were computed and discussed later. For the other elements, five concentrated multi-elemental stock solutions were diluted from 0.5 to 5 μg l^{-1} with 1% v/v high-purity nitric acid (Ultrapure® from Merck™, Darmstadt, Germany) in ultrapure water and used to calibrate the HR-ICP-MS. ICP-AES was calibrated using a 2–100 μg l^{-1} range. Correlation coefficient (R^2) values of the calibration regressions appeared to be always better than 0.99. Numerous analytical blanks were prepared with 10 ml of 1% v/v Romil UpA™ HNO_3 (Romil, Cambridge, UK) diluted with ultrapure water. Between three and seven blanks were inserted in each analytical set to assess the instrumental DLs, calculated in the usual manner: DLs = $t_{(\alpha=0.01,\nu=n-1)}.s$ (Table 2), with a one-sided t-value, and s corresponding to the standard deviation of the blanks. Ion fluxes of the blanks always appeared to be negligible with regard to those produced by SLRSs, so that blank corrections were not required. SLRS-4 and SLRS-5 solutions, already acidified by the supplier, were analysed using both ICPs (and both introduction systems for ICP-AES and HR-ICP-MS) over almost 1 year by different operators. All SLRS-5 and SLRS-4 measurements were run consecutively, regardless of the instrument used.

Statistical procedure

Tests, including Shapiro–Wilk normality tests and comparisons of means by t-tests, as well as 95% confidence intervals of the means, were computed using free R software (http://www.r-project.org/, R Development Core Team 2011), and the implemented 'stats' package. As several elements were determined, numerous statistical tests had to be performed. To maintain an overall type-1 error at 5%, a sequential Bonferroni correction (Holm 1979) was operated manually at the end of the whole process to adjust the threshold for significance of the p-values.

Results and discussion

Detection limits

These were calculated for HR-ICP-MS and ICP-AES (Table 2). They appeared to be widely below the SLRS-4 and SLRS-5 certified values (Tables 3–4) and the concentrations proposed by Yeghicheyan *et al.* (2001) and Rodushkin *et al.* (2005) (Table 5), demonstrating the efficiency of our washing procedure, as well as the sensitivity and the stability of the instruments. The lowest DLs were, as expected, attained by HR-ICP-MS, followed by ICP-AES coupled with USN, and finally ICP-AES mounted with the pneumatic nebuliser (Table 2). The only notable exception to this trend concerned Zn, where the DL for ICP-AES equipped with USN was better than that obtained using HR-ICP-MS. Certified concentrations of Zn, Cr and Ni were just three times greater than their respective DLs measured by ICP-AES coupled with pneumatic (for Zn) and USN (for Cr and Ni); these results were therefore disregarded in the discussion that follows.

Accuracy and reproducibility of measurements

As no instrumental drift correction was applied except for REE (where Ba was used as an internal standard because of the duration of runs), the accuracy of concentrations expressed from initial calibrations was probably not optimum. Recovery percentages of individual measurements with respect to SLRS-4 and SLRS-5 certified values or concentrations of SLRS-4 reported by Yeghicheyan *et al.* (2001) and Rodushkin *et al.* (2005) usually varied between 70% and 130%, except for As, Cd, Co, K, Mo, Pb, Sb, Tl and Zn (Tables 3–5). Reproducibility was computed from all the SLRS-4 and SLRS-5 measurements and expressed in terms of relative standard deviations (% RSD). Except for some elements (As, Cd, Co, K, Pb, Sn, Zn), % RSDs were $<$ 10% for both ICP-AES and HR-ICP-MS (Tables 3–5). It is known that K, along with heavier alkaline elements, cannot be measured accurately using ICP-AES. Random contaminations cannot be excluded for As, Cd, Co, Pb, Sn and Zn present at trace levels.

Table 2.
Acquisition settings and detection limits for all the measured elements

Element	m/z	Res.	DL MS (ng l^{-1})	λ (nm)	DL AES (ng l^{-1}) pneu/USN	Element	m/z	Res.	DL MS (ng l^{-1})	λ (nm)	DL AES (ng l^{-1}) pneu/USN
Al	27	m	60	167.1	800/200	Mo	95	l	3.6		
As	75	h	0.8			Na				330.2	7000/10000
B	11	l	15			Nb	93	l	0.04		
Ba	137	l	10	455.4	200/30	Nd	146	h	0.09^a		
Bi	209	l	0.05			Ni	60	m	2.7	231.6	NM/80
Br	79	h	NM			P	31	m	50	177.5	1000/300
Ca				317.9	30000/600	Pb	208	l	0.1		
Cd	111	l	0.7			Pd	105	l	NM		
Cs	133	l	NM			Pr	141	h	0.03^a		
Ce	140	h	0.3^a			Rb	85	l	0.6		
Co	59	m	0.3			Rh	103	l	NM		
Cr	52	m	0.3	267.7	NM/60	S				180.7	4000/1000
Cu	63	m	0.9			Sb	121	l	0.2		
Dy	163	h	0.02^a			Sc	45	m	0.3		
Eu	153	h	0.2^a			Si				251.6	5000/17000
Er	166	h	0.05^a			Sm	147	h	0.04^a		
Fe	56	m	2	259.9	500/200	Sn	118	l	0.3		
Ga	69	m	NM			Sr	88	l	2.7	407.8	40/20
Gd	157	h	0.2^a			Tb	159	h	0.02^a		
Ge	72	h	NM			Th	232	l	0.4		
Hf	178	l	0.1			Ti	47	m	18	336.1	300/40
Ho	165	h	0.01^a			Tl	205	l	0.01		
K				766.5	2000/200	Tm	169	h	0.01^a		
La	139	h	0.07^a			U	238	l	0.02		
Li	7	l	4.5	670.8	500/10	V	51	m	0.1	311.1	NM/90
Lu	175	h	0.01^a			Y	89	l	0.2		
Mg				285.2	2000/100	Yb	172	h	0.05^a		
Mn	55	m	3.2	257.6	100/10	Zn	66	m	90	206.2	300/50

m/z, mass of the isotope considered; Res., resolution; h, high resolution (~ 10000); m, medium resolution (≈ 4000); l, low resolution (≈ 300); DL MS, detection limits for HR-ICP-MS, in ng l^{-1}; λ, wavelength in nm; DL AES, detection limits for ICP-AES using a pneumatic nebuliser (pneu.) or an ultrasonic nebuliser (USN), in ng l^{-1}; NM, DL not measured.

[a] APEX as sample introduction system.

Table 3.
SLRS-4 certified concentrations, measured values expressed as recovery rate (mean, between brackets: minimum and maximum) and reproducibility expressed as % RSD

Element	Certified concentrations (µg l^{-1})	*n* by HR-ICP-MS	HR-ICP-MS (%)	% RSD	*n* by ICP-AES	ICP-AES (%)	% RSD
Al	54 ± 4	5	98 [87; 102]	2.4	26	108 [97; 119]	6.9
As	0.68 ± 0.06	25	123 [101; 145]	12			
Ba	12.2 ± 0.6	25	110 [101; 124]	6.2	25	108 [95; 120]	6.8
Cd	0.012 ± 0.002	25	132 [113; 164]	11			
Co	0.033 ± 0.006	25	126 [107; 154]	14			
Cr	0.33 ± 0.02	25	99 [95; 107]	3.7			
Cu	1.81 ± 0.08	25	109 [101; 120]	5.6			
Fe	103 ± 5	5	101 [100; 103]	1.1	25	98 [87; 106]	6.5
Mn	3.37 ± 0.18	25	107 [100; 118]	4.4	26	101 [81; 120]	11
Mo	0.21 ± 0.02	25	114 [102; 138]	9.1			
Ni	0.67 ± 0.08	25	116 [110; 128]	3.9			
Pb	0.086 ± 0.007	25	88 [65; 118]	24			
Sb	0.23 ± 0.04	25	138 [122; 150]	6.5			
Sr	26.3 ± 3.2	5	110 [109; 112]	1.4	24	111 [92; 129]	9.5
U	0.050 ± 0.003	25	92 [83; 99]	5.7			
V	0.32 ± 0.03	25	108 [89; 123]	12			
Zn	0.93 ± 0.10	25	117 [104; 140]	21	15	114 [88; 154]	26
Ca	6200 ± 200				25	91 [80; 99]	6.9
Mg	1600 ± 100				25	101 [89; 114]	8.9
K	680 ± 20				26	117 [98; 144]	19
Na	2400 ± 200				12	90 [78; 109]	9.8

n, number of measurements. Uncertainties of certified concentrations given at 2*s*.

Table 4.
SLRS-5 certified concentrations, measured values expressed as recovery rate (mean, between brackets: minimum and maximum) and reproducibility expressed as % RSD

Element	Certified concentrations (µg l^{-1})	*n* by HR-ICP-MS	HR-ICP-MS (%)	% RSD	*n* by ICP-AES	ICP-AES (%)	% RSD
Al	49.5 ± 5.0	5	94 [92; 96]	1.8	26	107 [94; 141]	7.2
As	0.413 ± 0.039	25	112 [93; 132]	11			
Ba	14.0 ± 0.5	25	106 [97; 117]	6.0	25	110 [96; 139]	5.9
Cd	0.0060 ± 0.0014	25	160 [123; 197]	13			
Co	0.05[a]	25	118 [103; 138]	10			
Cr	0.208 ± 0.023	25	112 [103; 120]	3.8			
Cu	17.4 ± 1.3	25	107 [99; 118]	4.8			
Fe	91.2 ± 5.8	5	101 [100; 103]	0.9	25	103 [91; 118]	6.7
Mn	4.33 ± 0.18	25	102 [95; 112]	3.8	26	99 [81; 123]	10
Mo	0.27 ± 0.04	25	90 [79; 105]	8.0			
Ni	0.476 ± 0.064	25	112 [101; 123]	5.9			
Pb	0.081 ± 0.006	25	89 [65; 119]	24			
Sb	0.3[a]	25	123 [112; 131]	5.0			
Sr	53.6 ± 1.3	5	102 [101; 103]	0.8	24	105 [87; 129]	9.1
U	0.093 ± 0.006	25	97 [92; 102]	2.9			
V	0.317 ± 0.033	25	108 [89; 123]	12			
Zn	0.845 ± 0.095	25	131 [93; 170]	20	15	114 [89; 158]	20
Ca	10500 ± 400				25	85 [80; 106]	5.9
Mg	2540 ± 160				25	104 [92; 122]	9.0
K	839 ± 36				26	138 [103; 195]	22
Na	5380 ± 100				12	96 [84; 117]	11

n, number of measurements. Uncertainties of certified concentrations given at 2.

[a] Information values provided without associated uncertainties by the NRC-CNRC.

Table 5.
SLRS-4 published concentrations; our measured values expressed as recovery rate (mean, between brackets: minimum and maximum) and reproducibility expressed as % RSD

	n	Published concentrations	Recovery percentage	% RSD
REE (ng l^{-1})				
La	3	287 ± 16	101 [92;110]	0.4
Ce	3	360 ± 24	101 [92;111]	1.3
Pr	3	69.3 ± 3.6	97 [88;106]	1.2
Nd	3	269 ± 28	97 [89;106]	2.0
Sm	3	57.4 ± 5.6	97 [90;107]	2.2
Eu	3	8.0 ± 1.2	96 [87;107]	2.3
Gd	3	34.2 ± 4.0	97 [90;108]	2.8
Tb	3	4.3 ± 0.8	93 [84;100]	2.5
Dy	3	24.2 ± 3.2	91 [83;98]	0.8
Ho	3	4.7 ± 0.3	92 [83;99]	2.3
Er	3	13.4 ± 1.2	88 [82;97]	2.5
Tm	3	1.7 ± 0.4	100 [93;108]	2.4
Yb	3	12.0 ± 0.8	92 [84;101]	3.2
Lu	3	1.9 ± 0.2	93 [86;101]	2.3
Other elements (µg l^{-1})				
B	15	5.95 ± 0.44	89 [85;94]	4.0
Bi	15	0.0022 ± 0.0004[a]	98 [87;111]	8.5
Hf	15	0.0033 ± 0.0012[a]	81 [64;96]	10.0
Li	31	0.54 ± 0.14	129 [121;137]	4.3
Nb	10	0.0041 ± 0.0006[a]	90 [84;98]	4.8
P	40	9.13 ± 1.56	71 [69;74]	2.0
Rb	15	1.53 ± 0.10	104 [99;110]	2.5
Sc	15	0.012 ± 0.002[a]	92 [85;103]	5.5
Si	6	1864 ± 96	107 [106;109]	1.2
Sn	15	0.0080 ± 0.0002[a]	91 [79;106]	11.2
Th	15	0.018 ± 0.006	102 [92;111]	3.8
Ti	39	1.46 ± 0.02	90 [86;95]	2.6
Tl	10	0.0076 ± 0.0012	66 [65;67]	1.2
Y	10	0.15 ± 0.02	87 [83;90]	2.4

n, number of measurements. Uncertainties of published concentrations given at 2*s*.
All concentrations used as reference values come from Yeghicheyan *et al.* (2001), except [a] from Rodushkin *et al.* (2005).

SLRS-5/SLRS-4 concentration ratios for certified elements

A ratio calculation was performed for each couple of measured SLRS-5 and SLRS-4 values. Distributions of As, Cd, Co, Cr, Cu, K, Mn, Mo, Ni, Pb, Sb, Sr, U, Zn, Ca, Mg and Na ratios obtained using HR-ICP-MS and ICP-AES did not appear to differ significantly from a normal distribution. When results from both ICPs were available for those elements, and when their means did not significantly differ, results were pooled. Averaged and 95% confidence intervals (CIs) were calculated (Table 6). The distribution of V concentrations, only available in HR-ICP-MS, differed significantly from normality, so that the 95% CI was calculated by bootstrapping (Efron 1979, Marques de Sá 2007). Aluminium, Fe and Ba ratios exhibited near normal distributions for both HR-ICP-MS and ICP-AES but, although only slight, the difference between their means was significant (Al: 0.877 ± 0.007 vs. 0.903 ± 0.011, Fe: 0.888 ± 0.010 vs. 0.914 ± 0.009, and Ba: 1.11 ± 0.01 vs. 1.16 ± 0.01, for HR-ICP-MS and ICP-AES, respectively – 95% confidence level of the mean, Table 6). There is no obvious reason, such as the presence of specific interferences, to favour one method over the other. As a consequence, both estimates were retained (Table 6).

Most of the measured elemental ratios were in perfect agreement with those computed from both certificates. The only exceptions to this trend concerned K ratios for which significant differences between certified and measured ratios were observed: 1.23 ± 0.06 vs. 1.40 ± 0.02 (not in Table 6).

Except Cd, for which the % RSD value of the measured SLRS-5/SLRS-4 ratio was greater than 10%, the % RSDs of the other elemental ratios were around 3–4%

Table 6.
SLRS-5/SLRS-4 elemental concentration ratios

Element	Certified concentrations ratios	Measured ratios	Associated % RSD
Al	0.92 ± 0.11	0.903 ± 0.011/0.877 ± 0.007[b]	3.1
As	0.61 ± 0.08	0.55 ± 0.01	3.1
Ba	1.15 ± 0.07	1.16 ± 0.01/1.11 ± 0.01[b]	3.1
Cd	0.50 ± 0.14	0.62 ± 0.04	14.3
Cr	0.63 ± 0.08	0.72 ± 0.01	2.2
Co	1.52 ± 0.28[a]	1.42 ± 0.03	4.6
Cu	9.61 ± 0.83	9.51 ± 0.06	1.6
Fe	0.89 ± 0.07	0.888 ± 0.010/0.914 ± 0.009[b]	2.4
Mn	1.28 ± 0.09	1.24 ± 0.01	3.3
Mo	1.29 ± 0.27	1.02 ± 0.01	3.4
Ni	0.71 ± 0.13	0.69 ± 0.02	6.0
Pb	0.94 ± 0.10	0.95 ± 0.01	2.1
Sb	1.30 ± 0.23[a]	1.17 ± 0.01	2.5
Sr	2.04 ± 0.25	1.91 ± 0.02	2.9
U	1.86 ± 0.17	1.97 ± 0.05	6.0
V	0.99 ± 0.14	0.96 ± 0.02	4.3
Zn	0.91 ± 0.14	0.85 ± 0.02	7.6
Ca	1.69 ± 0.08	1.75 ± 0.03	3.6
Mg	1.59 ± 0.14	1.59 ± 0.02	3.1
Na	2.24 ± 0.19	2.38 ± 0.06	3.8

For certified elements, combined uncertainties of the ratios are given at 2*s* considering both individual errors, except (a) for which only SLRS-4 uncertainties are provided. Uncertainties of the means for measured ratios are given at 95% confidence level. [b] Ratios calculated from HR-ICP-MS/ICP-AES measurements.

(Table 6) – in other words much better than the % RSDs calculated on the basis of the individual measurements. This demonstrates the efficiency of the ratio calculation process in reducing the influence of instrumental drift or problems related to interferences for both instruments; both standard measurements are likely to be affected in the same way. Interestingly, the 95% CIs of the mean ratios reported here were between 2 and 20 times lower than those issued from the error propagation of the certified and published values for both SLRS CRMs.

SLRS-5/SLRS-4 ratio and SLRS-5 concentrations for uncertified elements

Table 7 reports SLRS-5/SLRS-4 ratios for the REE, and other uncertified elements. None of the measured ratios for uncertified elements differed from a normal distribution. 95% CIs were therefore calculated as for certified elements. SLRS-5/SLRS-4 ratios of REE evolved in a narrower range (from 0.66 to 0.80, except for Sm: 0.56) than the other uncertified elements (from 0.39 to 2.06), probably because the REE reflect the geological nature of the weathered watershed, which is obviously not supposed to vary over such a short time scale. Values of % RSDs for SLRS-5/SLRS-4 ratios for uncertified elements were < 17% and even less than 5% for most of them, most notably the REE. Deduced SLRS-5 concentrations were computed by multiplying the measured ratios by the SLRS-4 concentrations proposed by Yeghicheyan *et al.* (2001), Rodushkin *et al.* (2005) or Lawrence *et al.* (2006). Because uncertified SRLS-5 values have not yet been published, it was impossible to check formally the accuracy of our deduced concentrations.

Conclusions

By measuring SLRS-5/SLRS-4 ratios and combining the values for SLRS-4 proposed by Yeghicheyan *et al.* (2001), Rodushkin *et al.* (2005) and Lawrence *et al.* (2006), we were able to calculate SLRS-5 concentrations for thirty-three uncertified elements. Our ratio measurements for certified elements corresponded closely to the actual certified value ratios. This demonstrates that the ratio calculation process from successive measurements compensated sufficiently for any eventual trouble relating to calibration and also reduced interference impacts. SLRS-5 concentrations deduced for uncertified elements, including REE, can therefore be used as initial guidelines for accuracy control in any future water analyses. A compilation of SLRS-5 concentrations based on a proper multiple-laboratory inter-calibration, similar to the one performed by Yeghicheyan *et al.* (2001), would nonetheless be very welcome.

Table 7.
SLRS-5/SLRS-4 elemental concentration ratios for uncertified elements and deducted SLRS-5 concentrations

Element	*n*	Measured ratios	Associated % RSD	Deducted SLRS-5 concentration
REE[a]		REE[a]		(ng l^{-1})
La	6	0.682 ± 0.003	0.4	196 ± 11[b]
Ce	6	0.655 ± 0.009	1.3	236 ± 16[b]
Pr	6	0.677 ± 0.009	1.2	46.9 ± 2.5[b]
Nd	6	0.687 ± 0.016	2.0	185 ± 20[b]
Sm	6	0.564 ± 0.015	2.2	32.4 ± 3.3[b]
Eu	6	0.694 ± 0.018	2.3	5.6 ± 1.4[c]
Gd	6	0.727 ± 0.024	2.8	24.9 ± 3.0[b]
Tb	6	0.748 ± 0.021	2.5	3.2 ± 0.6[b]
Dy	6	0.754 ± 0.007	0.8	18.2 ± 2.5[b]
Ho	6	0.766 ± 0.020	2.3	3.6 ± 0.5[b]
Er	6	0.784 ± 0.023	2.5	10.5 ± 1.0[b]
Tm	6	0.782 ± 0.022	2.4	1.3 ± 0.3[b]
Yb	6	0.774 ± 0.028	3.2	9.3 ± 0.7[b]
Lu	6	0.795 ± 0.021	2.3	1.5 ± 0.2[b]
Other elements				(µg l^{-1})
B	15	1.25 ± 0.03	4.2	7.46 ± 0.58[b]
Bi	15	0.39 ± 0.02	7.6	0.00086 ± 0.00016[d]
Br	10	0.39 ± 0.02	6.3	18.8 ± 1.8[b]
Cs	10	0.63 ± 0.02	3.3	0.0057 ± 0.0013[b]
Ga	10	1.24 ± 0.07	7.7	0.015 ± 0.001[b]
Ge	9	0.63 ± 0.02	5.1	0.0063 ± 0.0038[b]
Hf	15	0.87 ± 0.07	14.1	0.0029 ± 0.0011[d]
Li	31	0.93 ± 0.02	5.9	0.50 ± 0.13[b]
Nb	15	0.93 ± 0.03	4.0	0.0038 ± 0.0006[d]
P	40	1.43 ± 0.02	5.3	13.1 ± 2.2[b]
Pd	10	1.41 ± 0.04	3.5	0.003 ± 0.002[b]
Rb	15	0.80 ± 0.01	1.7	1.23 ± 0.08[b]
Rh	10	2.06 ± 0.12	8.2	[e]
S	24	1.00 ± 0.01	1.8	[e]
Sc	15	0.72 ± 0.02	6.0	0.0087 ± 0.0015[d]
Si	23	1.01 ± 0.01	2.4	1881 ± 99[b]
Sn	15	0.71 ± 0.06	16.4	0.0057 ± 0.0005[d]
Th	15	0.59 ± 0.02	4.7	0.011 ± 0.004[b]
Ti	39	1.56 ± 0.03	5.2	2.28 ± 0.05[b]
Tl	10	0.55 ± 0.02	4.0	0.0042 ± 0.0007[b]
Y	10	0.79 ± 0.01	1.4	0.12 ± 0.01[b]

n number of measurements. [a] Because of the duration of REE measurements using high-resolution mode (about 90 min per sample), the instrumental drift was checked (and corrected) using a Ba internal standard. [b] SLRS-4 values used from Yeghicheyan *et al.* (2001). [c] SLRS-4 values used from Lawrence *et al.* (2006). [d] SLRS-4 values used from Rodushkin *et al.* (2005). [e] No value available in the literature. All uncertainties are given at 95% confidence level.

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