

A Compilation of Silicon and Thirty One Trace Elements Measured in the Natural River Water Reference Material SLRS-4 (NRC-CNRC)

Delphine **Yeghicheyan** (1), Jean **Carignan** (1), Michel **Valladon** (2), Martine **Bouhnik Le Coz** (3), Florence **Le Cornec** (4), Maryse **Castrec-Rouelle** (5), Michel **Robert** (6), Luc **Aquilina** (3), Emmanuel **Aubry** (5), Carine **Churlaud** (6), Aline **Dia** (3), Samuel **Deberdt** (2), Bernard **Dupré** (2), Rémi **Freydier** (2), Gérard **Gruau** (3), Odile **Hénin** (3), Anne-Marie **de Kersabiec** (5), Joël **Macé** (3), Luc **Marin** (1), Nicole **Morin** (3), Patrice **Petitjean** (3) and Elodie **Serrat** (3)

(1) Service d'Analyse des Roches et des Minéraux (SARM), CNRS-CRPG, 15 rue Notre Dame des Pauvres, BP 20, 54501 Vandoeuvre-lès-Nancy, France. e-mail: yeghi@crpg.cnrs-nancy.fr

(2) Laboratoire de Géochimie, 38 rue des Trente-Six-Ponts, 31400 Toulouse Cedex, France

(3) Géosciences Rennes, bd du Général Leclerc, 35045 Rennes Cedex, France

(4) IRD, Laboratoire des Formations Superficielles, 32 avenue Henri Varagnat, 93143 Bondy Cedex, France

(5) Laboratoire de Géochimie et Métallogénie, Université Pierre et Marie Curie, casier 124, Tour 26/16, 4 Place Jussieu, 75252 Paris Cedex 05, France

(6) Centre Commun d'Analyses, Université de La Rochelle, 5 Perspective de l'Océan, 17000 La Rochelle, France

The natural river water certified reference material SLRS-4 (NRC-CNRC, National Research Council-Conseil National de Recherches Canada) has been routinely analysed for major and trace elements by six French laboratories. Most measurements were made using inductively coupled plasma-mass spectrometry. For silicon and thirty one trace elements (rare earth elements, Ag, B, Br, Cs, Ga, Ge, Li, P, Pd, Rb, Se, Th, Ti, Tl, W, Y and Zr), no certified values are assigned by NRC-CNRC. We propose some compilation values and related uncertainties according to the results obtained by the different laboratories.

Keywords: river water reference material, ICP-MS, silicon, rare earth elements, trace elements, compilation, SLRS-4.

Le standard d'eau de rivière SLRS-4 (NRC-CNRC, National Research Council-Conseil National de Recherches Canada) est analysé régulièrement comme contrôle qualité par six laboratoires français étudiant les éléments majeurs et en traces dans les solutions naturelles. La plupart des mesures sont réalisées par ICP-MS (Inductively Coupled Plasma-Mass Spectrometry). Le silicium et 31 éléments en traces (terres rares, Ag, B, Br, Cs, Ga, Ge, Li, P, Pd, Rb, Se, Th, Ti, Tl, W, Y and Zr) ne sont pas certifiés par NRC-CNRC. Nous proposons des valeurs de compilation pour ces éléments ainsi que les incertitudes associées d'après les concentrations moyennes obtenues par chaque laboratoire.

Mots-clés : standard d'eau de rivière, ICP-MS, silicium, terres rares, éléments en traces, compilation, SLRS-4.

The natural river water certified reference material SLRS-4 (prepared by the National Research Council-Conseil National de Recherches Canada) is widely used to control routine analysis by geochemists and hydrogeologists. However, some trace elements, useful to trace sources and geochemical processes, have not been assigned certified values. The six participating French laboratories (The Service d'Analyse des Roches et des Minéraux of Nancy, the Geosciences Laboratory

of Rennes, the Laboratoire de Géochimie of Toulouse, the Laboratoire de Géochimie et Métallogénie of the UPMC Paris, the Laboratoire des Formations Superficielles of IRD Bondy and the Centre Commun d'Analyses of La Rochelle) routinely analysed SLRS-4 by ICP-MS, ICP-AES and AAS as a control for the analysis of major and trace elements in water samples. In addition to the elements certified by NRC-CNRC and according to the aim of laboratories, uncertified elements were

Table 1.
Instrumentation and procedures of the participating laboratories

Laboratory	Instrument	Methods and introduction systems	Blank	Acid medium	Calibration	Interference corrections
Nancy	ICP-MS, Perkin Elmer ELAN 6000	direct (all elements except REE) Meinhard nebulizer and Scott spray chamber	distilled water	HNO ₃ purified by sub-boiling distillation 5% v/v	multi elemental mono elemental for B 10 µg l ⁻¹ 0.5 µg l ⁻¹ for REEs	Cd and Tb with CeO and NdO
	Spectrophotometry, Beckman DU 62	direct (Si)	De-ionised water purified with a UHQ (Elga) system	-	0, 0.25, 0.62, 1.25 mg l ⁻¹ (5 ml of sample in 10 ml)	-
Toulouse	ICP-MS, Perkin Elmer ELAN 6000	direct (all elements) Cross-flow nebulizer and Scott spray chamber	De-ionised water purified with a MilliQ (Millipore) system	HNO ₃ doubly purified by sub-boiling distillation 2% v/v and reacidification at 2% v/v of the SIRS-4 water	multi elemental with internal standards In, Re 10, 50 µg l ⁻¹ (In = Re = 10 µg l ⁻¹)	Aries <i>et al.</i> (2000)
	ICP-MS, Hewlett Packard 4500	direct (all elements) Cross-flow nebulizer and cooled Scott spray chamber (cooled by Peltier effect 2 °C)	De-ionised water purified with a MilliQ (Millipore) system internal standard In	HNO ₃ purified by sub-boiling distillation 2% v/v and reacidification at 2% v/v of the SIRS-4 water	multi elemental with internal standard In	Bouhnik-le Coz <i>et al.</i> (2001)
IRD Bondy	Spectrophotometry, Biotek - Uvikon XS	direct (Si)	De-ionised water purified with a MilliQ (Millipore) system	-	Si = 5, 10, 20, 30, 60 mg l ⁻¹	-
	Mass Spectrometry, Finnigan MAT 262	isotopic dilution (Rb)	-	-	Spikes 84Sr = 0.1184 µg g ⁻¹ (99.8%) 87Rb = 5.5750 µg g ⁻¹ (98%)	-
	ICP-MS, Varian UltraMass 700	direct or after off-line chromatography (all elements) V-groove nebulizer or ultrasonic nebulizer and Sturman-masters cyclonic spray chamber	De-ionised water purified with a MilliQ (Millipore) system	HNO ₃ 2% v/v	multi-elemental with or without internal standard Tm five calibration samples from 0.005 to 100 µg l ⁻¹ according to the concentration range of the element (Tm = 1 µg l ⁻¹)	51V = -3.1081*53X+0.3524*52Cr 75As = -3.1278*77X+1.0177*78Se 87Sr = -0.3856*85Rb 86Sr = -1.504*83Kr 138Ba = -0.0009008*La - 0.0003394*140Ce
UPMC Paris	ICP-AES, Jobin Yvon 238 sequential	direct (Mg, Ca, Sr, Fe, Ba, B) Meinhard nebulizer and cyclonic spray chamber with radial plasma viewing	De-ionised water purified with a MilliQ (Millipore) system	HNO ₃ 0.5% v/v	multi-elemental two or four calibration samples from 0 to 10 mg l ⁻¹ according to the concentration range of the element	-
	AAS, Hitachi Z5000 and TJA Solutions Solaar 989QZ	direct (Mn, Cu, Li, Rb)	-	-	multi-elemental	-
La Rochelle	ICP-MS, Varian UltraMass 700	direct (all elements) V-groove nebulizer and Sturman-masters cyclonic spray chamber	De-ionised water purified with a MilliQ (Millipore) system	HNO ₃ 2% v/v	multi elemental with internal standard Rh seven calibration samples from 0.01 to 10 µg l ⁻¹ according to the concentration range of the element (Rh = 0.1 or 1 µg l ⁻¹)	51V = -3.1081*53X+0.3524*52Cr 75As = -3.1278*77X+1.0177*78Se

* High temperature hydraulic High Pressure Nebulizer (Knauer®). nX Total signal on mass n.

Table 2.
Isotopes used for ICP-MS, wavelength used for ICP-AES and AAS by the participating laboratories

	Isotopes					Wavelength (nm)
	Nancy	Toulouse	Rennes	IRD Bondy	La Rochelle	UPMC Paris
Ag	-	107	-	-	-	-
Al	27	27	27	-	27	-
As	75	75	-	-	75	-
B	10, 11	11	-	-	-	249.773
Ba	138	137, 138	137	137, 138	137	455.403
Be	-	-	-	-	9	-
Br	-	35	-	-	-	-
Ca	-	43	44	-	-	422.673
Cd	114	114	111	-	111	-
Ce	140	140	140	140	-	-
Co	59	59	-	59	59	-
Cr	53	52, 53	53	52	52	-
Cu	63	63, 65	65	65	65	324.8
Cs	-	133	-	-	-	-
Dy	164	162, 163	163	163	-	-
Er	166	166, 167	166	166	-	-
Eu	153	151, 153	153	151, 153	-	-
Fe	-	57	57	-	-	238.21
Ga	-	69, 71	-	-	-	-
Gd	158	156, 157, 158	158	157	-	-
Ge	-	70, 74	-	-	-	-
Ho	165	165	165	165	-	-
In	-	115	115	-	-	-
K	-	39	39	-	-	-
La	139	139	139	139	-	-
Li	7	7	-	7	7	670.8
Lu	175	175	175	175	-	-
Mg	-	24	24	-	-	280.27
Mn	55	55	55	55	55	280.1
Mo	-	95	-	95, 98	-	-
Na	-	23	23	-	-	-
Nd	142	143, 146	146	146	-	-
Ni	-	60, 62	-	60	60	-
P	-	31	-	-	-	-
Pb	208	204, 206, 207, 208	206, 207, 208	-	-	-
Pd	-	105	-	-	-	-
Pr	141	141	141	141	-	-
Rb	85	85	85	85	85	780
Re	-	187	-	-	-	-
Rh	-	-	-	-	103	-
Sb	-	121	-	-	-	-
Se	-	77, 78	-	-	-	-
Si	-	29	29	-	-	-
Sm	152	147, 152	147	147	-	-
Sr	88	86, 88	88	86, 87	88	421.552
Tb	159	159	159	159	-	-
Th	-	232	232	-	-	-
Ti	-	47, 49	-	47	-	-
Tl	205	205	-	-	-	-
Tm	169	169	169	169	-	-
U	238	238	238	238	238	-
V	51	51	-	51	51	-
W	-	184	-	-	-	-
Y	-	89	-	-	-	-
Yb	174	172, 174	174	172	-	-
Zn	66	66, 68	66	66	-	-
Zr	-	90	-	-	-	-

Isotopes used as internal standards are shown in bold.

also measured in the reference water. Neither proficiency tests, nor interlaboratory schemes are considered in this paper. The compilation presented is based on two years of individual routine results and proposes working values for uncertified elements.

Instrumentation and statistical treatment

The equipment of each laboratory is reported in Table 1. Except for the UPMC laboratory, which used AAS and ICP-AES, all the other laboratories used quadrupole ICP-MS. The Rennes and Nancy laboratories also performed complementary analyses of Rb and Si using, respectively, isotope dilution TIMS and spectrophotometry. The instrument operating parameters were similar for all the ICP-MS but the sample introduction systems, the method of blank subtraction, the acid molarity of the analysed solutions and the method of calibration were specific to each laboratory. A desolvator (high temperature hydraulic high pressure nebulizer) was used by the Toulouse laboratory for some trace elements. This method was described in Jakubowski *et al.* (1992) and Berndt *et al.* (1996). The on-line liquid chromatography technique used by the team at Nancy is described in detail in this volume (Carignan *et al.* 2001). Oxides and doubly charged ions were less than 3% and laboratories applied different oxide and hydroxide interference corrections (Le Cornec *et al.* 1999, Aries *et al.* 2000, Bouhnik-Le Coz *et al.* 2001). Wavelengths free of spectral interferences were used by the UPMC Paris laboratory with the optical techniques. Some of these corrections are reported in Table 1.

Calibrations were performed using synthetic multi-elemental solutions except for B concentration measurements performed in Nancy, for which this laboratory used a mono-elemental B standard solution, as described in Rose *et al.* (2000). Some laboratories corrected instrumental drift by adding to samples an internal standard such as In (Rennes), In and Re (Toulouse), Tm (IRD Bondy) and Rh (La Rochelle). When no internal standard was used (Nancy and IRD Bondy), drift was controlled by measuring the standard solution every four to five samples. Blanks and acids used by laboratories are listed in Table 1: blanks were acidified with HNO₃ to reach 2 mol l⁻¹ for Nancy (Carignan *et al.* 2001) and 0.1 to 0.5 mol l⁻¹ for other laboratories. The Rennes laboratory added HNO₃ in samples to reach pH 1 (instead of pH 1.6 reported by NRC-CNRC for SLRS-4) because they observed a more stable signal

for all elements under this condition. Table 2 summarises isotopes and internal standards measured by the different teams. When several isotopes were measured, we chose the isotope with the smallest standard deviation after verifying the absence of interferences. For lead, ²⁰⁸Pb was used for the compilation.

Laboratories undertook the preliminary rejection of outliers by their own methods. Two of them (UPMC Paris, La Rochelle) eliminated values that exceeded the individual mean value by $\pm 2s$. The Dixon and Grubbs tests at the 95% confidence level (Miller and Miller 1993, Prichard *et al.* 1995, Feinberg 1996) were applied by the others. Analysis of variance (ANOVA) calculations (Neuilly and Cetama 1993) were also performed between the Nancy, Toulouse, Rennes and the IRD Bondy results in order to validate the compilation. Detailed data were not available from the other laboratories.

The aim of this paper is not to certify elemental concentrations in SLRS-4, but to document the homogeneity of results obtained from different laboratories, using different techniques, and then to propose working values for uncertified elements. The compilation data (mean and standard deviation) were calculated from the average values of each laboratory without taking into account the different number of results and the individual uncertainties (i.e. no weighting was applied). In general, an individual mean was rejected from the compilation when it exceeded the overall average by \pm twice the compiled standard deviation (95% confidence limits). The same calculations were performed for certified elements in order to assess the quality of laboratories analysis.

Results and discussion

Certified values

Table 3 reports average concentrations obtained by the different laboratories for elements having certified concentrations in SLRS-4. The compilation data represent the arithmetic mean calculated from values reported by each laboratory. Except in a few cases, most elements fall within the certified confidence limits, if we take into account the individual and the compiled uncertainties. Uncorrected/corrected polyatomic interferences (on Ca, Cr, Fe, K, Na, Zn) or possible contamination for elements like Cd and Zn might explain the outliers and some high standard deviations.

Table 3.
Average concentration values ($\mu\text{g l}^{-1}$), standard deviation and relative standard deviation of certified elements in the river water CRM SLRS-4

Element	Certified values			Nancy direct (n = 25)			Toulouse direct (n = 26)			Toulouse desolvator (n = 32)			Rennes direct (n = 84)		
	$\mu\text{g l}^{-1}$	CLs	rCLs (%)	Average	SD	% RSD	Average	SD	% RSD	Average	SD	% RSD	Average	SD	% RSD
Al	54	4	7.4	52.0	3.0	5.8	51.3	3.1	6.1	55.7	1.4	2.6	52.8	1.6	3.0
As	0.68	0.06	8.8	0.68	0.09	12.8	0.75	0.04	5.6	0.72	0.02	2.8	-	-	-
Ba	12.2	0.6	4.9	13.1	0.5	4.2	12.7	0.4	3.3	13.2	0.3	2.2	12.6	0.1	0.7
Be	0.007	0.002	28.6	-	-	-	-	-	-	-	-	-	-	-	-
Ca	6200	200	3.2	-	-	-	4267	253	5.9	-	-	-	5859	168	2.9
Cd	0.012	0.002	16.7	0.011	0.001	4.5	0.013	0.002	15.9	0.013	0.002	13.2	0.015	0.001	8.8
Co	0.033	0.006	18.2	0.046	0.007	14.3	0.053	0.017	32.8	0.035	0.001	2.3	-	-	-
Cr	0.33	0.02	6.1	0.40	0.03	6.6	0.34	0.14	41.4	0.42	0.05	12.8	0.31	0.01	4.4
Cu	1.81	0.08	4.4	2.0	0.2	9.3	1.87	0.09	4.7	2.45	0.72	29.2	1.87	0.06	3.1
Fe	103	5	4.9	-	-	-	116	8	6.8	109	3	2.4	107	6	5.3
K	680	20	2.9	-	-	-	671	89	13.3	597	18	2.9	603	15	2.4
Mg	1600	100	6.3	-	-	-	1695	91	5.4	1658	77	4.6	1593	38	2.4
Mn	3.37	0.18	5.3	3.44	0.15	4.2	3.39	0.14	4.2	3.53	0.08	2.3	3.37	0.07	2.0
Mo	0.21	0.02	9.5	-	-	-	0.24	0.07	28.4	0.18	0.02	10.1	-	-	-
Na	2400	200	8.3	-	-	-	2692	79	2.9	2580	126	4.9	2227	49	2.2
Ni	0.67	0.08	11.9	-	-	-	0.92	0.24	26.6	0.72	0.03	4.7	-	-	-
Pb	0.086	0.007	8.1	0.094	0.008	8.1	0.082	0.036	43.6	0.084	0.001	1.7	0.077	0.010	12.4
Sb	0.23	0.04	17.4	-	-	-	0.30	0.15	49.3	0.25	0.005	1.9	-	-	-
Sr	26.3	3.2	12.2	28.3	1.3	4.5	28.2	1.0	3.4	30.1	0.7	2.3	28.4	0.5	1.9
U	0.05	0.003	6.0	0.0522*	0.0003	0.6	0.046	0.003	6.7	0.045	0.002	3.4	0.050	0.002	4.6
V	0.32	0.03	9.4	0.366	0.025	6.9	0.349	0.032	9.1	0.343	0.004	1.3	-	-	-
Zn	0.93	0.1	10.8	1.09	0.10	8.7	1.42	0.41	29.0	0.93	0.03	3.4	1.20	0.08	6.6
Element	IRD Bondy (n = 14)			UPMC Paris (n = 10)			La Rochelle (n = 15)			Compilation					
	Average	SD	% RSD	Average	SD	% RSD	Average	SD	% RSD	Average	SD	% RSD			
Al	-	-	-	-	-	-	51.1	3.1	6.1	53	2	3.6			
As	-	-	-	-	-	-	0.67	0.06	8.3	0.70	0.04	5.5			
Ba	12.0	0.7	6.1	12.8	0.3	2.3	11.8	0.5	4.3	12.6	0.52	4.1			
Be	-	-	-	-	-	-	0.008	0.002	28.4	0.008	0.002	28.4			
Ca	-	-	-	5630	170	3.0	-	-	-	5252	861	16.4			
Cd	-	-	-	-	-	-	0.017	0.007	42.8	0.014	0.002	17.8			
Co	0.046	0.006	13.9	-	-	-	0.057	0.015	26.1	0.048	0.008	17.9			
Cr	0.41	0.08	19.1	-	-	-	0.32	0.05	16.9	0.37	0.05	12.5			
Cu	1.85	0.12	6.7	1.77	0.07	3.7	1.75	0.10	5.8	1.93	0.24	12.4			
Fe	-	-	-	100	2	1.5	-	-	-	108	7	6.1			
K	-	-	-	-	-	-	-	-	-	624	41	6.6			
Mg	-	-	-	1550	45	2.9	-	-	-	1624	65	4.0			
Mn	3.25	0.39	11.9	3.46	0.12	3.5	3.18	0.15	4.7	3.37	0.12	3.7			
Mo	0.20	0.02	8.9	-	-	-	-	-	-	0.21	0.03	16.2			
Na	-	-	-	-	-	-	-	-	-	2499	243	9.7			
Ni	0.97	0.19	19.1	-	-	-	0.67	0.12	18.1	0.82	0.15	18.0			
Pb	-	-	-	-	-	-	-	-	-	0.084	0.007	8.4			
Sb	-	-	-	-	-	-	-	-	-	0.27	0.04	13.5			
Sr	28.6	2.2	7.7	28.4	0.6	1.9	25.5	0.9	3.6	28.2	1.36	4.8			
U	0.055	0.006	10.5	-	-	-	0.043	0.012	27.4	0.05	0.00	10.0			
V	0.367	0.050	13.5	-	-	-	0.329	0.027	8.2	0.35	0.02	4.6			
Zn	1.59	0.29	18.3	-	-	-	-	-	-	1.24	0.26	21.0			

n number of results. SD standard deviation. % RSD relative standard deviation.
 * n = 3. - no measurement available. *Italics* outside the certified confidence limits.
 CLs 95% confidence limits. rCLs relative confidence limit.

Table 4.
Average concentration values ($\mu\text{g l}^{-1}$), standard deviation and relative standard deviation of REEs in the river water CRM SLRS-4

	Nancy on-line chromatography (n=16)			Toulouse direct (n=27)			Toulouse desolvator (n=32)		
	Average	SD	% RSD	Average	SD	% RSD	Average	SD	% RSD
La	275.6	10.3	3.7	292.1	2.6	0.9	295.5	6.5	2.2
Ce	340.5	20.1	5.9	363.0	4.9	1.4	371.5	7.2	1.9
Pr	67.4	3.0	4.4	68.6	1.9	2.8	70.8	1.4	1.9
Nd	255.1	12.8	5.0	287.8	9.4	3.3	280.4	6.1	2.2
Sm	54.3	3.2	5.9	56.5	1.4	2.6	59.2	1.4	2.4
Eu	7.9	1.2	15.4	7.4	0.3	3.5	8.7	1.0	12.0
Gd	36.2	4.5	12.6	31.6	2.1	6.6	33.0	3.5	10.6
Tb	4.4	0.7	16.7	3.8	0.3	8.5	4.3	0.1	2.2
Dy	24.3	1.2	4.8	22.3	1.0	4.7	24.3	0.7	2.9
Ho	4.8	0.7	13.7	4.2	0.4	8.9	4.7	0.1	3.1
Er	13.9	1.0	6.9	12.4	0.5	3.8	13.6	0.4	2.7
Tm	1.7	0.1	8.0	1.5	0.2	13.3	1.8	0.1	4.2
Yb	11.5	0.8	7.3	12.0	1.0	8.3	12.2	0.5	3.8
Lu	1.8	0.3	16.8	1.9	0.3	14.0	1.9	0.1	3.7
	Rennes direct (n=84)			IRD Bondy (n=15)			Compilation		
	Average	SD	% RSD	Average	SD	% RSD	Average	SD	% RSD
La	281.8	4.4	1.5	288.7	18.3	6.3	287	8	2.8
Ce	357.9	4.3	1.2	368.4	21.8	5.9	360	12	3.4
Pr	68.0	1.0	1.4	71.7	4.6	6.5	69.3	1.8	2.6
Nd	262.5	2.7	1.0	259.3	13.7	5.3	269	14	5.3
Sm	55.9	1.0	1.7	61.3	3.8	6.2	57.4	2.8	4.9
Eu	7.7	0.3	4.5	8.4	0.6	6.7	8.0	0.6	6.9
Gd	34.2	0.8	2.4	36.0	4.5	12.5	34.2	2.0	5.7
Tb	4.2	0.2	4.2	4.8	0.4	8.8	4.3	0.4	8.4
Dy	23.5	0.6	2.6	26.6	1.9	7.2	24.2	1.6	6.4
Ho	4.6	0.1	3.2	5.0	0.3	6.5	4.7	0.3	5.7
Er	13.3	0.5	3.8	13.8	0.8	5.8	13.4	0.6	4.5
Tm	1.9	0.2	8.6	-	-	-	1.7	0.2	10.4
Yb	11.8	0.4	3.5	12.4	0.7	6.0	12.0	0.4	3.2
Lu	2.0	0.2	8.3	1.9	0.2	9.0	1.9	0.1	3.1

n number of results. SD standard deviation. % RSD relative standard deviation.

Elements such as Co, Cr and Fe are known to often suffer interferences from ArO species (Date and Gray 1989, Reed *et al.* 1994, May and Wiedmeyer 1998). Interferences from sulfur and ArO species on Zn might explain the high values obtained by the participants except where the desolvation method was used. In the case of Ca, agreement between both ICP-MS and ICP-AES techniques confirmed a lower value than that obtained by NRC-CNRC with ICP-AES and FAAS and it is suggested that this value should be re-evaluated.

Individual laboratories obtained 83% of values for certified elements within the NRC-CNRC confidence

limits and 95% of compiled data fall within these limits. This demonstrates the proficiency of the participating laboratories in determining results for other elements and validates our mode of calculations for uncertified elements.

Uncertified values

Average concentrations obtained by the laboratories are reported in Tables 4 and 5.

Rare Earth Elements: Results for rare earth elements (REEs) are shown in Table 4. For all REEs, the relative

Table 5.
 Proposed mean concentration values ($\mu\text{g l}^{-1}$), number of measurements, standard deviation and relative standard deviation of uncertified elements in the river water CRM SLRS-4

	Nancy direct				Toulouse direct				Toulouse desolvator				Rennes			
	n	Average	SD	% RSD	n	Average	SD	% RSD	n	Average	SD	% RSD	n	Average	SD	% RSD
Ag	-	-	-	-	14	0.035	0.005	14	-	-	-	-	-	-	-	-
B	4	6.05	0.09	1	6	6.11	0.22	4	-	-	-	-	-	-	-	-
Br	-	-	-	-	6	48	2	5	-	-	-	-	-	-	-	-
Cs	-	-	-	-	28	0.008	0.002	23	16	0.009	0.002	23	-	-	-	-
Ga	-	-	-	-	29	0.012	0.002	19	16	0.012	0.001	9	-	-	-	-
Ge	-	-	-	-	28	0.012	0.004	33	16	0.008	0.002	26	-	-	-	-
Li	11	0.444	0.013	3	31	0.515	0.117	23	6	0.615	0.027	4	-	-	-	-
P	-	-	-	-	-	-	-	-	32	9.13	0.94	10	-	-	-	-
Pd	-	-	-	-	21	0.021	0.006	28	-	-	-	-	-	-	-	-
Rb	11	1.57	0.04	2	27	1.57	0.07	4	16	1.58	0.02	1	84	1.56	0.04	3
Rb ^a	-	-	-	-	-	-	-	-	-	-	-	-	4	1.54	0.01	1
Se	-	-	-	-	-	-	-	-	16	0.23	0.03	13	-	-	-	-
Si	-	-	-	-	21	1616 ^c	377	23	16	1443 ^c	266	18	84	1820	36	2
Si ^b	6	1916	26	1	-	-	-	-	-	-	-	-	9	1857	17	1
Th	-	-	-	-	27	0.018	0.003	18	32	0.018	0.003	20	84	0.014	0.002	14
Ti	-	-	-	-	31	1.56	0.14	9	16	1.43	0.06	4	-	-	-	-
Tl	11	0.007	0.001	14	-	-	-	-	16	0.008	0.001	13	-	-	-	-
W	-	-	-	-	2	0.013	0.001	4	-	-	-	-	-	-	-	-
Y	-	-	-	-	31	0.139	0.005	3	16	0.144	0.003	2	-	-	-	-
Zr	-	-	-	-	27	0.13	0.02	16	32	0.11	0.01	5	-	-	-	-
	IRD Bondy				UPMC Paris				La Rochelle				Compilation			
	n	Average	SD	% RSD	n	Average	SD	% RSD	n	Average	SD	% RSD	n	Average	SD	% RSD
Ag	-	-	-	-	-	-	-	-	-	-	-	-	14	0.035	0.005	14
B	-	-	-	-	3	5.70	0.45	8	-	-	-	-	13	5.95	0.22	4
Br	-	-	-	-	-	-	-	-	-	-	-	-	6	47.8	2.0	4
Cs	-	-	-	-	-	-	-	-	-	-	-	-	44	0.009	0.001	11
Ga	-	-	-	-	-	-	-	-	-	-	-	-	45	0.0119	0.0004	3
Ge	-	-	-	-	-	-	-	-	-	-	-	-	44	0.010	0.003	27
Li	6	0.524	0.066	13	11	0.610	0.015	2	15	0.504	0.026	5	80	0.54	0.07	12
P	-	-	-	-	-	-	-	-	-	-	-	-	32	9.13	0.78	9
Pd	-	-	-	-	-	-	-	-	-	-	-	-	21	0.021	0.006	29
Rb	6	1.43	0.16	11	15	1.49	0.09	6	15	1.53	0.10	6	178	1.53	0.05	3
Rb ^a	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Se	-	-	-	-	-	-	-	-	-	-	-	-	16	0.23	0.03	13
Si	-	-	-	-	-	-	-	-	-	-	-	-	99	1864	48	3
Si ^b	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Th	2	0.021	0.001	5	-	-	-	-	-	-	-	-	145	0.018	0.003	16
Ti	7	1.40	0.09	6	-	-	-	-	-	-	-	-	54	1.46	0.08	6
Tl	-	-	-	-	-	-	-	-	-	-	-	-	27	0.0076	0.0006	8
W	-	-	-	-	-	-	-	-	-	-	-	-	2	0.0133	0.0010	7
Y	4	0.155	0.019	12	-	-	-	-	-	-	-	-	51	0.146	0.008	5
Zr	-	-	-	-	-	-	-	-	-	-	-	-	59	0.12	0.015	13

n number of results. SD standard deviation. % RSD relative standard deviation.
 Italics compilation value from less than three different laboratories. ^a Rb value obtained by isotope dilution-TIMS.
^b Si values obtained by spectrophotometry. ^c excluded from the compilation value.

standard deviation (RSD) obtained for the compilation values ranges from 3% to 10% for concentrations varying between 360 ng l⁻¹ for Ce to 1.7 ng l⁻¹ for Tm, suggesting a fairly good homogeneity of results between laboratories and techniques. The RSD values are not correlated with the concentration, the highest values being associated with the middle REEs and Tm.

The high standard deviation for Tm is due to the low Tm concentration yielded by the direct introduction method used by the Toulouse laboratory, which was 20% lower than the mean obtained by the other laboratories. Higher variations for the middle REEs between laboratories may in part be explained by the fact that these elements are interfered by light REEs (LREEs) and

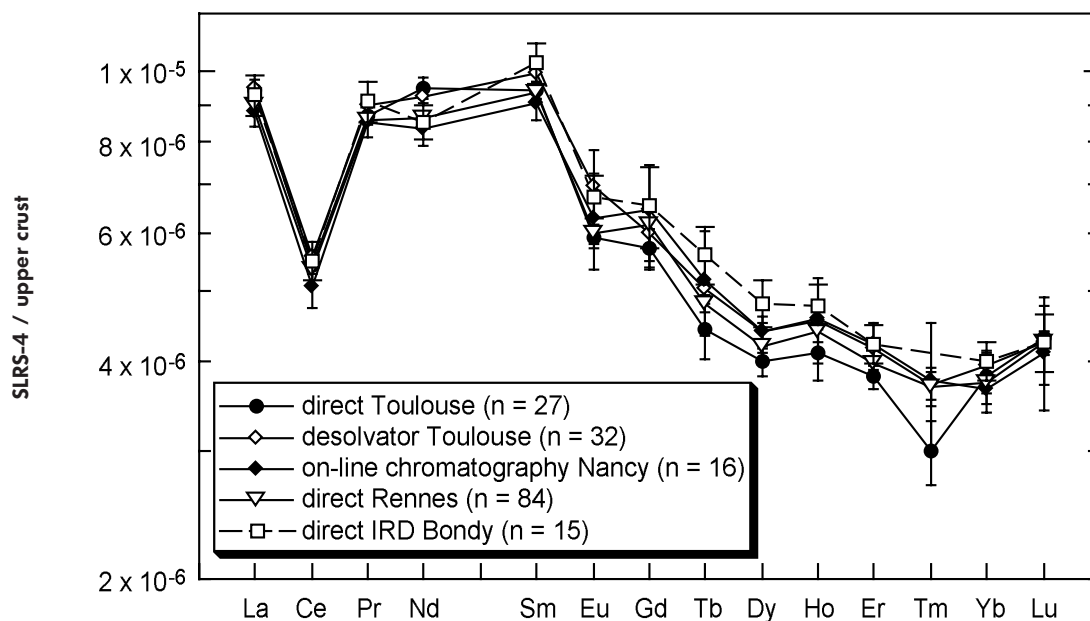


Figure 1. Upper crust-normalized REE patterns of the river water CRM SLRS-4 obtained by the different laboratories. n = number of results. Upper crust data from Taylor and McLennan (1985).

Ba oxides for which the correction (or lack of correction) introduces some noise. The low values of heavy REEs (HREEs), except for Yb and Lu, reported by the Toulouse laboratory with its direct introduction method, may result from the LREEs corrections applied by this laboratory (Ariès *et al.* 2000). This is supported by the fact that this laboratory yielded values closer to the compilation by using the desolvation technique, which generated a very low oxide formation. High values for Gd and Dy reported by the IRD (Bondy) may be explained by the fact that for these elements this laboratory applied no oxide corrections. However, the SARM (Nancy) did correct for Gd and obtained a similar value and did not correct for Dy and obtained a lower value.

The REE patterns normalized to concentrations of the upper crust (Taylor and McLennan 1985) for each laboratory are shown in Figure 1. The REE patterns display a LREE enrichment relative to the HREEs and an important negative Ce anomaly. The general pattern may reflect the composition of lithologies along the flow path of the river (Brookins 1989, Verplanck *et al.* 2001). The Ce anomaly is commonly observed for river waters and is probably due to the redox conditions and the trapping of Ce^{IV} by the Fe and Mn oxides (Fleet 1984, Brookins 1988).

Other elements: Eighteen other elements having no certified values were analysed. Results are reported

in Table 5. Six elements (B, Li, Th, Rb and Si) were determined by at least three different laboratories or methods (Figure 2). All the available data for B, Li, Th and Rb were used for the compilation values, including complementary data by ID-TIMS for Rb. Figure 2 shows that results from the different laboratories are within error (2s) except for Li (Nancy). Nancy and Toulouse (desolvator) reported the two extreme Li concentrations of $0.444 \pm 0.013 \mu\text{g l}^{-1}$ and $0.615 \pm 0.027 \mu\text{g l}^{-1}$ respectively and La Rochelle reported intermediate concentrations of $0.504 \pm 0.026 \mu\text{g l}^{-1}$. These results might be explained by some bias in the calibration between laboratories. Silicon concentration was measured by two techniques, ICP-MS and spectrophotometry (Table 5). Values obtained by spectrophotometry from Rennes and Nancy are similar. The ICP-MS value from Rennes is in agreement with those obtained by spectrophotometry, whereas Si concentrations determined by ICP-MS from Toulouse are lower and less reproducible (RSD of ~ 20% compared to ~ 1% obtained by spectrophotometry). The Si value measured in SLRS-4 is close to the estimated detection limit of the ICP-MS method for this element. The high Si background contribution observed by the Toulouse team in that concentration range certainly leads to inaccurate correction and explains the variability of the results. Therefore, we decided to exclude Si values reported by the Toulouse laboratory from the compilation calculations.

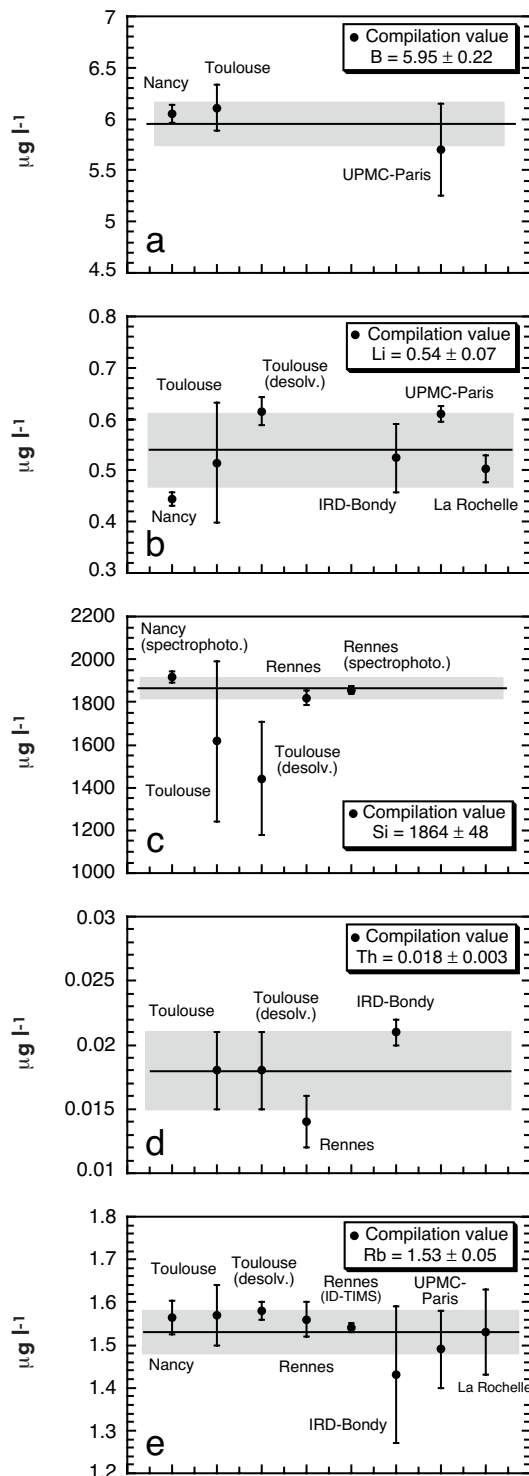


Figure 2. Average concentrations of B (a), Li (b), Si (c), Th (d) and Rb (e) in the river water CRM SLRS-4 determined by each participating laboratory. The compilation values are displayed in the legend. Full line: compilation value; shaded area: standard deviation of the compilation value; desolv.: desolvator; spectrophoto.: spectrophotometry; ID-TIMS: isotope dilution-TIMS. Error bars represent 1 s.

Three other trace elements (Ti, Tl, Y) were analysed by two laboratories (Table 5). Results for these elements are, within error, identical between the two laboratories. All other trace elements reported in Table 5 (Ag, Br, Cs, Ga, Ge, W, Zr, P, Pd, Se) were analysed only by the Toulouse laboratory. In all cases, when these elements were analysed by the two nebulisation systems, an identical concentration, within error, was obtained (Table 5).

Conclusions

We report a compilation of concentrations for uncertified elements in the natural river water reference material SLRS-4 (NRC-CNRC) from two years of routine analysis in six different French laboratories. The results reported for REE concentrations are coherent, with RSD for the compilation values ranging from 3% to 10%. Eight elements (Li, Th, Rb, B, Ti, Tl, Y, Si) analysed by at least two laboratories yielded compilation values having RSD ranging from 3% to 16%. Fourteen other trace element concentrations were reported, but with the availability of a more limited number of results.

References

Aries S., Valladon M., Polvé M. and Dupré B. (2000)

A routine method for oxide and hydroxide interference corrections in ICP-MS chemical analysis of environmental and geological samples. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 24, 19-31.

Berndt T.H. and Yanez J. (1996)

High temperature hydraulic high-pressure nebulization: A recent nebulization principle for sample introduction. *Journal of Analytical Atomic Spectrometry*, 11, 703-712.

Bouhnik-Le Coz M., Petitjean P., Serrat E. and Gruau G. (2001)

Validation d'un protocole permettant le dosage simultané des cations majeurs et traces dans les eaux douces naturelles par ICP-MS. *Les Cahiers Techniques*, Editions Géosciences Rennes, 1, 82pp.

Brookins D.G. (1988)

Eh-pH diagrams for geochemists. Springer-Verlag (New-York), 176pp.

Brookins D.G. (1989)

Aqueous geochemistry of rare earth elements. In: Ribbe P. (ed.), *Geochemistry and mineralogy of rare earth elements*. Mineralogical Society of America, *Reviews in Mineralogy*, 21, 201-223.



references

Carignan J., Hild P., Mevelle G., Morel J. and Yeghicheyan D. (2001)

Routine analysis of trace elements in geological samples using flow-injection and low-pressure on-line liquid chromatography ICP-MS: A study of geochemical reference materials BR, DR-N, UB-N, ANG and GH. *Geostandards Newsletter: The Journal of Geostandards and Geoanalysis*, 25, 187-198.

Date A.R. and Gray A.L. (1989)

Applications of inductively coupled plasma-mass spectrometry. Blackie (New York), 254pp.

Feinberg M. (1996)

La validation des méthodes d'analyse: Une approche chimométrique de l'assurance qualité au laboratoire. Masson (Paris), 397pp.

Fleet A.J. (1984)

Aqueous and sedimentary geochemistry of rare earth elements. In: Henderson P. (ed.), *Rare earth elements geochemistry*. Elsevier Science (Amsterdam), 343-373.

Jakubowski N., Feldmann I. and Stuewert D. (1992)

Analytical improvement of pneumatic nebulization in ICP-MS by desolvation. *Spectrochimica Acta*, 47B, 107-118.

Le Cornec F., Gerard M. and Giffard I. (1999)

Preconcentration and determination by ICP-MS of rare earth elements and some metal ions in water samples. 99 European Winter Conference on Plasma Spectrochemistry (Pau), abstract volume, 133pp.

May T.W. and Wiedmeyer R.H. (1998)

A table of polyatomic interferences in ICP-MS. *Atomic Spectroscopy*, 19, 150-155.

Miller J.C. and Miller J.N. (1993)

Statistics for analytical chemistry (3rd edition). Ellis Horwood PTR Prentice Hall (New York), 233pp.

Neuilly M. and Cetama (1993)

Modélisation et estimation des erreurs de mesures. Lavoisier (Paris), 644pp.

Prichard F.E., Crosby N.T., Day J.A., Hardcastle W.A., Holcombe D.G. and Treble R.D. (1995)

Quality in the analytical chemistry laboratory. In: Newman E.J. (ed.) *Analytical Chemistry by Open Learning*. John Wiley and Sons (Chichester), 307pp.

Reed N.M., Cairns R.O. and Hutton R.C. (1994)

Characterization of polyatomic ion interferences in inductively coupled plasma-mass spectrometry using a high resolution mass spectrometer. *Journal of Analytical Atomic Spectrometry*, 9, 881-896.

Rose E.F., Carignan J. and Chaussidon M. (2000)

Transfer of atmospheric boron from oceans to continents: An investigation using precipitation waters and epiphytic lichens. AGU and Geochemical Society publication, G3 1, 15pp.

Taylor S.R. and McLennan S.M. (1985)

The continental crust: Its composition and evolution. Blackwell (Oxford), 460pp.

Verplanck P.L., Antweiler R.C., Nordstrom D.K. and Taylor H.E. (2001)

Standard reference water samples for rare earth element determinations. *Applied Geochemistry*, 16, 231-244.