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**A COMPILATION OF SILICIUM AND THIRTY ONE TRACE ELEMENTS  
MEASURED IN THE NATURAL RIVER WATER STANDARD SLRS-4  
(NRC-CNRC)**

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Keywords : river water reference material, ICP-MS, rare earth elements, trace elements

The natural river water standard SLRS-4 (NRC-CNRC) has been routinely analysed for major and trace elements by six French laboratories. Most measurements were done using ICP-MS

(Inductively Coupled Plasma-Mass Spectrometry). For silicium 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.

Mots-clés : standard d'eau de rivière, ICP-MS, terres rares, éléments en traces

Le standard d'eau de rivière SLRS-4 (NRC-CNRC) 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.

The natural river water standard 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) analysed routinely 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 certified elements by NRC-CNRC and according to the aim of laboratories, uncertified elements are also measured in the reference water. No proficiency tests, neither interlaboratory schemes have been elaborated for this paper. The presented compilation only gathers two years of individual routine results and working values for uncertified elements are proposed.

## **I. Instrumentation and statistical treatments**

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 introduction sampling systems, the

subtracted blanks, the acid molarity of the analysed solutions and the calibration methods were specific for each laboratory. A desolvator (High temperature hydraulic High Pressure Nebulizer) is used by the laboratory of Toulouse for some trace elements. This method was described in Jakubowski *et al.* (1992) and Berndt *et al.* (1996). The on-line liquid chromatography used by the team of Nancy is described in detail in this volume (Carignan *et al.*, 2001). Oxides and doubly charged ions were less than 3% and the different laboratories have applied oxide and hydroxide interference corrections (Le Cornec *et al.*, 1999; Aries *et al.*, 2000; Bouhnik-Le Coz *et al.*, 2001). Wavelengths without spectral interferences were used by the UPMC Paris laboratory with the optical techniques. Some of these corrections are reported in Table 1.

Calibrations were done 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 the instrumental drift by adding an internal standard to samples such as In (Rennes), In and Re (Toulouse), Tm (IRD Bondy) and Rh (La Rochelle). When no internal standard is used (Nancy and IRD Bondy), the eventual drift is controlled by measuring the standard solution every 4-5 samples. Blanks and acids are consigned in Table 1: blanks are acidified with HNO<sub>3</sub> to reach 2 molar for Nancy (Carignan *et al.*, 2001) and 0.1 to 0.5 molar for other laboratories. The Rennes laboratory added HNO<sub>3</sub> 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 in these conditions. Table 2 summarises isotopes and internal standards measured by the different

teams. When several isotopes were measured, we choose the isotope with the smallest standard deviation after verifying the absence of interferences. For lead,  $^{208}\text{Pb}$  was used for the compilation.

Laboratories have preliminary rejected the outliers by their own methods. Two of them (UPMC Paris, La Rochelle) eliminate values out of the individual mean value  $\pm 2$  sd (standard deviation). The Dixon and Grubbs tests at 95% confidence level (Miller & Miller, 1993 ; Prichard, 1995; Feinberg, 1996) have been applied by the others. The 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 for the others.

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

## II. 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 for few ones, 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.

Elements like Co, Cr and Fe are known to be easily interfered by ArO species (Date and Gray, 1989, Reed *et al.*, 1994, May and Wiedmeyer, 1998). The sulfur and ArO species on Zn might explain the high values obtained by the participants except with the desolvation method. In the case of Ca, the use of both techniques, ICP-MS and ICP-AES confirmed a lower value than that obtained by NRC-CNRC with ICP-AES and FAAS and it should be interesting to re-evaluate the Ca concentration by other laboratories.

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 insures the proficiency of the participating laboratories for results on the 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 standard deviation (rsd) obtained for the compilation values ranges from 3% to 10% for concentrations varying between 360 ng.l<sup>-1</sup> for Ce to 1.7 ng.l<sup>-1</sup> for Tm suggesting a fairly good homogeneity of the results between laboratories and techniques. The rsd values are not correlated with the concentration, the highest values being affected to the middle REEs and Tm. The high standard deviation for Tm is due to the low Tm concentration yielded by Toulouse direct introduction method, which is 20% lower than the mean obtained by the other laboratories. Higher variations for the middle REEs between laboratories may in part explained by the fact that these elements are interfered by Light REEs (LREEs) and Ba oxides for which the corrections (or no correction) introduce some noise. The low values of Heavy REEs (HREEs), except for Yb and Lu, reported by Toulouse 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 generate a very low oxide formation. High values for Gd and Dy reported by the IRD Bondy may be explained by the fact that this laboratory for



these elements applied no oxide corrections. However, Nancy did correct for Gd and obtained similar value and did not correct for Dy and obtained lower value.

The REE patterns normalised to concentrations of the upper crust (Taylor and McLennan, 1985) for each laboratory are reported in Figure 1. The REE patterns display a LREE enrichment relative to the Heavy REEs 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<sup>IV</sup> by the Fe and Mn oxides (Fleet, 1984; Brookins, 1988).

### *II.b.2 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 3 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 except for Li (Nancy). Nancy and Toulouse (desolvator) reported the two extrem 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. Si concentration was measured by two techniques : ICP-MS and spectrophotometry (Table 5). Values obtained by spectrophotometry from Rennes and Nancy are rather 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 closed to the estimated determination 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 heterogeneity of the results. Therefore, we decided to exclude Si values reported by Toulouse from the compilation calculations.

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).

### **III. Conclusion**

We report a compilation of concentrations for uncertified elements in the natural river water standard SLRS-4 (NRC-CNRC) from two years of routine analysis in six different French laboratories. These reported coherent results for REE concentrations, with rsd for the compilation values ranging from 3% to 10%. Eight elements (Li, Th, Rb, B, Ti, Tl, Y, Si) analysed at least by two laboratories yielded compilation values having rsd ranging from 3%

to 16%. Fourteen other trace elements concentrations were reported, but with a more restrictive 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* 24,1, 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*, Ed. Géosciences Rennes, 1, 82 pp.

Brookins D.G. (1988)

*Eh-pH Diagrams for Geochemists*. Springer-Verlag Pubs., New-York, 176 pp.

Brookins D.G. (1989)

Aqueous geochemistry of rare earth elements. In P. Ribbe Ed., *Geochemistry and mineralogy of Rare Earth Elements*, Mineralogical Society of America, *Reviews in Mineralogy* 21, 201-223.

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 geostandards BR, DR-N, UB-N, ANG and GH, *Geostandards Newsletter*, *in this issue*.

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

Applications of inductively coupled plasma mass spectrometry. Blackie Ed., New York, 254 pp.

Feinberg M. (1996)

La validation des méthodes d'analyse : une approche chimiométrique de l'assurance qualité au laboratoire. Masson, Paris, 397 pp.

Fleet A.J. (1984)

Aqueous and sedimentary geochemistry of rare earth elements. In: P. Henderson Ed., Rare Earth Elements Geochemistry. Elsevier Science Pubs, Amsterdam, 343-373.

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

Analytical improvement of pneumatic nebulization in ICP-MS by desolvation. Spectrochimica Acta 47B,1,107-118.

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, 133.

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. 3<sup>rd</sup> ed., Ellis Horwood PTR Prentice Hall, New York, 233 pp.

Neuilly M. and Cetama (1993)

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

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* Analytical Chemistry by Open Learning. John Wiley and Sons Ed., 307 pp.

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)

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

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

The continental crust : its composition and evolution. Blackwell, Oxford, 460pp.

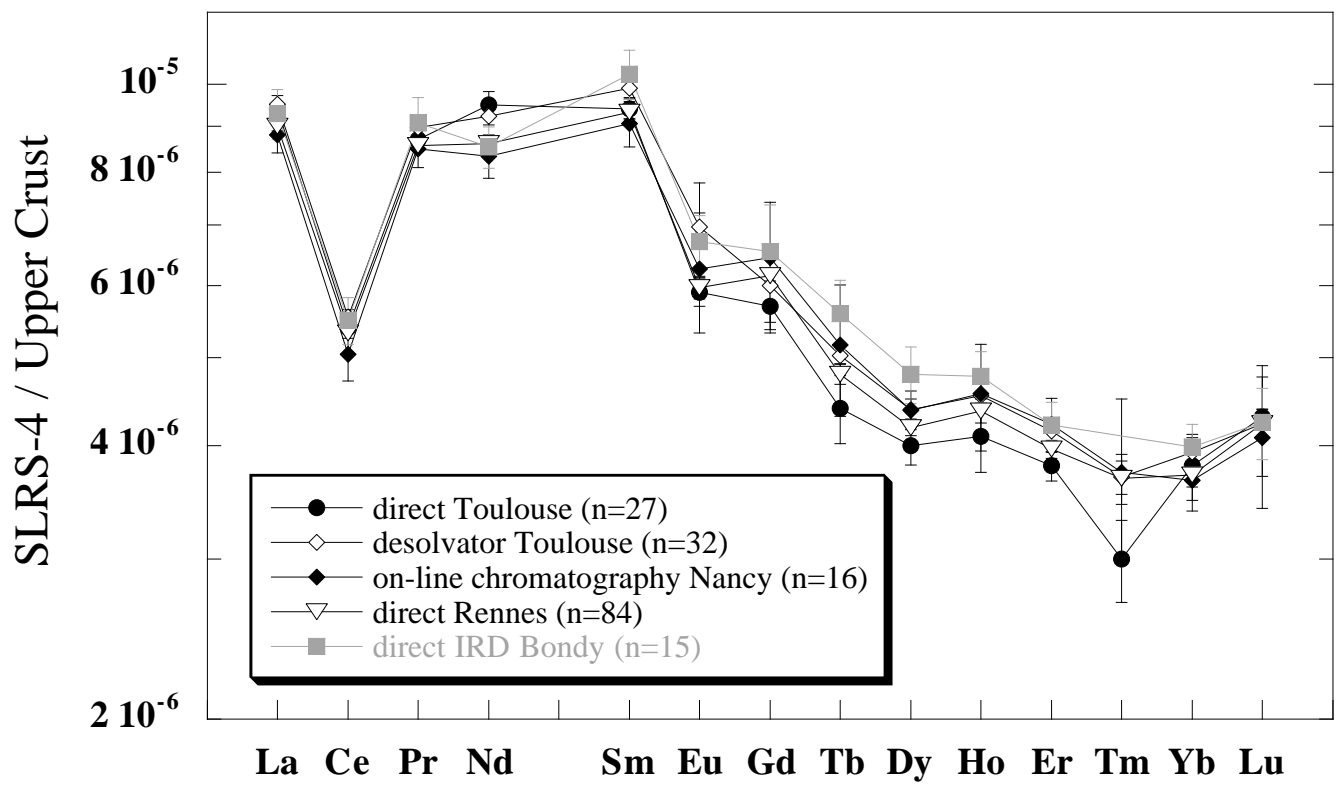
Verplanck P.L., Antweiler R.C., Nordstrom D.K. and Taylor H.E. (2001)

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

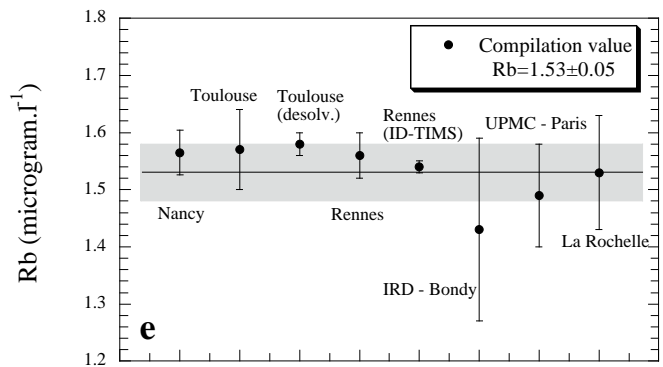
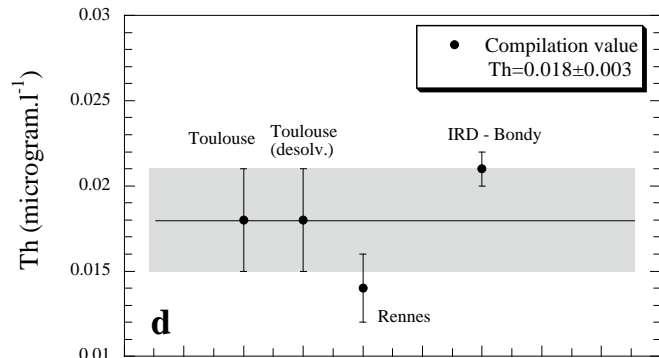
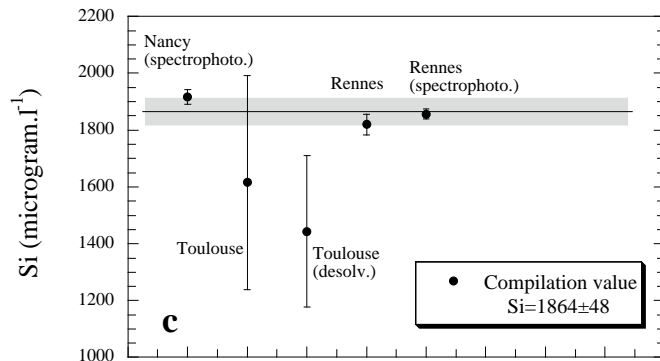
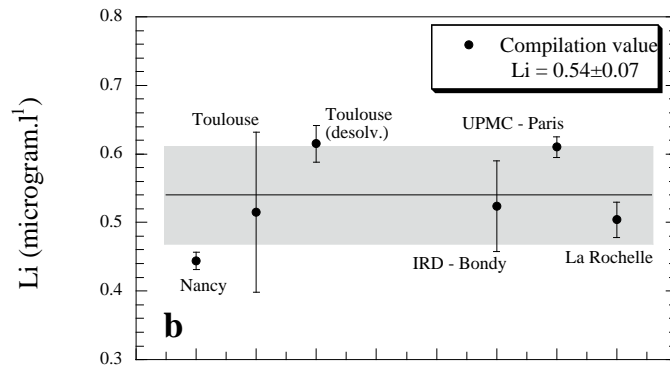
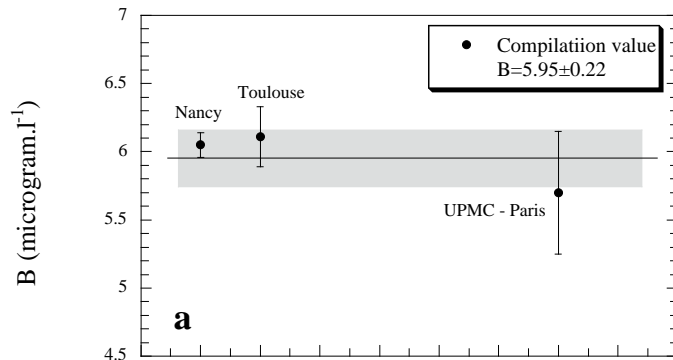
## Figure caption

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

Figure 2 : Average concentrations of B (a), Li (b), Si (c), Th (d) and Rb (e) determined by each participating laboratory in the river water standard SLRS-4. 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.







**Table 1: Instrumentation and procedures of the participating laboratories.**

Laboratory	Instrument	Methods and introduction systems		Blank	Acid medium	Calibration	Interferences corrections
Nancy	ICP-MS Perkin Elmer ELAN 6000	direct (all elements except REE) Meinhard nebulizer and Scott spray chamber	on-line chromatography (REE) 2 electrovalves with a microcolumn connected to a Meinhard nebulizer and a Scott spray chamber	distilled water	HNO <sub>3</sub> purified by sub-boiling distillation  5%	multi elemental mono elemental for B  10 µg.l <sup>-1</sup> 0.5 µg.l <sup>-1</sup> for REEs	Gd 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 <sup>-1</sup> (5 mL of sample in 10 mL)	-
Toulouse	ICP-MS Perkin Elmer ELAN 6000	direct (all elements) Cross-flow nebulizer and Scott spray chamber	HHPN* desolvator (all elements) Meinhard nebulizer and cyclonic spray chamber	De-ionised water purified with a MilliQ (Millipore) system	HNO <sub>3</sub> doubly purified by sub-boiling distillation  2% and reacidification at 2% of the SLRS-4 water	multi elemental with internal standards In, Re  10, 50 µg.l <sup>-1</sup> (In = Re = 10 µg.l <sup>-1</sup> )	Aries <i>et al.</i> (2000)
Rennes	ICP-MS Hewlett Packard 4500	direct (all elements) Cross-flow nebulizer and cooled Scott spray chamber (Peltier effect 2°C)		De-ionised water purified with a MilliQ (Millipore) system  internal standard In	HNO <sub>3</sub> purified by sub-boiling distillation  2% and reacidification at 2% of the SLRS-4 water	multi elemental with internal standard In	Bouhnik-le Coz <i>et al.</i> (2001)
	Spectrophotometry Biotek - Uvikon XS	direct (Si)		De-ionised water purified with a MilliQ (Millipore) system	-	Si = 5, 10, 20, 30, 60 mg.l <sup>-1</sup>	-
	Mass Spectrometry Finnigan MAT 262	isotopic dilution (Rb)		-	-	Spikes <sup>84</sup> Sr = 0.1184 µg.g <sup>-1</sup> (99,8%) <sup>87</sup> Rb = 5.5750 µg.g <sup>-1</sup> (98%)	-
IRD Bondy	ICP-MS Varian UltraMass 700	direct or after off-line chromatography (all elements) V-groove nebulizer or ultrasonic nebulizer and Sturm-masters cyclonic spray chamber		De-ionised water purified with a MilliQ (Millipore) system	HNO <sub>3</sub>  2%	multi elemental with or without internal standard Tm  five standards from 0.005 to 100 µg.l <sup>-1</sup> according to the concentration range of the element (Tm = 1 µg.l <sup>-1</sup> )	<sup>51</sup> V = -3.1081 * <sup>53</sup> ? + 0.3524 * <sup>52</sup> Cr <sup>75</sup> As = -3.1278 * <sup>77</sup> ? + 1.0177 * <sup>76</sup> Se <sup>87</sup> Sr = -0.3856 * <sup>85</sup> Rb <sup>86</sup> Sr = -1.504 * <sup>83</sup> Kr <sup>138</sup> Ba = -0.0009008 * La - 0.003394 * <sup>140</sup> Ce
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 <sub>3</sub>	multi elemental  two or four standards from 0 to 10 mg.l <sup>-1</sup> according to the concentration range of the element	-
	AAS Hitachi Z5000 and TJA Solutions Solaar989QZ	direct (Mn, Cu, Li, Rb)			0.5%	multi elemental	
La Rochelle	ICP-MS Varian UltraMass 700	direct (all elements) V-groove nebulizer and Sturm-masters cyclonic spray chamber		De-ionised water purified with a MilliQ (Millipore) system	HNO <sub>3</sub>  2%	multi elemental with internal standard Rh  seven standards from 0.01 to 10 µg.l <sup>-1</sup> according to the concentration range of the element (Rh = 0.1 or 1 µg.l <sup>-1</sup> )	<sup>51</sup> V = -3.1081 * <sup>53</sup> ? + 0.3524 * <sup>52</sup> Cr <sup>75</sup> As = -3.1278 * <sup>77</sup> ? + 1.0177 * <sup>76</sup> Se

\* : High temperature hydraulic High Pressure Nebulizer (Knauer®)

? Total signal on mass x

**Table 2: Isotopes used for ICP-MS, wavelength used for ICP-AES and AAS by the participating laboratories. Internal standards isotopes are in bold faces.**

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

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

Element	certified values			Nancy direct (n=25)			Toulouse direct (n=26)			Toulouse desolvator (n=32)			Rennes direct (n=84)			IRD Bondy (n=14)			UPMC Paris (n=10)			La Rochelle (n=15)			COMPILATION			
	$\mu\text{g.l}^{-1}$	CLs	rCLs (%)	average	sd	rsd (%)	average	sd	rsd (%)	average	sd	rsd (%)	average	sd	rsd (%)	average	sd	rsd (%)	average	sd	rsd (%)	average	sd	rsd (%)	Element	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	-	-	-	-	-	-	51.1	3.1	6.1	Al	53	2	3.6
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	-	-	-	-	-	-	-	-	0.67	0.06	8.3	As	0.70	0.04	5.5	
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	12.0	0.7	6.1	12.8	0.3	2.3	11.8	0.5	4.3	Ba	12.6	0.52	4.1
Be	0.007	0.002	28.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.008	0.002	28.4	Be	0.008	0.002	28.4	
Ca	6200	200	3.2	-	-	-	4267	253	5.9	-	-	-	5859	168	2.9	-	-	-	5630	170	3.0	-	-	-	Ca	5252	861	16.4
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	-	-	-	-	-	0.017	0.007	42.8	Cd	0.014	0.002	17.8	
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	-	-	-	0.046	0.006	13.9	-	-	-	0.057	0.015	26.1	Co	0.048	0.008	17.9
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	0.41	0.08	19.1	-	-	-	0.32	0.05	16.9	Cr	0.37	0.05	12.5
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	1.85	0.12	6.7	1.77	0.07	3.7	1.75	0.10	5.8	Cu	1.93	0.24	12.4
Fe	103	5	4.9	-	-	-	116	8	6.8	109	3	2.4	107	6	5.3	-	-	-	100	2	1.5	-	-	-	Fe	108	7	6.1
K	680	20	2.9	-	-	-	671	89	13.3	597	18	2.9	603	15	2.4	-	-	-	-	-	-	-	-	-	K	624	41	6.6
Mg	1600	100	6.3	-	-	-	1695	91	5.4	1658	77	4.6	1593	38	2.4	-	-	-	1550	45	2.9	-	-	-	Mg	1624	65	4.0
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	3.25	0.39	11.9	3.46	0.12	3.5	3.18	0.15	4.7	Mn	3.37	0.12	3.7
Mo	0.21	0.02	9.5	-	-	-	0.24	0.07	28.4	0.18	0.02	10.1	-	-	-	0.20	0.02	8.9	-	-	-	-	-	-	Mo	0.21	0.03	16.2
Na	2400	200	8.3	-	-	-	2692	79	2.9	2580	126	4.9	2227	49	2.2	-	-	-	-	-	-	-	-	-	Na	2499	243	9.7
Ni	0.67	0.08	11.9	-	-	-	0.92	0.24	26.6	0.72	0.03	4.7	-	-	-	0.97	0.19	19.1	-	-	-	0.67	0.12	18.1	Ni	0.82	0.15	18.0
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	-	-	-	-	-	-	-	-	-	Pb	0.084	0.007	8.4
Sb	0.23	0.04	17.4	-	-	-	0.30	0.15	49.3	0.25	0.005	1.9	-	-	-	-	-	-	-	-	-	-	-	-	Sb	0.27	0.04	13.5
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	28.6	2.2	7.7	28.4	0.6	1.9	25.5	0.9	3.6	Sr	28.2	1.36	4.8
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	0.055	0.006	10.5	-	-	-	0.043	0.012	27.4	U	0.05	0.00	10.0
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	-	-	-	0.367	0.050	13.5	-	-	-	0.329	0.027	8.2	V	0.35	0.02	4.6
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	1.59	0.29	18.3	-	-	-	-	-	-	Zn	1.24	0.26	21.0

n= number of results

sd : standard deviation  
CLs : 95% confidence limits

rsd : relative standard deviation  
rCLs : relative confidence limit

\* n=3

- : no measurement available

italics : outside the certified confidence limits

**Table 4 : Average concentration values (ng.l<sup>-1</sup>), standard deviation and relative standard deviation of REEs in the river water standard SLRS-4.**

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

n = number of results      sd : standard deviation      rsd : relative standard deviation

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 standard SLRS-4.

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

n = number of results      sd : standard deviation      rsd : relative standard deviation      italics : compilation value from less than 3 different laboratories

\* : Rb value obtained by Isotope Dilution-TIMS

\*\* : Si values obtained by spectrophotometry

\*\*\* : excluded from the compilation value