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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 HNO₃ to reach 2 molar for Nancy (Carignan *et al.*, 2001) and 0.1 to 0.5 molar 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 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}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 ± 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⁻¹ for Ce to 1.7 ng.l⁻¹ 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^{IV} 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.

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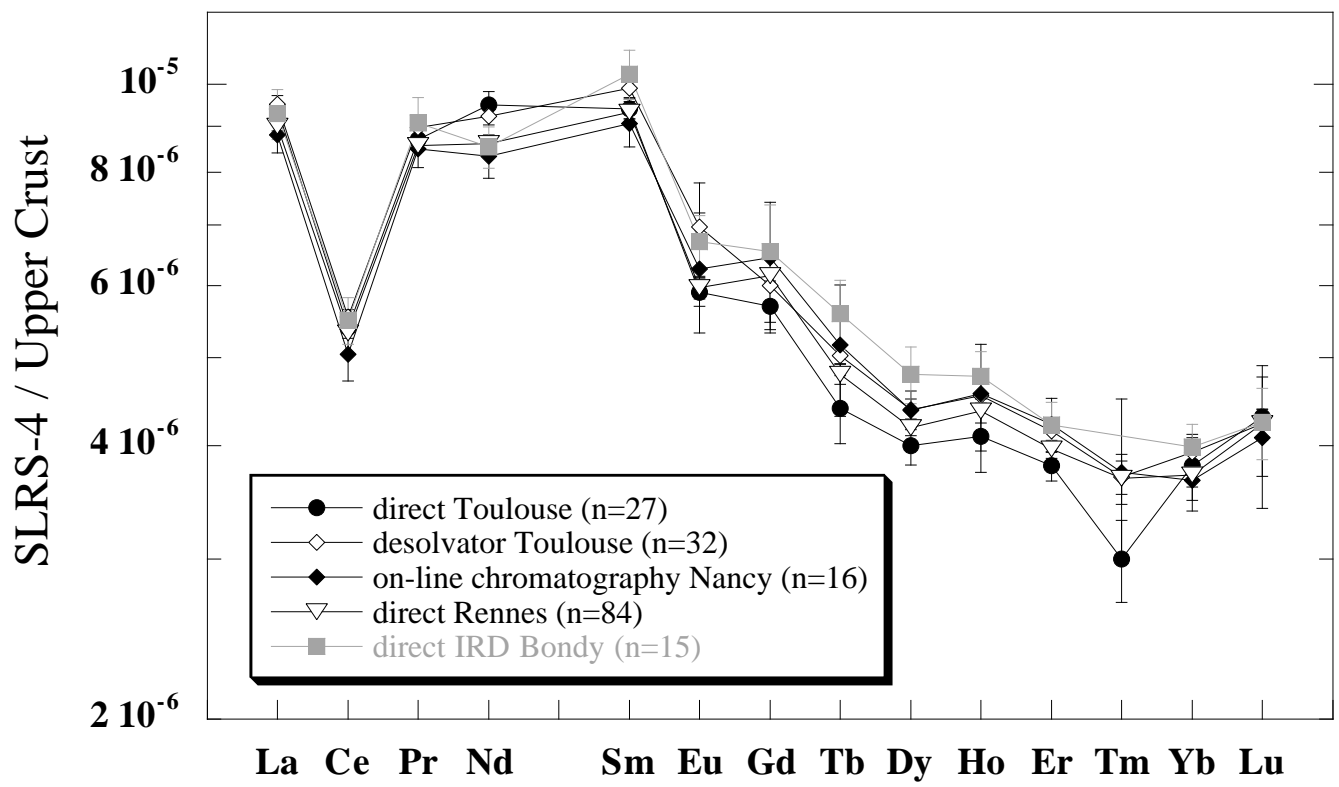
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Figure caption

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.



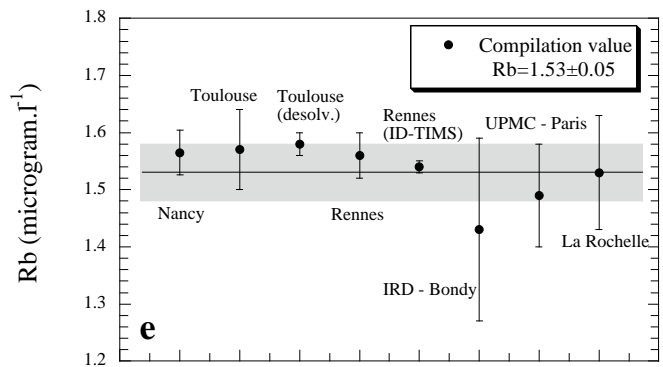
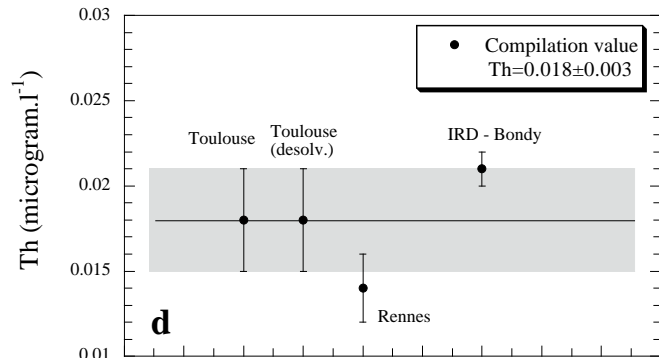
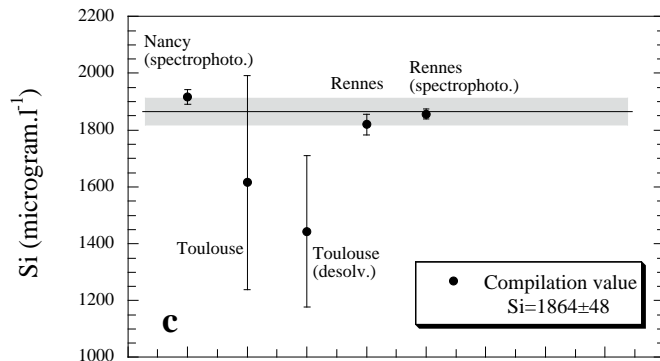
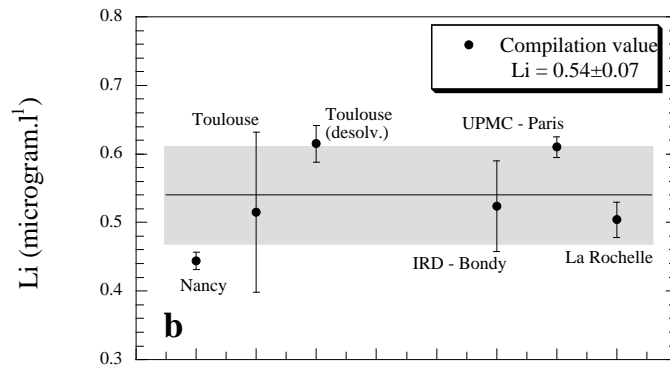
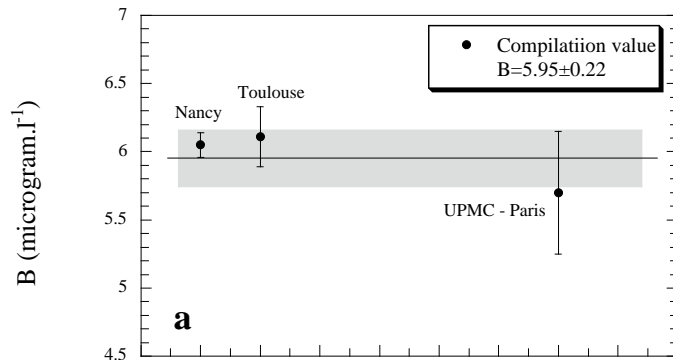


Table 1: Instrumentation and procedures of the participating laboratories.

| 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 ₃ purified by sub-boiling distillation 5% | multi elemental mono elemental for B 10 µg.l ⁻¹ 0.5 µg.l ⁻¹ 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 ⁻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 | HHPN* desolvator (all elements) Meinhard nebulizer and cyclonic spray chamber | De-ionised water purified with a MilliQ (Millipore) system | HNO ₃ 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 ⁻¹ (In = Re = 10 µg.l ⁻¹) | 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 ₃ 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 ⁻¹ | - |
| | Mass Spectrometry Finnigan MAT 262 | isotopic dilution (Rb) | | - | - | Spikes ⁸⁴ Sr = 0.1184 µg.g ⁻¹ (99,8%) ⁸⁷ Rb = 5.5750 µg.g ⁻¹ (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 ₃ 2% | multi elemental with or without internal standard Tm five standards from 0.005 to 100 µg.l ⁻¹ according to the concentration range of the element (Tm = 1 µg.l ⁻¹) | ⁵¹ V = -3.1081 * ⁵³ ? + 0.3524 * ⁵² Cr ⁷⁵ As = -3.1278 * ⁷⁷ ? + 1.0177 * ⁷⁶ Se ⁸⁷ Sr = -0.3856 * ⁸⁵ Rb ⁸⁶ Sr = -1.504 * ⁸³ Kr ¹³⁸ Ba = -0.0009008 * La - 0.003394 * ¹⁴⁰ 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 ₃ | multi elemental two or four standards from 0 to 10 mg.l ⁻¹ 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 ₃ 2% | multi elemental with internal standard Rh seven standards from 0.01 to 10 µg.l ⁻¹ according to the concentration range of the element (Rh = 0.1 or 1 µg.l ⁻¹) | ⁵¹ V = -3.1081 * ⁵³ ? + 0.3524 * ⁵² Cr ⁷⁵ As = -3.1278 * ⁷⁷ ? + 1.0177 * ⁷⁶ 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 | 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 | | | | |

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⁻¹), 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 (%) |
| La | 275.6 | 10.3 | 3.7 | 292.1 | 2.6 | 0.9 | 295.5 | 6.5 | 2.2 | 281.8 | 4.4 | 1.5 | 288.7 | 18.3 | 6.3 | La | 287 | 8 | 2.8 |
| Ce | 340.5 | 20.1 | 5.9 | 363.0 | 4.9 | 1.4 | 371.5 | 7.2 | 1.9 | 357.9 | 4.3 | 1.2 | 368.4 | 21.8 | 5.9 | Ce | 360 | 12 | 3.4 |
| Pr | 67.4 | 3.0 | 4.4 | 68.6 | 1.9 | 2.8 | 70.8 | 1.4 | 1.9 | 68.0 | 1.0 | 1.4 | 71.7 | 4.6 | 6.5 | Pr | 69.3 | 1.8 | 2.6 |
| Nd | 255.1 | 12.8 | 5.0 | 287.8 | 9.4 | 3.3 | 280.4 | 6.1 | 2.2 | 262.5 | 2.7 | 1.0 | 259.3 | 13.7 | 5.3 | Nd | 269 | 14 | 5.3 |
| Sm | 54.3 | 3.2 | 5.9 | 56.5 | 1.4 | 2.6 | 59.2 | 1.4 | 2.4 | 55.9 | 1.0 | 1.7 | 61.3 | 3.8 | 6.2 | Sm | 57.4 | 2.8 | 4.9 |
| Eu | 7.9 | 1.2 | 15.4 | 7.4 | 0.3 | 3.5 | 8.7 | 1.0 | 12.0 | 7.7 | 0.3 | 4.5 | 8.4 | 0.6 | 6.7 | Eu | 8.0 | 0.6 | 6.9 |
| Gd | 36.2 | 4.5 | 12.6 | 31.6 | 2.1 | 6.6 | 33.0 | 3.5 | 10.6 | 34.2 | 0.8 | 2.4 | 36.0 | 4.5 | 12.5 | Gd | 34.2 | 2.0 | 5.7 |
| Tb | 4.4 | 0.7 | 16.7 | 3.8 | 0.3 | 8.5 | 4.3 | 0.1 | 2.2 | 4.2 | 0.2 | 4.2 | 4.8 | 0.4 | 8.8 | Tb | 4.3 | 0.4 | 8.4 |
| Dy | 24.3 | 1.2 | 4.8 | 22.3 | 1.0 | 4.7 | 24.3 | 0.7 | 2.9 | 23.5 | 0.6 | 2.6 | 26.6 | 1.9 | 7.2 | Dy | 24.2 | 1.6 | 6.4 |
| Ho | 4.8 | 0.7 | 13.7 | 4.2 | 0.4 | 8.9 | 4.7 | 0.1 | 3.1 | 4.6 | 0.1 | 3.2 | 5.0 | 0.3 | 6.5 | Ho | 4.7 | 0.3 | 5.7 |
| Er | 13.9 | 1.0 | 6.9 | 12.4 | 0.5 | 3.8 | 13.6 | 0.4 | 2.7 | 13.3 | 0.5 | 3.8 | 13.8 | 0.8 | 5.8 | Er | 13.4 | 0.6 | 4.5 |
| Tm | 1.7 | 0.1 | 8.0 | 1.5 | 0.2 | 13.3 | 1.8 | 0.1 | 4.2 | 1.9 | 0.2 | 8.6 | | | | Tm | 1.7 | 0.2 | 10.4 |
| Yb | 11.5 | 0.8 | 7.3 | 12.0 | 1.0 | 8.3 | 12.2 | 0.5 | 3.8 | 11.8 | 0.4 | 3.5 | 12.4 | 0.7 | 6.0 | Yb | 12.0 | 0.4 | 3.2 |
| Lu | 1.8 | 0.3 | 16.8 | 1.9 | 0.3 | 14.0 | 1.9 | 0.1 | 3.7 | 2.0 | 0.2 | 8.3 | 1.9 | 0.2 | 9.0 | Lu | 1.9 | 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 (%) | Element | n | average | sd | rsd (%) |
| Ag | | | | | 14 | 0.035 | 0.005 | 14 | | | | | | | | | | | | | | | | | | | | Ag | 14 | <i>0.035</i> | <i>0.005</i> | 14 | |
| B | 4 | 6.05 | 0.09 | 1 | 6 | 6.11 | 0.22 | 4 | | | | | | | | | 3 | 5.70 | 0.45 | 8 | | | | | | | B | 13 | 5.95 | 0.22 | 4 | | |
| Br | | | | | 6 | 48 | 2 | 5 | | | | | | | | | | | | | | | | | | | Br | 6 | <i>47.8</i> | <i>2.0</i> | 4 | | |
| Cs | | | | | 28 | 0.008 | 0.002 | 23 | 16 | 0.009 | 0.002 | 23 | | | | | | | | | | | | | | | Cs | 44 | <i>0.009</i> | <i>0.001</i> | 11 | | |
| Ga | | | | | 29 | 0.012 | 0.002 | 19 | 16 | 0.012 | 0.001 | 9 | | | | | | | | | | | | | | | Ga | 45 | <i>0.0119</i> | <i>0.0004</i> | 3 | | |
| Ge | | | | | 28 | 0.012 | 0.004 | 33 | 16 | 0.008 | 0.002 | 26 | | | | | | | | | | | | | | | Ge | 44 | <i>0.010</i> | <i>0.003</i> | 27 | | |
| Li | 11 | 0.444 | 0.013 | 3 | 31 | 0.515 | 0.117 | 23 | 6 | 0.615 | 0.027 | 4 | | 6 | 0.524 | 0.066 | 13 | 11 | 0.610 | 0.015 | 2 | 15 | 0.504 | 0.026 | 5 | Li | 80 | 0.54 | 0.07 | 12 | | | |
| P | | | | | | | | | 32 | 9.13 | 0.94 | 10 | | | | | | | | | | | | | | | P | 32 | <i>9.13</i> | <i>0.78</i> | 9 | | |
| Pd | | | | | 21 | 0.021 | 0.006 | 28 | | | | | | | | | | | | | | | | | | | Pd | 21 | <i>0.021</i> | <i>0.006</i> | 29 | | |
| 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 | 6 | 1.43 | 0.16 | 11 | 15 | 1.49 | 0.09 | 6 | 15 | 1.53 | 0.10 | 6 | Rb | 178 | 1.53 | 0.05 | 3 |
| Rb* | | | | | | | | | | | | | 4 | 1.54 | 0.01 | 1 | | | | | | | | | | | | | | | | | |
| Se | | | | | | | | | 16 | 0.23 | 0.03 | 13 | | | | | | | | | | | | | | | Se | 16 | <i>0.23</i> | <i>0.03</i> | 13 | | |
| Si | | | | | 21 | 1616*** | 377 | 23 | 16 | 1443*** | 266 | 18 | 84 | 1820 | 36 | 2 | | | | | | | | | | | Si | 99 | <i>1864</i> | <i>48</i> | 3 | | |
| Si** | 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 | 2 | 0.021 | 0.001 | 5 | | | | | | | Th | 145 | 0.018 | 0.003 | 16 | | |
| Ti | | | | | 31 | 1.56 | 0.14 | 9 | 16 | 1.43 | 0.06 | 4 | | | | | 7 | 1.40 | 0.09 | 6 | | | | | | | Ti | 54 | <i>1.46</i> | <i>0.08</i> | 6 | | |
| Tl | 11 | 0.007 | 0.001 | 14 | | | | | 16 | 0.008 | 0.001 | 13 | | | | | | | | | | | | | | | Tl | 27 | <i>0.0076</i> | <i>0.0006</i> | 8 | | |
| W | | | | | 2 | 0.013 | 0.001 | 4 | | | | | | | | | | | | | | | | | | | W | 2 | <i>0.0133</i> | <i>0.0010</i> | 7 | | |
| Y | | | | | 31 | 0.139 | 0.005 | 3 | 16 | 0.144 | 0.003 | 2 | | 4 | 0.155 | 0.019 | 12 | | | | | | | | | | Y | 51 | <i>0.146</i> | <i>0.008</i> | 5 | | |
| Zr | | | | | 27 | 0.13 | 0.02 | 16 | 32 | 0.11 | 0.01 | 5 | | | | | | | | | | | | | | | Zr | 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