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The natural river water reference material SLRS-6 (NRC-CNRC) is the newest batch of a quality control material routinely used in many international environmental laboratories. This work presents a nine-laboratory compilation of measurements of major and trace element mass fractions and their related uncertainties, unavailable in the NRC-CNRC certificate (B, Cs, Li, Ga, Ge, Hf, Nb, P, Rb, Rh, Re, S, Sc, Se, Si, Sn, Th, Ti, Tl, W, Y, Y, Zr and REEs). Measurements were mostly made using inductively coupled plasma-mass spectrometry. The results are compared with equivalent data for the last batch of the material, SLRS-5, measured simultaneously with SLRS-6 in this study. In general, very low mass fractions, close to the quantification limits, were found in the new batch. The Sr isotopic ratio is also reported.

Keywords: river water reference material, ICP-MS, CRM, interlaboratory comparison, rare earth elements, trace elements.

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Natural river water chemistry varies greatly worldwide. For hydrochemists and geochemists, analytical procedures include the use of quality controls with chemical compositions close to those of the waters studied. Among these quality controls, the Ottawa river water, SLRS, prepared by the National Research Council (NRC-CNRC Canada), is particularly useful and is one of the best candidates for routine analysis and method development and validation (Katarina et *al.* 2009, Serafimovska et *al.* 2011, Bolotov et *al.* 2015, Al-Sid-Cheikh et *al,* 2015). This study is a follow-up to the SLRS-4 and SLRS-5 compilations performed by laboratories within the framework of the CNRS (French National Centre for Scientific Research) "ISOTRACE" network (Yeghicheyan *et al.* 2001, 2013).

The most recent batch of the SLRS quality control, SLRS-6, has been available since 2015 and is used for trace element measurements, notably for the study of sources and/or processes in the environment. The nine participating laboratories (*cf.* the authors' affiliations) routinely analyse the SLRS-6 reference material by ICP-MS and to a lesser extent by ICP-OES. This new work is the result of a sharing of routine measurement data between laboratories, and we chose to share it here simply as a way to make the data available to other analysts who use this river water.

As with the previous batch, mass fractions of certified elements and uncertified elements were measured simultaneously. The present compilation includes fifteen individual routine measurements for each laboratory and proposes mass fraction values for uncertified elements.

Although the participating laboratories are not qualified to certify analyses, it was considered appropriate to use the statistical tools proposed in the current standards for certification or laboratory proficiency testing procedures. Robust statistical treatment using the A algorithm was specifically performed for this compilation, as based on ISO Guide recommendations (detailed below) and summarised by the Analytical Methods Committee (AMC) of the Royal Society of Chemistry (AMC 2001). The advantages of this type of statistical treatment (compared with methods used for previous batches) are that each laboratory has the same weight and possible outliers do not influence the compilation values.

The mass fractions obtained for certified and uncertified elements are discussed and compared with those determined for the previous batch, SLRS-5, analysed simultaneously. The strontium isotope ratio ($^{87}Sr/^{86}Sr$) has also been proposed by one laboratory.

Instrumentation, methods and statistical treatment

Instruments and methods

The nine laboratories all analysed the SLRS-6 reference material water by ICP-MS (quadrupole or High Resolution) and one laboratory also used ICP-OES to quantify Si and S (Appendix A). Whereas SLRS solutions were directly introduced into the instrument at most laboratories, the LEGOS laboratory diluted the reference material by a factor of 2 and the UFF-Niteroi laboratory (Rio) preconcentrated it by a factor of 2 to 3 by evaporation. The instrumental operating parameters were similar for all ICP-MS measurements but the sample introduction systems, the blank subtractions, the pH of analysed solutions, and the data processing, including calibration methods and interference corrections, were specific to each laboratory. Instruments were tuned for oxide and doubly-charged ion formation and the laboratories applied oxide and hydroxide interference corrections (based on Aries *et al*. 2000) when necessary. Furthermore, CCT (Collision Cell Technology) and the KED mode (Kinetic Energy Discrimination) with He gas, or medium/high resolutions, were used to limit or eliminate potential interferences. The corresponding corrections are detailed in Table 1 and Appendix A. For the optical technique, Si and S measurements were performed using two to three wavelengths free of spectral interferences. Strontium isotopes were analysed using a TIMS instrument (Triton ThermoScientific).

Most calibrations were carried out with synthetic multi elemental solutions (home-made with mono elemental solutions or customised solutions from various manufacturers) acidified with 0.28 mol l^{-1} HNO_3. Some laboratories worked with a more acidic medium (0.32 mol l^{-1} or 0.37 mol l^{-1} HNO_3) with a pH close to 1, while the SLRS batch was stabilised at pH 1.6 by the producer. The Rennes and LEGOS laboratories added HNO_3 to their SLRS-6 vials in order to obtain the same matrix as the standard and because more-reproducible measurements were obtained by reducing the initial pH. Only the Montpellier laboratory worked with higher pH calibration solutions (0.14 mol l^{-1} HNO_3).

Instrumental drift was monitored and corrected for using either (i) addition of an internal standard into samples such as Be-Sc-Ge-In-Rh-Re-Ir, and/or (ii) measurement of a standard solution every 4-5 samples and use of a linear regression correction. One laboratory spiked some of the SLRS-6 aliquots with ^{146}Nd, ^{151}Eu and ^{172}Yb to determine rare earth elements (REEs) mass fractions using isotopic dilution and external calibration.

The measured masses, modes (standard, CCT (KED), medium/high resolutions), spikes and internal standards used by the different teams are summarised in Appendix A.

Statistical methods: In contrast to the previous SLRS-5 compilation (Yeghicheyan et *al.* 2013), in which each laboratory reported a variable number of results, in the present study, all laboratories were required to report the results of fifteen measurements *per* element. The measurements had to be obtained independently or during at least three distinct series of five replicates (i.e., three different calibrations and days). In rare instances, fewer than fifteen replicates were available, however these exceptions were negligible and do not require any weight to be assigned to the corresponding data. In addition, it should be noted that participants purchased the bottles within 6 months and that the mass fractions reported here were taken from one or two different SLRS-6 bottles *per* laboratory (serial numbers between 3830 and 4042). When the SLRS-5 batch was available, the laboratory made measurements of this batch together with the SLRS-6 measurements.

We chose to report our compilation using robust statistics (Algorithm A), which allows any possible outliers in such a small sampling database to be retained. Calculations are detailed in NF/ISO 5725-5 (1998) and summarised in an AMC technical brief (2001) and in an IUPAC document (2006).

The median was determined first, and the standard deviation, *s** (also noted MAD for Median of Absolute Deviates), was then calculated using the following equation:

$$s^* = 1.483 \times Median\ (|x_i - x^*|)$$

where x* is the median of *j* repeats and x_i is the measurement *i* (from 1 from *n* measurements).

The robust compilation mean and associated standard deviation were found by iterations. If we consider the correction criteria to be $\varphi = 1.5 \times s^*$, for each x_i (1,2…*n*), the new median x_i^* can be calculated as follows:

$$x_i^* = \begin{cases} x^* - \varphi \ \ if \ \ x_i < x^* - \varphi \\ x^* + \varphi \ \ if \ \ x_i > x^* + \varphi \\ \quad x_i \quad otherwise \end{cases}$$

The new values of the robust median x^* and the standard deviation s^* were then recalculated as:

$$x^* = \sum_{i=1}^{n} x_i^* / n$$

$$s^* = 1.134 \sqrt{\sum_{i=1}^{n} (x_i^* - x^*)^2/(n-1)}$$

as long as the difference between the new and previous values for x^* and s^* was greater than 10^{-4}. The factor 1.134 was derived from the normal distribution.

The assigned expanded uncertainty, U, was then calculated using:

$$U = k.u = 2 \times 1.25 \times {s^*}/{\sqrt{p}}$$

where k is the coverage factor (derived from Student's coefficient 2 and defining an interval with a confidence level of about 95%), u is the assigned standard uncertainty and p is the number of laboratories. Note that the assigned expanded uncertainty for each individual laboratory was calculated using the same equation with p replaced by n, the number of measurements ($n = 15$).

In traditional statistics, this expanded uncertainty, U, would be similar to a 95% confidence limit (i.e., twice the standard deviation).

Although the present study is not a proficiency test, the confidence degree for each individual laboratory was assessed by calculating the E_n number, a performance statistic typically used in measurement comparison schemes and described in the ISO 13528 and ISO 17043 recommendations, using:

$$E_n = \frac{\bar{\bar{y}} - \mu}{\sqrt{U_{lab}^2 + U_{ref}^2}}$$

where μ is the reference target value, U_{lab} is the uncertainty in a participant's result and U_{ref} is the uncertainty from the reference provider's assigned value.

Note that the individual U_{lab} values and the U_{lab} for the compilation are calculated by combining measurement uncertainties (type B bias).

We used a critical value of 1 with the E_n numbers. When E_n were < 1, we considered the results compatible (good performance) and when E_n were > 1, we considered them inconsistent within uncertainties. In the present study, this proficiency test is only used with the certified mass fraction values provided by the NRC-CNRC.

All reported means and uncertainties (for both the compiled and individual mass fraction data) were therefore calculated using robust statistical methods and are discussed without outlier exclusion. Note that the calculation based on individual means lead to very small expanded uncertainties; we decided therefore to consider all measurements as a single dataset and made the calculation on that dataset. For simplification in the rest of the text, we designate as “mean” this robust MAD for individual and compiled data.

Results and discussion

Certified values

First, measurements of the SLRS-5 batch were made in order to check the analytical capabilities of four of the participants.

SLRS-5: Results are reported in Table 2. As this batch is now out of stock, participants use it sparingly. Moreover, two of the four laboratories reported fewer than 15 replicates (n = 5 for all elements at Clermont laboratory, and $3 \le n \le 8$, depending on the element, at LEGOS). Nevertheless, the reported means are in good agreement with the certified ranges (*cf*. E_n compilation scores in Table 2). Values for Be, Co and Sb are only indicative (without uncertainty) and E_n scores could not be calculated for these elements.

Despite the good performances observed, significant variation in Cd (+31%) was observed. It should be noted that Cd mass fractions are very low. The laboratories also chose different Cd masses (111,112 or 114). The observed differences can probably be explained by inadequate calibration or by the correction or absence of a correction for certain interferences such as MoO^+ or Ar_2O_2 for this element.

Thus, in the case of significant variation (> 20%) or very low mass fraction (as in the case of Cd), individual results have to be considered first rather than the compiled mass fraction. The combined expanded uncertainty is, therefore, biased and underestimated because the associated measurements errors are difficult to quantify.

SLRS-6: For the new river water batch SLRS-6, individual and compiled data are reported for 8 participants in Table 3. Concentrations range from 0.0063 (Cd) to 2760 µg l^{-1} (Na). For the compiled data, all values fall within the certified expanded uncertainties, with relative values ranging from 2.4% for Ca to 22.6% for Cd. Furthermore, all E_n scores show satisfactory performance for the compiled values (Table 3). As with the SLRS-5 batch, a small but significant difference in Cd mass fraction is observed (+17%).

Concerning the results for individual laboratories, more than 80% of the values obtained for certified elements were within the range of the NRC-CNRC expanded uncertainties for SLRS-5 and SLRS-6. Moreover, all compilation data fall within the range of the certified expanded uncertainties for SLRS-5 and SLRS-6 batches and all E_n numbers were < 1. This indicates the proficiency of the participating laboratories and suggests that they can propose results for uncertified elements.

Uncertified values

SLRS-5: Table 4a, b and Appendix B show compiled data for SLRS-5 and robust mean mass fractions obtained by the laboratories with expanded uncertainty *U* for uncertified elements. In the following sections, these values are compared with those proposed by Yeghicheyan *et al.* (2013), Heimburger *et al.* (2013) and Rousseau *et al.* (2013).

- Rare earth elements. All mass fractions are in agreement with the range proposed in the literature (Table 4a). The REE patterns for the compilation and values proposed by Yeghicheyan *et al*. (2013), Heimburger *et al*. (2013) and Rousseau *et al*. (2013) are presented in Figure 1.

Note that, with the exception of the light REEs (LREEs: La to Nd) from Rousseau *et al.* (2013), the mass fractions obtained by Heimburger *et al.* (2013) and Rousseau *et al.* (2013) are slightly lower than the present compilation (Table 4a and Figure 1).

The differences are less than 4%. Slightly lower mass fractions of heavy REEs (HREEs), notably Lu (Figure 1), were found during the course of these new measurements.

The higher Eu mass fraction of the compilation (6.5 ng l^{-1}) compared with the literature 6.1, 5.6 and 5.9 ng l^{-1}) is mainly due to the higher value obtained by the Nancy laboratory (Appendix B).

Imperfect oxyhydroxide interference corrections (notably, from Ce and Ba on middle REE and middle REE on heavy REE) likely explain these discrepancies. The choice of mass or the calibration methods used might also contribute to the observed discrepancies.

- Other elements. Figure 2 compares this compilation with the mass fractions proposed by Yeghicheyan *et al.* (2013) and Heimburger *et al.* (2013) for other uncertified elements (Table 4b). Only the compiled values obtained from at least three participants are discussed here. The other values are given for information. Discrepancies of greater than ± 20% (grey area) between this compilation and the literature values were observed for Ge (+42%), Nb (+41% or +44%), Th (-143% and -200%) and W (-41%).

Note that expanded uncertainties in some cases reach as high as 100%, as is the case for Ge and Th, which have proposed values of 0.011 ± 0.011 μg l^{-1} and 0.0045 ± 0.0054 μg l^{-1}, respectively, in this compilation. Very low mass fractions, close to the instrument detection limits, as well as uncorrected interferences, calibrations and blanks are likely responsible for producing such discrepancies.

SLRS-6: Table 5 summarises the compiled mass fractions for the SLRS-6 batch including individual measurements for each laboratory.

- Rare earth elements. Compiled REE mass fractions vary from 292.7 ng l^{-1} (Ce) to 1.79 ng l^{-1} (Tm) and the relative expanded uncertainty U ranges from 3% (Pr) to 12% (Lu), reflecting homogeneous results between laboratories and techniques. Individual REE patterns normalised to upper crust mass fractions (Taylor and McLennan 1985) are reported in Figure 3a for the complied REE pattern and in Figures 3b, 3c from five or four individual laboratories respectively. Some differences in mass fraction are observed for Gd (Rio and Nancy showing the two extreme values) and HREEs such as Er, (Montpellier), Eu, Tm and Lu (Perpignan), and Dy (Bondy) relative to the compiled data. The sources of these discrepancies are not easy to identify, though imperfect oxyhydroxide interference corrections might be assumed to be involved. Despite these variations, and given the use of robust statistics in this study, we decided not to exclude any data from the compilation. Patterns display enrichment in light REEs (LREEs) relative to heavy REEs as well as a large negative Ce anomaly.

- Other elements. Twenty-three uncertified elements, including silicon, were also characterised in SLRS-6. The compiled results and individual laboratory data are reported in Table 6. Twelve elements (B, Cs, Ga, Ge, Li, Rb, Si, Th, Ti, Tl, Y and Zr) were determined by at least three different laboratories or methods (in bold in Table 6). All of the available data were used to calculate the compiled values, including the complementary data by ICP-OES for Si.

Mass fractions range from 0.0046 to 2231 μg l^{-1} (for Cs and Si respectively). The associated expanded uncertainties are not proportional to the mass fraction; low mass fractions are not systematically associated with a high expanded relative uncertainty. Thus, Ga, Ge, Th and Tl show relatively high relative expanded uncertainties of 34 to 70% in the 0.01 μg l^{-1} range whereas the lowest mass fraction of Cs (0.0045 μg l^{-1}) is characterised by a U value of 10%. Even though the three laboratories used the same ^{71}Ga isotope, the isobaric interferences from sulfide, argide and chloride species, as described by May and Weidmeyer (1998), are perhaps not well estimated. The use of a high resolution ICP-MS at the LEGOS laboratory (Ga = 0.0059 ± 0.0002 μg l^{-1}) suggests that the Nancy and Perpignan values (Ga = 0.017 ± 0.002 and 0.0093 ± 0.007 μg l^{-1}, respectively) may have been affected by such interferences and are probably not as accurate as the LEGOS determination.

Eleven other trace elements were measured by only one (Bi, Hf, Re, Rh, Sc, Se, W) or two (Nb, P, S, Sn) laboratories (indicated in italics in Table 6). Note that relative expanded uncertainties are very high for Bi (79.1%), Nb (70.5%), Rh (95.5%) and Sn (82.6%) with mass fractions below or close to the ng l^{-1} level. When mass fractions are in the μg l^{-1} range, relative expanded uncertainties tend to be less than 20% (P = 5.18 μg l^{-1} ± 19.6%, S = 1790 μg l^{-1} ± 7.9%). These last eleven values are only given as indicative mass fractions.

- Sr isotopic ratio. For the Sr isotope measurements of SLRS-6, four 5 ml aliquots from the same bottle were evaporated before purification and measurement. The measured $^{87}Sr/^{86}Sr$ ratios range from 0.712034 to 0.712075, with an mean value of 0.712051 (Table 6), indicating that the batch is slightly more radiogenic than SLRS-5 (0.711011, Yeghicheyan *et al.* 2013). In parallel, Sr and Ca mass fractions are slightly lower than in the SLRS-5 batch (- 24% and -16.5%, respectively) and the Ca/Sr ratio is thus 1% higher. The main contributions to the Sr isotope ratios in rivers are usually defined by two end-members (Wadleight *et al.* 1985 and Palmer and Edmond 1992): limestones, which are easily eroded and are characterised by high strontium mass fractions and low $^{87}Sr/^{86}Sr$ ratios (between 0.706 to 0.709); and silicate rocks, which are more resistant to weathering and have lower strontium contents and more radiogenic $^{87}Sr/^{86}Sr$ ratios (between 0.710 to 0.730). The chemistry of the St Lawrence river is known to be mainly controlled by limestones that have an $^{87}Sr/^{86}Sr$ signature close to 0.709 (Wadleight *et al.* 1985). The higher ratio of 0.712 observed in SLRS-6 could indicate that the contribution from silicate rock is greater in the SLRS-6 batch than it is in the SLRS-5 batch.

SLRS-6 versus SLRS-5

The relative differences between SLRS-5 and SLRS-6 mass fractions are reported in Appendix C. The comparison of the two batches indicates only slight differences in the mass fraction for all elements except Al, Mn, Na and Ti. Mass fractions of these four elements are usually controlled by secondary mineralogical phases such as oxides or chlorides. They are strongly depleted in the SLRS-6 batch, implying variations in redox conditions and lithological background during sampling. Regarding Rh and Re, the large discrepancies that are observed (- 95.5% and + 92% respectively) are questionable as the mass fractions of these elements were close to the instrumental detection limits (1 ng l^{-1}).

Surprisingly, Si, Sc, Ge, Cs, Sn and Y, which mostly represent the detrital fraction, are stable across the two batches even though higher mass fractions might be expected in SLRS-6 given the Sr isotopic results. However, variations in Sr isotopic ratios are more likely driven by another mineralogical phase namely, zircons. Indeed, Zr, Pb, Th and REEs all show some degree of enrichment, from 15 to 50%, in the SLRS-6 river water. In addition, As, Be, Cr, Cu, Ni, Zn, Bi, Nb, Tl and W mass fractions are all higher in SLRS-6 than in SLRS-5, again reflecting a larger detrital contribution in SLRS-6 than in SLRS-5. Mass fractions of the other elements, Ca, Mg, Ga, Mo, Sr, P and S, are lower in SLRS-6 than in SLRS-5.

Conclusions

We reported a compilation of mass fractions of certified and uncertified elements in the natural river water reference material SLRS-6 (NRC-CNRC), measured routinely in nine different laboratories. For all certified elements, our results (provided by eight participating laboratories) are compatible with the certified values. We report REE mass fraction values with relative expanded uncertainties ranging from 3% to 12% (nine laboratories). The Sr isotopic composition of SLRS-6 is also reported (one laboratory).

Twelve elements (B, Cs, Ga, Ge, Li, Rb, Si, Sn, Th, Ti, Tl, Y and Zr) uncertified by NRC-CNRC were analysed by at least three laboratories. Finally, mass fractions of eleven more trace elements (Bi, Hf, Nb, P, R, Rh, S, Sc, Se, Sn and W) were reported (one or two participating laboratories).

In total, this interlaboratory comparison exercise provides mass fractions for twenty-six elements (determined by at least three different laboratories) in addition to the twenty-two elements certified by the manufacturer of the SLRS-6 river water reference material (as well as eleven more elements measured by only one or two laboratories). Such a dataset will undoubtedly be of value for the many ICP-MS environmental laboratories worldwide that use this reference material as a quality control.

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Supporting information

The following supporting information may be found in the online version of this article:

Appendix A. Masses, modes (no gas or He), and resolution (low, medium or high) used by the participating laboratories for ICP-MS, and wavelengths used for ICP-OES. Internal standards are in bold type. Spikes are in bold italics. When several isotopes reported, an mean value was calculated.

Appendix B. Compiled and individual robust mass fractions (in ng l^{-1} for REEs and in µg l^{-1} for the others), expanded uncertainty (*U*) and relative expanded uncertainty (r*U*) of proposed values for the river water certified reference material SLRS-5 per laboratory.

Appendix C. Plot of relative differences between SLRS-5 and SLRS-6 river water batches (%). Comparisons are based on the NRC values for certified elements and this compilation for uncertified elements. $100 \times (1 - [X]_{SLRS\text{-}5} / [X]_{SLRS\text{-}6})$

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Figure captions

Figure 1. Upper crust-normalised REE patterns (mass fraction) of the river water certified reference material SLRS-5 obtained in this work (circles) and values reported by Yeghicheyan *et al.* 2013 (squares), Heimburger *et al.* 2013 (triangles) and Rousseau *et al.* 2013 (diamonds). Errors bars correspond to expanded uncertainty for this study (*U*) and standard deviation for the others (1*s*). Upper crust data from Taylor and McLennan (1985).

Figure 2. Relative differences between compiled data (this work) and values reported by Yeghicheyan *et al.* 2013 (squares) and by Heimburger *et al.* 2013 (triangles) for the SLRS-5 river water certified reference material. Grey area corresponds to ± 20% (this work).

Figure 3. REE patterns of the river water certified reference material SLRS-6 normalised to upper crustal values (Taylor and McLennan 1985): (a) compilation for SLRS-6 (this work); (b) and (c) values from five and four individual laboratories (this work), respectively.

Table 1.

Instruments and procedures in each of the participating laboratories

<table>
<tr><th>Laboratory</th><th colspan="2">Instrument</th><th colspan="2">Methods and introduction systems</th><th colspan="2">Blank with acid medium</th><th>Calibration</th><th>Interference correction</th></tr>
<tr><td>Magmas et Volcans - Clermont Ferrand</td><td>ICP-MS</td><td>Agilent 7500</td><td colspan="2">Direct (all elements), micromist nebuliser and Scott spray chamber</td><td>De-ionised water, purified with a ASD GenPure xCAD system and acidified</td><td>HNO_3 purified by sub-boiling distillation 0.4 mol l^{-1} and HF ultrapur 0.05 mol l^{-1}</td><td>multi elemental without internal standard</td><td></td></tr>
<tr><td>LOCEAN-IRD Bondy</td><td>ICP-MS</td><td>Agilent 7500</td><td colspan="2">Direct (all elements), micromist nebuliser and Scott spray chamber</td><td>De-ionised water purified with a Milli-Q (Millipore) system</td><td>HNO_3 ultrapur 0.28 mol l^{-1}</td><td>multi elemental calibration (8 levels) : 0,2,5,10,50,100,200,400 ng l^{-1}</td><td></td></tr>
<tr><td rowspan="2">AETE ISO Platform OSU OREME Montpellier</td><td rowspan="2">ICP-MS</td><td rowspan="2">Thermo Scientific iCap Q</td><td colspan="2">direct</td><td rowspan="2">De-ionised water purified with a Milli-Q (Millipore) system</td><td rowspan="2">HNO_3 ultrapur 0.14 mol l^{-1}</td><td>multi elemental with internal standards Be, Sc, Ge, Rh, Ir</td><td>No interference correction, Kinetic Energy Discrimination Mode with CeO/Ce < 1%</td></tr>
<tr><td colspan="2">Cyclonic Spray Chamber, PFA ST Nebuliser 400 µl min^{-1}</td><td>0, 1, 5, 10 µg l^{-1}</td><td></td></tr>
<tr><td rowspan="2">CEFREM-Perpignan</td><td rowspan="2">ICP-MS</td><td rowspan="2">Agilent 7700x</td><td colspan="2">direct</td><td rowspan="2">De-ionised water purified with a Milli-Q (Millipore) system</td><td rowspan="2">HNO_3 0.28 mol l^{-1}</td><td>multi elemental with internal standards Sc, Ge, Re</td><td rowspan="2"></td></tr>
<tr><td colspan="2">Micromist nebuliser Scott quartz spray chamber</td><td>five standards from 0.01 to 500 µg l^{-1}</td></tr>
<tr><td rowspan="2">OMP-Toulouse</td><td rowspan="2">ICP-MS</td><td rowspan="2">Agilent 7500Ce</td><td colspan="2">direct</td><td rowspan="2">De-ionised water purified with a Milli-Q (Millipore) system</td><td>HNO_3 doubly purified by sub-boiling distillation</td><td>multi elemental</td><td rowspan="2"></td></tr>
<tr><td colspan="2">Micromist nebuliser and thermostated spray chamber</td><td>HNO_3 0.35 mol l^{-1}</td><td>from 2 µg to 100 mg l^{-1} (depends on the element) for dil 0 and diluted 3/10/30 and 100 times</td></tr>
<tr><td rowspan="2">Géosciences - Rennes</td><td rowspan="2">ICP-MS</td><td rowspan="2">Agilent 7700x</td><td colspan="2">direct</td><td rowspan="2">De-ionised water purified with a Milli-Q (Millipore) system</td><td rowspan="2">HNO_3 purified by sub-boiling distillation - All samples: 0.37 mol l^{-1} nitric acid - Acidification SLRS-6- 0.37 mol l^{-1} nitric acid</td><td rowspan="2">multi-elemental calibration (7 levels) with online internal standards Rh-Re</td><td rowspan="2">Correction oxide on REE measurements:
Eu(153) corrected from ^{137}BaO interference
Tb(159) corrected from ^{143}NdO interference
Dy(163) corrected from ^{147}SmO interfrence
Ho(165) corrected from ^{149}SmO intreference
Er(166) corrected from ^{150}SmO interference
Yb(174) corrected from ^{158}GdO interference
Lu(175) corrected from ^{159}TbO interference</td></tr>
<tr><td colspan="2">Micro-Mist nebuliser and Scott spray chamber</td></tr>
<tr><td rowspan="2">UFF-Niteroi "Rio"</td><td rowspan="2">ICP-MS</td><td rowspan="2">Thermo Scientific X-Series II</td><td>2 to 3 fold preconcentration by evaporation / dissolution on hot plate for REE elements</td><td>Glass nebuliser impact bead spray chamber</td><td rowspan="2">De-ionised water purified with a Milli-Q (Millipore) system</td><td rowspan="2">Bi-distilled HNO_3 0.28 mol l^{-1}</td><td>1 point REE solution (0.5 µg l^{-1}) plus a triple ^{146}Nd (97.35%), ^{151}Eu (97.70 %) and ^{172}Yb (95.84%) spike solution</td><td rowspan="2">Aries *et al*. (2000)</td></tr>
<tr><td>Direct (other elements)</td><td>Glass nebuliser impact bead spray chamber + Colision Cell (CCT) with He Gas</td><td>In house multi elementar 5 points calibration curve for other elements</td></tr>
<tr><td>LEGOS-OMP Toulouse</td><td>HR-ICP-MS</td><td>Thermo Element XR (from the Midi Pyrenees Observatory)</td><td colspan="2">Micromist nebuliser with mini-SIS spray chamber (cyclonic +Scott), at ~ 0.3 ml min^{-1}</td><td>De-ionised water purified with a Milli-Q (Millipore) system</td><td>Bi-distilled HNO_3 0.32 mol l^{-1}</td><td>multi elemental (same as OMP; 3 levels) with In and Re as internal standards.</td><td>Aries *et al*. (2000) for REE; MoO for ^{111}Cd; Sr^{2+} for ^{43}Ca and ^{44}Ca; TiO for ^{66}Zn</td></tr>
<tr><td rowspan="5">SARM-Nancy</td><td rowspan="2">ICP-MS</td><td rowspan="2">Agilent 7700x</td><td colspan="2">direct</td><td rowspan="2">De-ionised water purified with a PureLab Option-Q (Elga) system</td><td rowspan="2">HNO_3 ultrapur 0.28 mol l^{-1}</td><td rowspan="2">multi elemental with linear correction post-treatment</td><td rowspan="2">specific correction for masses 47,51,60,63,66,115,139,140,146,147,151,157,159,163,165,166,169,175 or He mode with CeO/Ce < 1%</td></tr>
<tr><td colspan="2">OpalMist nebuliser and Scott spray chamber</td></tr>
<tr><td rowspan="2">ICP-OES</td><td rowspan="2">Thermo Scientific iCap 6500</td><td colspan="2">direct</td><td rowspan="2">De-ionised water purified with an Aquadem (Véolia) system</td><td rowspan="2">Superpur HNO_3 0.28 mol l^{-1}</td><td rowspan="2">multi elemental 6-point calibration curve</td><td rowspan="2"></td></tr>
<tr><td colspan="2">OpalMist nebuliser and cyclonic spray chamber with radial plasma viewing</td></tr>
<tr><td>TIMS</td><td>Thermo Scientific Triton Plus</td><td colspan="2">5 ml evaporated and eluted on Sr Spec resin (Eichrom)</td><td>De-ionised water purified with a PureLab Option-Q (Elga) system</td><td>HNO_3 ultrapur 0.28 mol l^{-1}</td><td>NBS 987</td><td>Internal normalisation wih exponential law $^{86}Sr/^{87}Sr$ = 0.1194</td></tr>
</table>

Table 2.
Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and E_n score of certified elements in the river water certified reference material SLRS-5

Certified values				Compilation					E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	***p***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**49.5**	5	10.1	43	4	**49.3**	4.2	8.5	0.04	Yes
As	**0.413**	0.039	9.4	39	4	**0.384**	0.046	11.9	0.48	Yes
Ba	**14**	0.5	3.6	43	4	**14.6**	1.0	6.9	0.51	Yes
Be	**0.005**			43	4	**0.0053**	0.0015	27.4	0.20	Yes
Ca	**10500**	400	3.8	38	3	**10341**	509	4.9	0.25	Yes
Cd	**0.006**	0.0014	23.3	38	3	**0.0079**	0.0019	24.5	0.78	Yes
Co	**0.05**			43	4	**0.054**	0.005	8.8	0.76	Yes
Cr	**0.208**	0.023	11.1	43	4	**0.211**	0.032	15.3	0.07	Yes
Cu	**17.4**	1.3	7.5	35	3	**18.5**	1.5	8.3	0.56	Yes
Fe	**91.2**	5.8	6.4	43	4	**90.2**	4.7	5.2	0.13	Yes
K	**839**	36	4.3	37	3	**862**	62	7.2	0.32	Yes
Mg	**2540**	160	6.3	43	4	**2701**	312	11.5	0.46	Yes
Mn	**4.33**	0.18	4.2	43	4	**4.29**	0.28	6.5	0.12	Yes
Mo	**0.27**	0.04	14.8	43	4	**0.209**	0.015	7.3	0.21	Yes
Na	**5380**	100	1.9	38	3	**5636**	577	10.2	0.44	Yes
Ni	**0.476**	0.064	13.4	38	4	**0.475**	0.035	7.4	0.01	Yes
Pb	**0.081**	0.006	7.4	43	4	**0.082**	0.011	13.8	0.08	Yes
Sb	**0.3**			43	4	**0.306**	0.029	9.6	0.21	Yes
Sr	**53.6**	1.3	2.4	43	4	**53.3**	1.9	3.5	0.14	Yes
U	**0.093**	0.006	6.5	42	4	**0.091**	0.012	12.8	0.76	Yes
V	**0.317**	0.033	10.4	43	4	**0.324**	0.024	7.4	0.17	Yes
Zn	**0.845**	0.1	11.2	34	3	**0.894**	0.152	17.1	0.27	Yes

n number of results
p number of laboratories

Table 2.

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and E_n score of certified elements in the river water certified reference material SLRS-5

Certified values				Clermont-Ferrand				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**49.5**	5	10.1	5	45.5	3.3	7.2	0.67	Yes
As	**0.413**	0.039	9.4	5	0.428	0.008	1.8	0.39	Yes
Ba	**14**	0.5	3.6	5	13.8	0.4	3.0	0.35	Yes
Be	**0.005**			5	0.0052	0.0003	5.0		
Ca	**10500**	400	3.8						
Cd	**0.006**	0.0014	23.3						
Co	**0.05**			5	0.056	0.003	4.7		
Cr	**0.208**	0.023	11.1	5	0.243	0.016	6.4	1.24	**No**
Cu	**17.4**	1.3	7.5	5	18.5	0.5	2.5	0.78	Yes
Fe	**91.2**	5.8	6.4	5	92.0	1.4	1.5	0.14	Yes
K	**839**	36	4.3						
Mg	**2540**	160	6.3	5	2602	98	3.8	0.3	Yes
Mn	**4.33**	0.18	4.2	5	4.49	0.09	1.9	0.78	Yes
Mo	**0.27**	0.04	14.8	5	0.215	0.003	1.4	1.38	**No**
Na	**5380**	100	1.9						
Ni	**0.476**	0.064	13.4	5	0.485	0.046	9.6	0.11	Yes
Pb	**0.081**	0.006	7.4	5	0.059	0.007	11.5	2.38	**No**
Sb	**0.3**			5	0.294	0.004	1.5		
Sr	**53.6**	1.3	2.4	5	53.3	1.4	2.7	0.16	Yes
U	**0.093**	0.006	6.5	5	0.078	0.001	1.1	2.45	**No**
V	**0.317**	0.033	10.4	5	0.363	0.016	4.5	1.24	**No**
Zn	**0.845**	0.1	11.2						

n number of results

Table 2 (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and E_n score of certified elements in the river water certified reference material SLRS-5

Certified values				OMP-Toulouse				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compatibility**
Al	**49.5**	5	10.1	15	49.1	1.2	2.5	0.07	Yes
As	**0.413**	0.039	9.4	15	0.36	0.00	1.2	1.34	**No**
Ba	**14**	0.5	3.6	15	14.1	0.2	1.8	0.10	Yes
Be	**0.005**			15	0.0050	0.0007	14.4		
Ca	**10500**	400	3.8	15	10598	395	3.7	0.17	Yes
Cd	**0.006**	0.0014	23.3	15	0.0076	0.0005	6.7	1.06	**No**
Co	**0.05**			15	0.053	0.001	1.4		
Cr	**0.208**	0.023	11.1	15	0.216	0.009	4.2	0.30	Yes
Cu	**17.4**	1.3	7.5	15	18.8	0.7	3.9	0.96	Yes
Fe	**91.2**	5.8	6.4	15	90.1	1.4	1.5	0.18	Yes
K	**839**	36	4.3	15	862	30	3.5	0.50	Yes
Mg	**2540**	160	6.3	15	2676	250	9.3	0.46	Yes
Mn	**4.33**	0.18	4.2	15	4.32	0.13	2.9	0.03	Yes
Mo	**0.27**	0.04	14.8	15	0.200	0.003	1.7	1.74	**No**
Na	**5380**	100	1.9	15	5942	353	5.9	1.53	**No**
Ni	**0.476**	0.064	13.4	15	0.476	0.014	2.9	0.01	Yes
Pb	**0.081**	0.006	7.4	15	0.083	0.003	3.8	0.31	Yes
Sb	**0.3**			15	0.284	0.004	1.3		
Sr	**53.6**	1.3	2.4	15	53.0	0.6	1.1	0.43	Yes
U	**0.093**	0.006	6.5	15	0.086	0.001	1.4		
V	**0.317**	0.033	10.4	15	0.310	0.007	2.3	0.21	Yes
Zn	**0.845**	0.1	11.2	15	0.87	0.03	3.6	0.24	Yes

n number of results

Table 2 (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and E_n score of certified elements in the river water certified reference material SLRS-5

Certified values				E_n score		LEGOS-Toulouse				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**49.5**	5	10.1	0.07	Yes	8	51.3	2.5	4.8	0.32	Yes
As	**0.413**	0.039	9.4	1.34	**No**	4	0.429	0.069	16.1	0.20	Yes
Ba	**14**	0.5	3.6	0.10	Yes	8	14.3	0.2	1.6	0.53	Yes
Be	**0.005**					8	0.0064	0.0006	8.9		
Ca	**10500**	400	3.8	0.17	Yes	8	10259	248	2.4	0.51	Yes
Cd	**0.006**	0.0014	23.3	1.06	**No**	8	0.0076	0.0012	15.5	0.88	Yes
Co	**0.05**					8	0.057	0.006	10.7		
Cr	**0.208**	0.023	11.1	0.30	Yes	8	0.230	0.008	3.6	0.92	Yes
Cu	**17.4**	1.3	7.5	0.96	Yes						
Fe	**91.2**	5.8	6.4	0.18	Yes	8	89.8	2.7	3.0	0.22	Yes
K	**839**	36	4.3	0.50	Yes	7	824	44	5.3	0.26	Yes
Mg	**2540**	160	6.3	0.46	Yes	8	2720	407	15.0	0.41	Yes
Mn	**4.33**	0.18	4.2	0.03	Yes	8	4.22	0.11	2.6	0.51	Yes
Mo	**0.27**	0.04	14.8	1.74	**No**	8	0.218	0.014	6.6	1.21	**No**
Na	**5380**	100	1.9	1.53	**No**	8	5243	462	8.8	0.29	Yes
Ni	**0.476**	0.064	13.4	0.01	Yes	3	0.507	0.025	4.9	0.44	Yes
Pb	**0.081**	0.006	7.4	0.31	Yes	8	0.078	0.005	6.5	0.38	Yes
Sb	**0.3**					8	0.321	0.020	6.1		
Sr	**53.6**	1.3	2.4	0.43	Yes	8	53.9	0.9	1.7	0.21	Yes
U	**0.093**	0.006	6.5			7	0.090	0.004	4.9		
V	**0.317**	0.033	10.4	0.21	Yes	8	0.324	0.019	6.0	0.17	Yes
Zn	**0.845**	0.1	11.2	0.24	Yes	4	0.87	0.04	5.1	0.26	Yes

n number of results

Table 2 (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (*U*), relative expanded uncertainty (r*U*) and E_n score of certified elements in the river water certified reference material SLRS-5

Certified values				Nancy				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**49.5**	5	10.1	15	49.3	2.3	4.8	0.04	Yes
As	**0.413**	0.039	9.4	15	0.387	0.022	5.7	0.57	Yes
Ba	**14**	0.5	3.6	15	15.3	0.2	1.4	2.43	**No**
Be	**0.005**			15	0.005	0.001	15.1		
Ca	**10500**	400	3.8	15	10258	131	1.3	0.58	Yes
Cd	**0.006**	0.0014	23.3	15	0.008	0.001	12.8	1.28	**No**
Co	**0.05**			15	0.053	0.004	6.8		
Cr	**0.208**	0.023	11.1	15	0.188	0.009	4.6	0.80	Yes
Cu	**17.4**	1.3	7.5	15	18.2	0.8	4.3	0.52	Yes
Fe	**91.2**	5.8	6.4	15	91.6	4.9	5.3	0.05	Yes
K	**839**	36	4.3	15	877	23	2.6	0.88	Yes
Mg	**2540**	160	6.3	15	2748	35	1.3	1.27	**No**
Mn	**4.33**	0.18	4.2	15	4.22	0.17	4.0	0.44	Yes
Mo	**0.27**	0.04	14.8	15	0.212	0.007	3.4	1.44	**No**
Na	**5380**	100	1.9	15	5593	66	1.2	1.78	**No**
Ni	**0.476**	0.064	13.4	15	0.467	0.018	3.8	0.14	Yes
Pb	**0.081**	0.006	7.4	15	0.090	0.006	6.3	1.07	**No**
Sb	**0.3**			15	0.325	0.008	2.6		
Sr	**53.6**	1.3	2.4	15	53.1	1.5	2.7	0.24	Yes
U	**0.093**	0.006	6.5	15	0.101	0.003	3.1		
V	**0.317**	0.033	10.4	15	0.328	0.006	1.8	0.34	Yes
Zn	**0.845**	0.1	11.2	15	0.95	0.11	11.2	0.75	Yes

n number of results

Table 3.

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and En score of certified elements in the river water certified reference material SLRS-6

certified values				Compilation					E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	***p***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**33.8**	2.2	6.5	105	7	33.4	1.0	3.0	0.15	Yes
As	**0.57**	0.08	14.0	105	7	0.56	0.03	5.8	0.06	Yes
Ba	**14.28**	0.48	3.4	117	8	14.1	0.4	2.9	0.21	Yes
Be	**0.0066**	0.0022	33.3	75	5	0.0066	0.0011	16.5	0.01	Yes
Ca	**8760**	200	2.3	102	7	8611	206	2.4	0.52	Yes
Cd	**0.0063**	0.0014	22.2	90	6	0.0074	0.0017	22.6	0.51	Yes
Co	**0.053**	0.012	22.6	120	8	0.055	0.003	5.6	0.14	Yes
Cr	**0.252**	0.012	4.8	119	8	0.247	0.012	5.0	0.31	Yes
Cu	**23.9**	1.8	7.5	105	7	24.7	0.6	2.6	0.43	Yes
Fe	**84.3**	3.6	4.3	120	8	82.1	2.7	3.3	0.49	Yes
K	**651**	54	8.3	96	7	629	24	3.9	0.38	Yes
Mg	**2133**	58	2.7	111	8	2132	72	3.4	0.01	Yes
Mn	**2.12**	0.1	4.7	120	8	2.14	0.06	2.8	0.21	Yes
Mo	**0.215**	0.018	8.4	105	7	0.196	0.018	9.1	0.75	Yes
Na	**2760**	220	8.0	85	6	2735	128	4.7	0.10	Yes
Ni	**0.616**	0.022	3.6	119	8	0.608	0.028	4.6	0.23	Yes
Pb	**0.17**	0.026	15.3	105	7	0.166	0.013	8.1	0.15	Yes
Sb	**0.3372**	0.0058	1.7	85	7	0.335	0.010	3.1	0.18	Yes
Sr	**40.66**	0.32	0.8	120	8	41.03	0.97	2.4	0.37	Yes
U	**0.0698**	0.0034	4.9	105	8	0.067	0.003	4.5	0.54	Yes
V	**0.351**	0.006	1.7	120	8	0.361	0.014	3.7	0.65	Yes
Zn	**1.76**	0.12	6.8	90	6	1.78	0.11	5.9	0.13	Yes

n number of results

p number of laboratories

Table 3. (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and En score of certified elements in the river water certified reference material SLRS-6

certified values				Clermont-Ferrand				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**33.8**	2.2	6.5						
As	**0.57**	0.08	14.0	15	0.59	0.01	1.4	0.26	Yes
Ba	**14.28**	0.48	3.4	15	13.5	0.1	1.0	1.55	**No**
Be	**0.0066**	0.0022	33.3	15	0.0066	0.0003	4.6	0.01	Yes
Ca	**8760**	200	2.3						
Cd	**0.0063**	0.0014	22.2						
Co	**0.053**	0.012	22.6	15	0.055	0.001	1.5	0.18	Yes
Cr	**0.252**	0.012	4.8	15	0.250	0.005	1.9	0.13	Yes
Cu	**23.9**	1.8	7.5	15	25.2	0.3	1.4	0.73	Yes
Fe	**84.3**	3.6	4.3	15	79.2	1.3	1.6	1.33	**No**
K	**651**	54	8.3						
Mg	**2133**	58	2.7	15	2128	43	2.0	0.07	Yes
Mn	**2.12**	0.1	4.7	15	2.19	0.04	1.6	0.64	Yes
Mo	**0.215**	0.018	8.4	15	0.184	0.003	1.7	1.69	**No**
Na	**2760**	220	8.0						
Ni	**0.616**	0.022	3.6	15	0.593	0.019	3.1	0.81	Yes
Pb	**0.17**	0.026	15.3	15	0.144	0.003	2.2	0.98	Yes
Sb	**0.3372**	0.0058	1.7	15	0.332	0.004	1.1	0.72	Yes
Sr	**40.66**	0.32	0.8	15	39.85	0.49	1.2	1.38	**No**
U	**0.0698**	0.0034	4.9	15	0.0623	0.0014	2.2	2.04	**No**
V	**0.351**	0.006	1.7	15	0.368	0.008	2.1	1.74	**No**
Zn	**1.76**	0.12	6.8						

n number of results

Table 3. (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (*U*), relative expanded uncertainty (r*U*) and En score of certified elements in the river water certified reference material SLRS-6

certified values				Montpellier				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compatibility**
Al	**33.8**	2.2	6.5	15	32.6	0.4	1.2	0.53	Yes
As	**0.57**	0.08	14.0	15	0.56	0.01	2.1	0.14	Yes
Ba	**14.28**	0.48	3.4	12	14.8	0.1	0.9	1.07	**No**
Be	**0.0066**	0.0022	33.3						
Ca	**8760**	200	2.3	15	8606	140	1.6	0.63	Yes
Cd	**0.0063**	0.0014	22.2	15	0.0081	0.0004	5.2	1.25	**No**
Co	**0.053**	0.012	22.6	15	0.055	0.001	1.5	0.16	Yes
Cr	**0.252**	0.012	4.8	14	0.250	0.004	1.6	0.18	Yes
Cu	**23.9**	1.8	7.5	15	24.8	0.3	1.3	0.48	Yes
Fe	**84.3**	3.6	4.3	15	82.0	1.4	1.7	0.59	Yes
K	**651**	54	8.3	15	622	7	1.2	0.54	Yes
Mg	**2133**	58	2.7	15	2014	21	1.0	1.93	**No**
Mn	**2.12**	0.1	4.7	15	2.15	0.03	1.4	0.32	Yes
Mo	**0.215**	0.018	8.4	15	0.216	0.004	1.9	0.04	Yes
Na	**2760**	220	8.0	10	2584	42	1.6	0.78	Yes
Ni	**0.616**	0.022	3.6	14	0.597	0.009	1.6	0.81	Yes
Pb	**0.17**	0.026	15.3	15	0.165	0.005	2.9	0.21	Yes
Sb	**0.3372**	0.0058	1.7	11	0.358	0.009	2.6	1.85	**No**
Sr	**40.66**	0.32	0.8	15	42.65	0.57	1.3	3.06	**No**
U	**0.0698**	0.0034	4.9	15	0.0715	0.0011	1.6	0.46	Yes
V	**0.351**	0.006	1.7	15	0.375	0.009	2.3	2.23	**No**
Zn	**1.76**	0.12	6.8	15	1.78	0.03	1.6	0.15	Yes

n number of results

Table 3. (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and En score of certified elements in the river water certified reference material SLRS-6

certified values				Perpignan				E_n score	
Element	µg l^{-1}	*U*	r*U* (%)	*n*	mean	*U*	r*U* (%)	E_n	Compati-bility
Al	**33.8**	2.2	6.5	15	33.6	0.5	1.4	0.09	Yes
As	**0.57**	0.08	14.0	15	0.58	0.02	2.7	0.18	Yes
Ba	**14.28**	0.48	3.4	15	14.2	0.2	1.1	0.14	Yes
Be	**0.0066**	0.0022	33.3						
Ca	**8760**	200	2.3	15	8686	132	1.5	0.31	Yes
Cd	**0.0063**	0.0014	22.2	15	0.0103	0.0020	19.1	1.67	**No**
Co	**0.053**	0.012	22.6	15	0.048	0.005	10.7	0.42	Yes
Cr	**0.252**	0.012	4.8	15	0.242	0.006	2.6	0.73	Yes
Cu	**23.9**	1.8	7.5	15	25.2	0.3	1.3	0.72	Yes
Fe	**84.3**	3.6	4.3	15	82.7	0.9	1.1	0.43	Yes
K	**651**	54	8.3	15	637	17	2.7	0.25	Yes
Mg	**2133**	58	2.7	15	2125	30	1.4	0.12	Yes
Mn	**2.12**	0.1	4.7	15	2.18	0.07	3.1	0.53	Yes
Mo	**0.215**	0.018	8.4	15	0.249	0.022	8.8	1.19	**No**
Na	**2760**	220	8.0	15	2691	59	2.2	0.30	Yes
Ni	**0.616**	0.022	3.6	15	0.588	0.022	3.8	0.89	Yes
Pb	**0.17**	0.026	15.3	15	0.182	0.004	2.4	0.46	Yes
Sb	**0.3372**	0.0058	1.7						
Sr	**40.66**	0.32	0.8	15	40.97	0.45	1.1	0.56	Yes
U	**0.0698**	0.0034	4.9	15	0.0661	0.0018	2.7	0.97	Yes
V	**0.351**	0.006	1.7	15	0.366	0.010	2.8	1.23	**No**
Zn	**1.76**	0.12	6.8	15	2.00	0.13	6.3	1.35	**No**

n number of results

Table 3. (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and En score of certified elements in the river water certified reference material SLRS-6

certified values				OMP - Toulouse				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compatibility**
Al	**33.8**	2.2	6.5	15	33.3	1.1	3.4	0.19	Yes
As	**0.57**	0.08	14.0	15	0.52	0.01	2.2	0.66	Yes
Ba	**14.28**	0.48	3.4	15	13.9	0.2	1.2	0.82	Yes
Be	**0.0066**	0.0022	33.3	15	0.0069	0.0011	16.4	0.12	Yes
Ca	**8760**	200	2.3	15	8658	219	2.5	0.34	Yes
Cd	**0.0063**	0.0014	22.2	15	0.0073	0.0010	13.2	0.58	Yes
Co	**0.053**	0.012	22.6	15	0.054	0.002	3.9	0.04	Yes
Cr	**0.252**	0.012	4.8	15	0.244	0.018	7.2	0.39	Yes
Cu	**23.9**	1.8	7.5	15	24.8	1.0	4.2	0.43	Yes
Fe	**84.3**	3.6	4.3	15	81.3	1.9	2.3	0.73	Yes
K	**651**	54	8.3	15	620	42	6.8	0.45	Yes
Mg	**2133**	58	2.7	15	2179	101	4.6	0.39	Yes
Mn	**2.12**	0.1	4.7	15	2.09	0.04	1.7	0.28	Yes
Mo	**0.215**	0.018	8.4	15	0.176	0.003	1.7	2.15	**No**
Na	**2760**	220	8.0	15	2863	238	8.3	0.32	Yes
Ni	**0.616**	0.022	3.6	15	0.630	0.047	7.5	0.28	Yes
Pb	**0.17**	0.026	15.3	15	0.158	0.003	2.0	0.46	Yes
Sb	**0.3372**	0.0058	1.7	15	0.316	0.004	1.4	2.87	**No**
Sr	**40.66**	0.32	0.8	15	40.70	0.45	1.1	0.07	Yes
U	**0.0698**	0.0034	4.9	15	0.0667	0.0007	1.1	0.89	Yes
V	**0.351**	0.006	1.7	15	0.349	0.008	2.4	0.20	Yes
Zn	**1.76**	0.12	6.8	15	1.78	0.05	2.8	0.17	Yes

n number of results

Table 3. (Continued).

Compiled and individual robust mass fractions (μg l^{-1}), expanded uncertainty (*U*), relative expanded uncertainty (r*U*) and En score of certified elements in the river water certified reference material SLRS-6

certified values				Rennes				E_n score	
Element	**μg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**33.8**	2.2	6.5	15	33.6	0.3	0.7	0.11	Yes
As	**0.57**	0.08	14.0	15	0.57	0.01	0.9	0.04	Yes
Ba	**14.28**	0.48	3.4	15	14.3	0.1	0.7	0.14	Yes
Be	**0.0066**	0.0022	33.3	15	0.0063	0.0004	5.7	0.16	Yes
Ca	**8760**	200	2.3	15	8765	68	0.8	0.02	Yes
Cd	**0.0063**	0.0014	22.2	15	0.0065	0.0002	3.1	0.12	Yes
Co	**0.053**	0.012	22.6	15	0.053	0.001	1.7	0.02	Yes
Cr	**0.252**	0.012	4.8	15	0.255	0.003	1.1	0.27	Yes
Cu	**23.9**	1.8	7.5	15	24.3	0.1	0.4	0.21	Yes
Fe	**84.3**	3.6	4.3	15	86.3	0.5	0.5	0.54	Yes
K	**651**	54	8.3	15	642	3	0.4	0.16	Yes
Mg	**2133**	58	2.7	15	2144	12	0.6	0.19	Yes
Mn	**2.12**	0.1	4.7	15	2.15	0.02	1.0	0.32	Yes
Mo	**0.215**	0.018	8.4						
Na	**2760**	220	8.0	15	2759	20	0.7	0.00	Yes
Ni	**0.616**	0.022	3.6	15	0.619	0.009	1.5	0.13	Yes
Pb	**0.17**	0.026	15.3	15	0.165	0.002	1.2	0.20	Yes
Sb	**0.3372**	0.0058	1.7	15	0.337	0.002	0.5	0.09	Yes
Sr	**40.66**	0.32	0.8	15	40.88	0.12	0.3	0.66	Yes
U	**0.0698**	0.0034	4.9	15	0.0688	0.0009	1.4	0.28	Yes
V	**0.351**	0.006	1.7	15	0.358	0.002	0.5	1.08	**No**
Zn	**1.76**	0.12	6.8	15	1.75	0.01	0.6	0.05	Yes

n number of results

Table 3. (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (*U*), relative expanded uncertainty (r*U*) and En score of certified elements in the river water certified reference material SLRS-6

certified values				Rio				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**33.8**	2.2	6.5	15	33.2	0.7	2.1	0.26	Yes
As	**0.57**	0.08	14.0						
Ba	**14.28**	0.48	3.4	15	14.6	0.1	0.5	0.56	Yes
Be	**0.0066**	0.0022	33.3						
Ca	**8760**	200	2.3	12	8208	283	3.4	1.59	**No**
Cd	**0.0063**	0.0014	22.2						
Co	**0.053**	0.012	22.6	15	0.057	0.002	3.9	0.36	Yes
Cr	**0.252**	0.012	4.8	15	0.250	0.006	2.3	0.14	Yes
Cu	**23.9**	1.8	7.5	15	24.5	0.4	1.5	0.31	Yes
Fe	**84.3**	3.6	4.3	15	84.3	1.2	1.4	0.01	Yes
K	**651**	54	8.3	6	630	2	0.3	0.38	Yes
Mg	**2133**	58	2.7	6	2230	12	0.5	1.63	**No**
Mn	**2.12**	0.1	4.7	15	2.11	0.06	2.9	0.04	Yes
Mo	**0.215**	0.018	8.4	15	0.201	0.004	2.1	0.75	Yes
Na	**2760**	220	8.0						
Ni	**0.616**	0.022	3.6	15	0.600	0.016	2.7	0.58	Yes
Pb	**0.17**	0.026	15.3						
Sb	**0.3372**	0.0058	1.7						
Sr	**40.66**	0.32	0.8	15	42.65	0.89	2.1	2.11	**No**
U	**0.0698**	0.0034	4.9						
V	**0.351**	0.006	1.7	15	0.353	0.004	1.3	0.25	Yes
Zn	**1.76**	0.12	6.8						

n number of results

Table 3. (Continued).

Compiled and individual robust mass fractions (μg l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU) and En score of certified elements in the river water certified reference material SLRS-6

certified values				LEGOS-Toulouse				E_n score	
Element	μg l^{-1}	U	rU (%)	n	mean	U	rU (%)	E_n	Compatibility
Al	**33.8**	2.2	6.5	15	35.0	0.8	2.4	0.52	Yes
As	**0.57**	0.08	14.0	15	0.58	0.02	4.0	0.11	Yes
Ba	**14.28**	0.48	3.4	15	14.1	0.1	1.1	0.34	Yes
Be	**0.0066**	0.0022	33.3	15	0.0074	0.0005	6.9	0.37	Yes
Ca	**8760**	200	2.3	15	8506	138	1.6	1.05	**No**
Cd	**0.0063**	0.0014	22.2	15	0.0080	0.0003	4.1	1.15	**No**
Co	**0.053**	0.012	22.6	15	0.053	0.002	2.8	0.02	Yes
Cr	**0.252**	0.012	4.8	15	0.256	0.006	2.2	0.27	Yes
Cu	**23.9**	1.8	7.5						
Fe	**84.3**	3.6	4.3	15	81.0	1.5	1.8	0.84	Yes
K	**651**	54	8.3	15	623	15	2.4	0.50	Yes
Mg	**2133**	58	2.7	15	2149	60	2.8	0.19	Yes
Mn	**2.12**	0.1	4.7	15	2.15	0.03	1.5	0.27	Yes
Mo	**0.215**	0.018	8.4	15	0.190	0.005	2.4	1.34	**No**
Na	**2760**	220	8.0	15	2853	77	2.7	0.40	Yes
Ni	**0.616**	0.022	3.6	15	0.611	0.023	3.8	0.16	Yes
Pb	**0.17**	0.026	15.3	15	0.163	0.004	2.5	0.27	Yes
Sb	**0.3372**	0.0058	1.7	14	0.337	0.005	1.4	0.07	Yes
Sr	**40.66**	0.32	0.8	15	40.97	0.52	1.3	0.51	Yes
U	**0.0698**	0.0034	4.9	15	0.0694	0.0018	2.6	0.10	Yes
V	**0.351**	0.006	1.7	15	0.375	0.008	2.0	2.50	**No**
Zn	**1.76**	0.12	6.8	15	1.86	0.18	9.6	0.46	Yes

n number of results

Table 3. (Continued).

Compiled and individual robust mass fractions (µg l^{-1}), expanded uncertainty (*U*), relative expanded uncertainty (r*U*) and En score of certified elements in the river water certified reference material SLRS-6

certified values				Nancy				E_n score	
Element	**µg l^{-1}**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	**E_n**	**Compati-bility**
Al	**33.8**	2.2	6.5	15	33.2	0.6	1.8	0.26	Yes
As	**0.57**	0.08	14.0	15	0.55	0.04	6.7	0.21	Yes
Ba	**14.28**	0.48	3.4	15	13.8	0.2	1.4	0.83	Yes
Be	**0.0066**	0.0022	33.3	15	0.0060	0.0005	9.1	0.27	Yes
Ca	**8760**	200	2.3	15	8673	107	1.2	0.38	Yes
Cd	**0.0063**	0.0014	22.2	15	0.0044	0.0005	10.4	1.28	**No**
Co	**0.053**	0.012	22.6	15	0.061	0.002	2.9	0.62	Yes
Cr	**0.252**	0.012	4.8	15	0.196	0.008	4.3	3.80	**No**
Cu	**23.9**	1.8	7.5	15	24.2	0.6	2.3	0.18	Yes
Fe	**84.3**	3.6	4.3	15	80.3	2.1	2.6	0.97	Yes
K	**651**	54	8.3	15	630	32	5.1	0.33	Yes
Mg	**2133**	58	2.7	15	2165	28	1.3	0.50	Yes
Mn	**2.12**	0.1	4.7	15	2.12	0.09	4.4	0.02	Yes
Mo	**0.215**	0.018	8.4	15	0.182	0.006	3.2	1.75	**No**
Na	**2760**	220	8.0	15	2692	29	1.1	0.31	Yes
Ni	**0.616**	0.022	3.6	15	0.628	0.016	2.5	0.45	Yes
Pb	**0.17**	0.026	15.3	15	0.186	0.006	3.3	0.59	Yes
Sb	**0.3372**	0.0058	1.7	15	0.339	0.007	1.9	0.22	Yes
Sr	**40.66**	0.32	0.8	15	40.59	0.46	1.1	0.13	Yes
U	**0.0698**	0.0034	4.9	15	0.0660	0.0016	2.4	1.00	**No**
V	**0.351**	0.006	1.7	15	0.343	0.010	3.0	0.64	Yes
Zn	**1.76**	0.12	6.8	15	1.69	0.02	1.1	0.57	Yes

n number of results

Table 4a.

Compiled robust mass fractions for REEs (in ng l^{-1}), expanded uncertainty (*U*), relative expanded uncertainty (r*U*), in the river water certified reference material SLRS-5 (this work), compared with literature values (see Appendix B for details)

	Compilation (ng l^{-1})					Yeghicheyan *et al.* (2013)		
REE	***n***	***p***	**mean**	***U***	**r*U* (%)**	**mean**	***U***	**r*U* (%)**
La	41	4	**204.4**	6.7	3.3	207.2	12.8	6.2
Ce	41	4	**250.0**	9.6	3.8	252.3	59.7	23.7
Pr	41	4	**50.2**	1.2	2.4	49.1	7.2	14.6
Nd	41	4	**190.5**	5.0	2.6	192.1	46.4	24.2
Sm	41	4	**34.4**	1.0	2.9	33.7	4.4	13.1
Eu	34	3	**6.5**	0.2	3.4	6.1	1.1	18.4
Gd	41	4	**25.5**	1.1	4.4	26.7	4.4	16.4
Tb	41	4	**3.7**	0.1	3.5	3.4	0.6	17.7
Dy	41	4	**19.2**	0.6	3.3	19.1	2.0	10.5
Ho	41	4	**3.7**	0.1	3.5	3.7	0.4	11.8
Er	41	4	**10.8**	0.4	3.3	10.9	1.2	11.2
Tm	40	4	**1.5**	0.1	4.4	1.5	0.5	31.3
Yb	41	4	**10.0**	0.4	4.4	10.1	1.6	15.7
Lu	41	4	**1.6**	0.1	4.9	1.7	0.4	22.9

n number of results
p number of laboratories
1*s* standard deviation
% RSD relative standard deviation (per cent)

Table 4a. (Continued).

Compiled robust mass fractions for REEs (in ng l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU), in the river water certified reference material SLRS-5 (this work), compared with literature values (see Appendix B for details)

	Compilation (ng l^{-1})					Heimburger *et al.* (2013)			Rousseau *et al.* (2013)		
REE	***n***	***p***	**mean**	***U***	**r*U* (%)**	**mean**	**1*s***	**% RSD**	**mean**	**1*s***	**% RSD**
La	41	4	**204.4**	6.7	3.3	196.0	11.0	5.6	213.6	9.3	4.3
Ce	41	4	**250.0**	9.6	3.8	236.0	16.0	6.8	254.8	6.1	2.4
Pr	41	4	**50.2**	1.2	2.4	46.9	2.5	5.3	50.3	1.2	2.4
Nd	41	4	**190.5**	5.0	2.6	185.0	20.0	10.8	197.1	4.6	2.3
Sm	41	4	**34.4**	1.0	2.9	32.4	3.3	10.2	33.1	0.2	0.6
Eu	34	3	**6.5**	0.2	3.4	5.6	1.4	25.0	5.9	0.09	1.5
Gd	41	4	**25.5**	1.1	4.4	24.9	3.0	12.0	26.1	0.6	2.4
Tb	41	4	**3.7**	0.1	3.5	3.2	0.6	18.8	3.4	0.11	3.2
Dy	41	4	**19.2**	0.6	3.3	18.2	2.5	13.7	18.9	0.2	1.2
Ho	41	4	**3.7**	0.1	3.5	3.6	0.5	13.9	3.7	0.05	1.4
Er	41	4	**10.8**	0.4	3.3	10.5	1.0	9.5	10.6	0.09	0.8
Tm	40	4	**1.5**	0.1	4.4	1.3	0.3	23.1	1.5	0.02	1.3
Yb	41	4	**10.0**	0.4	4.4	9.3	0.7	7.5	10.1	0.15	1.5
Lu	41	4	**1.6**	0.1	4.9	1.5	0.2	13.3	1.6	0.02	1.2

n number of results
p number of laboratories
1*s* standard deviation
% RSD relative standard deviation (per cent)

Table 4a. (Continued).

Compiled robust mass fractions for REEs (in ng l^{-1}), expanded uncertainty (U), relative expanded uncertainty (rU), in the river water certified reference material SLRS-5 (this work), compared with literature values (see Appendix B for details)

	Compilation (µg l^{-1})					Yeghicheyan *et al.* (2013)			Heimburger *et al.* (2013)		
	n	***p***	**mean**	***U***	**r*U* (%)**	**mean**	***U***	**r*U* (%)**	**mean**	**1*s***	**% RSD**
B	15	1	**8.18**	3.80	46.5	6.56	0.91	13.9	7.46	0.58	7.8
Bi	28	2	**0.0007**	0.0008	114.5	0.0009	0.0003	38.0	0.00086	0.00016	18.6
Cs	38	3	**0.0044**	0.0009	19.5	0.0049	0.0019	38.5	0.0057	0.0013	22.8
Ga	36	3	**0.017**	0.007	40.2	0.021	0.014	67.0	0.015	0.001	6.7
Ge	34	3	**0.011**	0.011	96.9	0.015	0.014	92.9	0.0063	0.0038	60.3
Li	23	2	**0.46**	0.09	20.4	0.45	0.09	20.4	0.50	0.13	26.0
Nb	38	3	**0.0065**	0.0048	74.3	*0.0036*	*0.0016*	*44.4*	0.0038	0.0006	15.8
P	23	2	**6.08**	5.25	86.2	*8.19*	*3.40*	*41.5*	13.1	2.2	16.8
Rb	38	3	**1.24**	0.11	8.6	1.24	0.37	30.0	1.23	0.08	6.5
Re	15	1	**0.067**	0.010	14.7	*0.066*	*0.012*	*18.2*			
Rh	15	1	**0.0011**	0.0005	47.7	0.0009	0.0015	161.0			
S	15	1	**2466**	55	2.2	2368	244	10.3			
Sc	15	1	**0.317**	0.082	25.9	0.28	0.46	163.5	0.0087	0.0015	17.2
Si	38	3	**2077**	218	10.5	1922	165	8.6	1881	99	5.3
Sn	15	1	**0.0095**	0.0060	63.3	0.29	0.44	150.9	0.0057	0.0005	8.8
Th	38	3	**0.0045**	0.0054	119.3	0.0136	0.0033	24.1	0.011	0.004	36.4
Ti	38	3	**1.88**	0.44	23.4	1.86	0.34	18.3	2.28	0.05	2.2
Tl	38	3	**0.0043**	0.0017	39.5	0.0039	0.0024	61.7	0.0042	0.0007	16.7
W	23	2	**0.010**	0.003	31.5	0.014	0.018	125.1			
Y	38	3	**0.109**	0.008	7.0	0.112	0.009	8.3	0.120	0.010	8.3
Zr	30	2	**0.030**	0.007	22.0	0.02	0.03	113.1			

n number of results
p number of laboratories
1*s* standard deviation
% RSD relative standard deviation (per cent)

Table 5.

Compiled and individual robust mass fractions of rare earth elements (in ng l^{-1}), with the corresponding expanded uncertainty (*U*) and relative expanded uncertainty (r*U*) in the river water certified reference material SLRS-6

	Compilation (ng l^{-1})					Clermont-Ferrand				Bondy			
	n	*p*	mean	*U*	r*U* (%)	*n*	mean	*U*	r*U* (%)	*n*	mean	*U*	r*U* (%)
La	135	9	**248.3**	12.1	4.9	15	**231.9**	4.5	2.0	15	**273.0**	4.6	1.7
Ce	135	9	**292.7**	15.1	5.1	15	**273.4**	4.5	1.7	15	**325.8**	5.9	1.8
Pr	135	9	**59.1**	1.9	3.2	15	**55.4**	0.9	1.7	15	**65.0**	1.2	1.9
Nd	135	9	**227.8**	9.4	4.1	15	**214.3**	3.9	1.8	15	**261.1**	6.1	2.3
Sm	135	9	**39.5**	1.7	4.3	15	**36.5**	0.8	2.3	15	**44.5**	1.3	2.9
Eu	120	8	**7.26**	0.35	4.9	15	**7.0**	0.2	3.5	15	**7.3**	0.2	2.4
Gd	135	9	**31.6**	2.5	8.0	15	**28.9**	0.9	3.2	15	**32.7**	0.6	1.7
Tb	135	9	**4.07**	0.27	6.5	15	**3.8**	0.2	4.1	15	**4.0**	0.0	0.0
Dy	135	9	**21.9**	1.1	5.1	15	**20.1**	0.7	3.4	15	**25.6**	0.3	1.2
Ho	135	9	**4.3**	0.3	6.4	15	**4.1**	0.1	2.6	15	**4.7**	0.1	1.4
Er	135	9	**12.4**	0.7	5.7	15	**11.4**	0.5	4.3	15	**12.8**	0.4	2.8
Tm	120	8	**1.79**	0.18	9.8	0				15	**1.9**	0.0	2.4
Yb	135	9	**11.2**	0.7	6.5	15	**10.2**	0.4	3.6	15	**13.3**	0.2	1.2
Lu	120	8	**1.91**	0.23	12.0	0				15	**2.0**	0.1	2.9

n number of results

p number of laboratories

Table 5. (Continued).

Compiled and individual robust mass fractions of rare earth elements (in ng l^{-1}), with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

Compilation (ng l^{-1})						**Montpellier**				**Perpignan**			
	n	***p***	**mean**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**
La	135	9	**248.3**	12.1	4.9	15	**259.5**	2.1	0.8	15	**247.1**	3.8	1.5
Ce	135	9	**292.7**	15.1	5.1	15	**304.5**	3.5	1.1	15	**295.0**	3.9	1.3
Pr	135	9	**59.1**	1.9	3.2	15	**61.5**	1.0	1.7	15	**59.0**	1.1	1.9
Nd	135	9	**227.8**	9.4	4.1	15	**239.1**	3.3	1.4	15	**220.6**	3.4	1.5
Sm	135	9	**39.5**	1.7	4.3	15	**40.9**	0.6	1.6	15	**37.5**	2.4	6.4
Eu	120	8	**7.26**	0.35	4.9	15	**7.8**	0.4	4.7	15	**10.4**	0.5	5.1
Gd	135	9	**31.6**	2.5	8.0	15	**33.6**	0.9	2.7	15	**32.5**	1.5	4.5
Tb	135	9	**4.07**	0.27	6.5	15	**4.4**	0.2	4.8	15	**4.6**	0.4	7.6
Dy	135	9	**21.9**	1.1	5.1	15	**22.7**	0.6	2.8	15	**21.7**	1.1	5.1
Ho	135	9	**4.3**	0.3	6.4	15	**4.5**	0.3	6.6	15	**4.7**	0.3	5.9
Er	135	9	**12.4**	0.7	5.7	15	**13.2**	0.7	4.3	15	**12.8**	0.5	3.9
Tm	120	8	**1.79**	0.18	9.8	15	**1.9**	0.2	9.9	15	**2.1**	0.3	13.4
Yb	135	9	**11.2**	0.7	6.5	15	**11.8**	0.3	2.8	15	**11.0**	0.8	7.7
Lu	120	8	**1.91**	0.23	12.0	15	**2.0**	0.1	7.4	15	**2.3**	0.3	15.2

n number of results
p number of laboratories

Table 5. (Continued).

Compiled and individual robust mass fractions of rare earth elements (in ng l^{-1}), with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

Compilation (ng l^{-1})						OMP-Toulouse				Rennes			
	n	*p*	**mean**	***U***	**r*U* (%)**	*n*	**mean**	***U***	**r*U* (%)**	*n*	**mean**	***U***	**r*U* (%)**
La	135	9	**248.3**	12.1	4.9	15	**230.6**	1.7	0.8	15	**248.9**	1.3	0.5
Ce	135	9	**292.7**	15.1	5.1	15	**275.8**	1.6	0.6	15	**297.2**	1.7	0.6
Pr	135	9	**59.1**	1.9	3.2	15	**57.0**	0.9	1.5	15	**59.1**	0.3	0.6
Nd	135	9	**227.8**	9.4	4.1	15	**216.2**	2.6	1.2	15	**230.1**	2.1	0.9
Sm	135	9	**39.5**	1.7	4.3	15	**39.9**	0.8	1.9	15	**38.7**	0.2	0.5
Eu	120	8	**7.26**	0.35	4.9	15	**7.2**	0.3	3.6	15	**7.3**	0.1	1.8
Gd	135	9	**31.6**	2.5	8.0	15	**32.1**	1.1	3.5	15	**31.4**	0.2	0.7
Tb	135	9	**4.07**	0.27	6.5	15	**4.0**	0.2	5.7	15	**4.0**	0.1	2.2
Dy	135	9	**21.9**	1.1	5.1	15	**21.7**	0.7	3.0	15	**21.3**	0.1	0.5
Ho	135	9	**4.3**	0.3	6.4	15	**3.9**	0.2	4.7	15	**4.2**	0.1	2.1
Er	135	9	**12.4**	0.7	5.7	15	**11.6**	0.5	4.7	15	**12.1**	0.1	0.8
Tm	120	8	**1.79**	0.18	9.8	15	**1.6**	0.1	4.8	15	**1.7**	0.1	4.1
Yb	135	9	**11.2**	0.7	6.5	15	**10.3**	0.6	6.0	15	**11.1**	0.1	0.9
Lu	120	8	**1.91**	0.23	12.0	15	**1.6**	0.1	3.6	15	**1.9**	0.0	0.8

n number of results
p number of laboratories

Table 5. (Continued).

Compiled and individual robust mass fractions of rare earth elements (in ng l^{-1}), with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

Compilation (ng l^{-1})						Rio				LEGOS-Toulouse			
	n	*p*	**mean**	***U***	**r*U* (%)**	*n*	**mean**	***U***	**r*U* (%)**	*n*	**mean**	***U***	**r*U* (%)**
La	135	9	**248.3**	12.1	4.9	15	**247.6**	4.8	2.0	15	**238.8**	1.9	0.8
Ce	135	9	**292.7**	15.1	5.1	15	**277.5**	3.5	1.3	15	**282.1**	3.1	1.1
Pr	135	9	**59.1**	1.9	3.2	15	**58.6**	0.7	1.2	15	**59.7**	1.1	1.8
Nd	135	9	**227.8**	9.4	4.1	15	**232.5**	2.3	1.0	15	**224.5**	2.9	1.3
Sm	135	9	**39.5**	1.7	4.3	15	**40.8**	0.5	1.2	15	**39.3**	1.0	2.5
Eu	120	8	**7.26**	0.35	4.9	15	**6.8**	0.5	7.3	0			
Gd	135	9	**31.6**	2.5	8.0	15	**36.1**	1.1	3.1	15	**29.4**	0.6	2.0
Tb	135	9	**4.07**	0.27	6.5	15	**4.3**	0.2	5.3	15	**3.7**	0.1	2.5
Dy	135	9	**21.9**	1.1	5.1	15	**23.3**	0.8	3.3	15	**21.4**	0.5	2.1
Ho	135	9	**4.3**	0.3	6.4	15	**4.5**	0.2	4.6	15	**4.2**	0.1	3.1
Er	135	9	**12.4**	0.7	5.7	15	**13.1**	0.4	3.2	15	**12.3**	0.3	2.8
Tm	120	8	**1.79**	0.18	9.8	15	**1.9**	0.1	7.5	15	**1.7**	0.0	2.2
Yb	135	9	**11.2**	0.7	6.5	15	**12.1**	0.8	6.5	15	**10.8**	0.3	2.8
Lu	120	8	**1.91**	0.23	12.0	15	**2.1**	0.2	8.8	15	**1.7**	0.0	2.2

n number of results
p number of laboratories

Table 5. (Continued).

Compiled and individual robust mass fractions of rare earth elements (in ng l^{-1}), with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

Compilation (ng l^{-1})						Nancy			
	n	***p***	**mean**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**
La	135	9	**248.3**	12.1	4.9	15	**261.7**	6.1	2.3
Ce	135	9	**292.7**	15.1	5.1	15	**313.0**	7.2	2.3
Pr	135	9	**59.1**	1.9	3.2	15	**60.2**	1.3	2.2
Nd	135	9	**227.8**	9.4	4.1	15	**229.1**	6.7	2.9
Sm	135	9	**39.5**	1.7	4.3	15	**39.3**	1.4	3.5
Eu	120	8	**7.26**	0.35	4.9	15	**7.1**	0.4	5.7
Gd	135	9	**31.6**	2.5	8.0	15	**24.6**	2.3	9.5
Tb	135	9	**4.07**	0.27	6.5	15	**3.8**	0.2	4.9
Dy	135	9	**21.9**	1.1	5.1	15	**20.9**	0.8	4.0
Ho	135	9	**4.3**	0.3	6.4	15	**4.1**	0.2	5.4
Er	135	9	**12.4**	0.7	5.7	15	**11.8**	0.5	4.1
Tm	120	8	**1.79**	0.18	9.8	15	**1.6**	0.1	4.4
Yb	135	9	**11.2**	0.7	6.5	15	**11.3**	0.8	6.9
Lu	120	8	**1.91**	0.23	12.0	15	**1.7**	0.1	6.7

n number of results
p number of laboratories

Table 6.

Compiled and indvidual robust mass fractions of other uncertified elements in µg l-1, with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

Compilation (µg l^{-1})						Clermont-Ferrand				Montpellier			
	n	*p*	mean	*U*	r*U* (%)	*n*	mean	*U*	r*U* (%)	*n*	mean	*U*	r*U* (%)
B	45	3	**7.39**	1.28	17.3					15	**7.2**	0.2	2.8
Bi	*15*	*1*	*0.0013*	*0.0003*	20.4								
Cs	60	4	**0.0046**	0.0005	10.1					15	**0.0051**	0.0004	7.9
Ga	45	3	**0.011**	0.007	70.0								
Ge	45	3	**0.010**	0.007	64.8								
Hf	15	1	*0.0095*	0.0004	4.3								
Li	90	6	**0.530**	0.025	4.8	15	**0.536**	0.009	1.7	15	**0.53**	0.01	2.4
Nb	30	*2*	*0.0081*	0.0057	70.5								
P	30	*2*	*5.18*	1.02	19.6					15	**4.9**	0.4	8.3
Rb	120	8	**1.41**	0.05	3.5	15	**1.41**	0.01	1.0	15	**1.44**	0.03	2.1
Re	15	*1*	*0.0135*	0.0002	1.4	15	**0.0135**	0.0002	1.4				
Rh	15	*1*	*0.00069*	0.00017	24.6								
S	30	*2*	*1790*	142	7.9					15	**1711**	97	5.7
Sc	15	*1*	*0.333*	0.015	4.5								
Se	15	*1*	*0.072*	0.009	12.1					15	**0.072**	0.009	12.1
Si	75	5	**2231**	128	5.8					15	**2119**	34	1.6
Sn	30	*2*	*0.010*	0.008	82.6					15	**0.009**	0.004	43.8
Th	75	5	**0.016**	0.007	46.4					15	**0.018**	0.002	10.0
Ti	75	5	**0.525**	0.082	15.6					15	**0.486**	0.035	7.3
Tl	60	4	**0.0085**	0.0029	34.4					15	**0.011**	0.002	15.6
W	15	*1*	*0.0165*	0.0004	2.6								
Y	105	7	**0.128**	0.006	4.5	15	**0.124**	0.001	1.2	15	**0.135**	0.001	1.0
Zr	45	3	**0.062**	0.011	18.2								
^{87}Sr/^{86}Sr	*4*	*1*	*0.71205*	0.00002	0.003								

n number of results
p number of laboratories

Table 6. (Continued).

Compiled and indvidual robust mass fractions of other uncertified elements in µg l-1, with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

Compilation (µg l^{-1})						**Perpignan**				**OMP-Toulouse**			
	n	***p***	**mean**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**
B	45	3	**7.39**	1.28	17.3					15	**9.2**	0.4	4.2
Bi	*15*	*1*	*0.0013*	*0.0003*	20.4					15	**0.0013**	0.0003	20.4
Cs	60	4	**0.0046**	0.0005	10.1	15	**0.0099**	0.0012	12.0	15	**0.0045**	0.0002	5.4
Ga	45	3	**0.011**	0.007	70.0	15	**0.0093**	0.0007	7.5				
Ge	45	3	**0.010**	0.007	64.8					15	**0.014**	0.003	18.5
Hf	15	1	*0.0095*	0.0004	4.3								
Li	90	6	**0.530**	0.025	4.8	15	**0.536**	0.013	2.4	15	**0.512**	0.037	7.2
Nb	30	*2*	*0.0081*	0.0057	70.5						**0.0056**	0.0008	14.9
P	30	*2*	*5.18*	1.02	19.6								
Rb	120	8	**1.41**	0.05	3.5	15	**1.44**	0.04	2.7	15	**1.37**	0.01	0.9
Re	15	*1*	*0.0135*	0.0002	1.4								
Rh	15	*1*	*0.00069*	0.00017	24.6					15	**0.00069**	0.00017	24.6
S	30	*2*	*1790*	142	7.9								
Sc	15	*1*	*0.333*	0.015	4.5					15	**0.333**	0.015	4.5
Se	15	*1*	*0.072*	0.009	12.1								
Si	75	5	**2231**	128	5.8					15	**2182**	100	4.6
Sn	30	*2*	*0.010*	0.008	82.6								
Th	75	5	**0.016**	0.007	46.4					15	**0.010**	0.002	23.6
Ti	75	5	**0.525**	0.082	15.6	15	**0.633**	0.024	3.8	15	**0.525**	0.036	6.8
Tl	60	4	**0.0085**	0.0029	34.4					15	**0.007**	0.000	6.0
W	15	*1*	*0.0165*	0.0004	2.6								
Y	105	7	**0.128**	0.006	4.5	15	**0.130**	0.002	1.9	15	**0.123**	0.001	1.1
Zr	45	3	**0.062**	0.011	18.2						**0.058**	0.004	7.1
$^{87}Sr/^{86}Sr$	*4*	*1*	*0.71205*	0.00002	0.003								

n number of results
p number of laboratories

Table 6. (Continued).

Compiled and indvidual robust mass fractions of other uncertified elements in µg l-1, with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

Compilation ($\mu g\ l^{-1}$)						Rennes				Rio			
	n	***p***	**mean**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**	***n***	**mean**	***U***	**r*U* (%)**
B	45	3	**7.39**	1.28	17.3	15	**7.04**	0.09	1.3				
Bi	*15*	*1*	*0.0013*	*0.0003*	20.4								
Cs	60	4	**0.0046**	0.0005	10.1								
Ga	45	3	**0.011**	0.007	70.0								
Ge	45	3	**0.010**	0.007	64.8								
Hf	15	1	*0.0095*	0.0004	4.3								
Li	90	6	**0.530**	0.025	4.8	15	**0.519**	0.009	1.8				
Nb	30	*2*	*0.0081*	0.0057	70.5								
P	30	*2*	*5.18*	1.02	19.6								
Rb	120	8	**1.41**	0.05	3.5	15	**1.42**	0.01	0.6	15	**1.50**	0.03	1.9
Re	15	*1*	*0.0135*	0.0002	1.4								
Rh	15	*1*	*0.00069*	0.00017	24.6								
S	30	*2*	*1790*	142	7.9								
Sc	15	*1*	*0.333*	0.015	4.5								
Se	15	*1*	*0.072*	0.009	12.1								
Si	75	5	**2231**	128	5.8	15	**2216**	10	0.5				
Sn	30	*2*	*0.010*	0.008	82.6								
Th	75	5	**0.016**	0.007	46.4	15	**0.022**	0.0004	1.6				
Ti	75	5	**0.525**	0.082	15.6								
Tl	60	4	**0.0085**	0.0029	34.4								
W	15	*1*	*0.0165*	0.0004	2.6								
Y	105	7	**0.128**	0.006	4.5					15	**0.135**	0.001	0.7
Zr	45	3	**0.062**	0.011	18.2								
$^{87}Sr/^{86}Sr$	*4*	*1*	*0.71205*	0.00002	0.003								

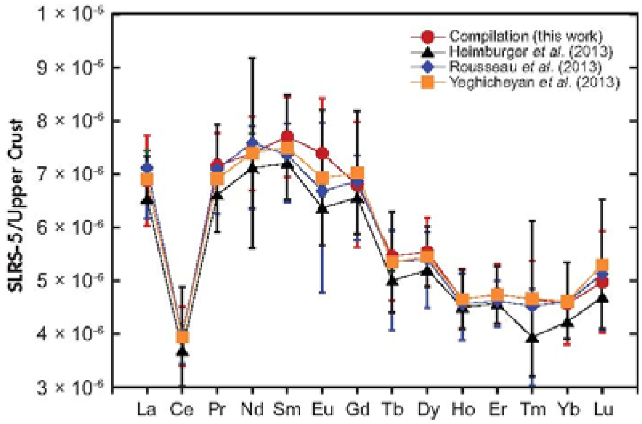
n number of results
p number of laboratories

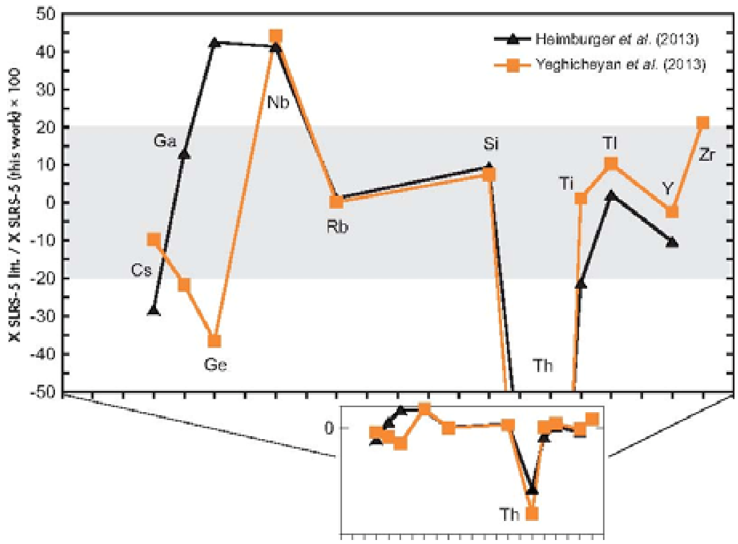
Table 6. (Continued).

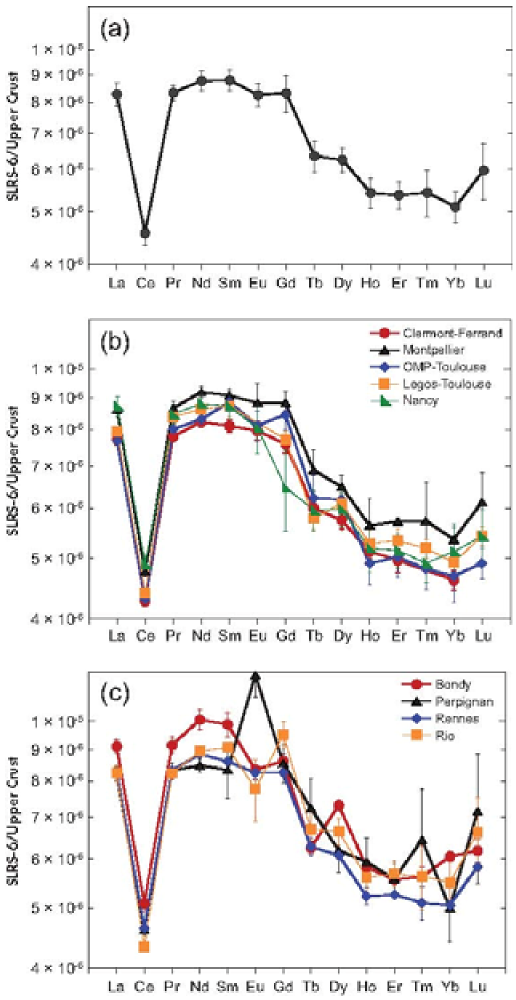
Compiled and indvidual robust mass fractions of other uncertified elements in µg l-1, with the corresponding expanded uncertainty (U) and relative expanded uncertainty (rU) in the river water certified reference material SLRS-6

	Compilation (µg l^{-1})					LEGOS-Toulouse				Nancy			
	n	*p*	mean	*U*	r*U* (%)	*n*	mean	*U*	r*U* (%)	*n*	mean	*U*	r*U* (%)
B	45	3	**7.39**	1.28	17.3								
Bi	*15*	*1*	*0.0013*	*0.0003*	20.4								
Cs	60	4	**0.0046**	0.0005	10.1	15	**0.0047**	0.0001	1.9	15			
Ga	45	3	**0.011**	0.007	70.0	15	**0.0059**	0.0002	3.6	15	**0.017**	0.002	12.0
Ge	45	3	**0.010**	0.007	64.8	15	**0.0068**	0.0007	10.1	15	**0.010**	0.003	30.2
Hf	15	1	*0.0095*	0.0004	4.3	15	**0.0095**	0.0004	4.3				
Li	90	6	**0.530**	0.025	4.8	15	**0.537**	0.019	3.5				
Nb	30	*2*	*0.0081*	0.0057	70.5	15	**0.0104**	0.0005	4.7				
P	30	*2*	*5.18*	1.02	19.6	15	**5.38**	0.34	6.4				
Rb	120	8	**1.41**	0.05	3.5	15	**1.38**	0.03	1.9	15	**1.35**	0.04	2.9
Re	15	*1*	*0.0135*	0.0002	1.4								
Rh	15	*1*	*0.00069*	0.00017	24.6								
S	30	*2*	*1790*	142	7.9					15	**1813**	18	1.0
Sc	15	*1*	*0.333*	0.015	4.5								
Se	15	*1*	*0.072*	0.009	12.1								
Si	75	5	**2231**	128	5.8	15	**2338**	109	4.7	15	**2277**	30	1.3
Sn	30	*2*	*0.010*	0.008	82.6	15	**0.011**	0.002	18.2				
Th	75	5	**0.016**	0.007	46.4	15	**0.020**	0.002	8.4	15	**0.009**	0.001	7.7
Ti	75	5	**0.525**	0.082	15.6	15	**0.481**	0.016	3.3	15	**0.62**	0.02	4.0
Tl	60	4	**0.0085**	0.0029	34.4	15	**0.0073**	0.0002	3.2	15	**0.0077**	0.0003	4.3
W	15	*1*	*0.0165*	0.0004	2.6	15	**0.017**	0.0004	2.6				
Y	105	7	**0.128**	0.006	4.5	15	**0.126**	0.002	1.8	15	**0.124**	0.003	2.8
Zr	45	3	**0.062**	0.011	18.2	15	**0.0612**	0.0062	10.1	15	**0.067**	0.002	3.7
^{87}Sr/^{86}Sr	*4*	*1*	*0.71205*	0.00002	0.003					4	**0.71205**	0.00002	0.003

n number of results
p number of laboratories


Compilation (this work)
Heimburger et al. (2013)
Rousseau et al. (2013)
Yeghicheyan et al. (2013)
SLRS-5/Upper Crust
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu


Heimburger et al. (2013)
Yeghicheyan et al. (2013)
X SLRS-5 lit. / X SLRS-5 (this work) × 100
Ga
Nb
Si
Ti
Tl
Y
Zr
Rb
Cs
Ge
Th


(a)
SLRS-6/Upper Crust
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
(b)
Clermont-Ferrand
Montpellier
OMP-Toulouse
Legos-Toulouse
Nancy
(c)
Bondy
Perpignan
Rennes
Rio