Analysis of Seventeen Certified Water Reference Materials for Trace and Technology-Critical Elements

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Concentrations of elements in the aquatic environment are a key parameter for various scientific fields such as biogeochemistry, biology and environmental science. Within this context, the scientific community asks for new analytical protocols to be able to quantify more and more elements of the periodic table. Therefore, the requirements for aqueous reference materials have increased drastically. Even though a wide variety of CRMs of different water matrices are available, certified values of many elements (e.g., rare earth elements (REE), technology-critical elements, such as Ga and In, and generally those elements which are not part of current monitoring regulations) do not yet exist. Therefore, the scientific community relies on published elemental concentrations of many CRMs provided by other researchers. Some elements of interest, such as the REE, are well studied and plenty of literature values exist. However, less studied elements, such as Ga and In, are rarely studied. In this study, an ‘externally’ calibrated quantification method based on an optimised online preconcentration method coupled with ICP-MS/MS was used for the quantification of thirty-four elements. The method was applied to seventeen water CRMs covering freshwater, brackish water and seawater. The measured data are combined with a comprehensive literature review on non-certified values in selected water CRMs, and new consensus values are suggested for various non-certified elements.

Keywords: ICP-MS, multi-elemental analysis, seaFAST, natural waters, consensus values.

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Table 1.
Literature overview of studies (listed alphabetically by CRM) providing concentration values of elements of interest (printed in bold) for the water CRM, together with details on the analytical method that lead to the publication of the literature values

| Authors                  | Water CRM | Analytes*                                                                 | Direct/diluted/preconcentration + matrix reduction | Online/offline preconcentration |
|--------------------------|-----------|---------------------------------------------------------------------------|---------------------------------------------------|--------------------------------|
| Griesel et al. (2001)    | BCR-505   | As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, V, Zn                             | Electro-deposition                                 | Offline                        |
| Wang et al. (2014)       | BCR-505   | Cd, Co, Cu, Dy, Er, Eu, Fe, Gd, Ho, La, Lu, Nd, Ni, Pb, Pr, Sm, Tb, Tm, V, Y, Yb, Zn | Preconcentration-chelating medium                  | Offline                        |
| Rodushkin and Ruth (1997)| CASS-2    | Al, Ba, Cd, Ca, Cu, Fe, Mn, Mo, Ni, Pb, Sb, U, V, Zn                     | Dilution (fivefold)                                | -                              |
| Kühn and Kriews (2000)   | CASS-3    | Bi, Cd, Co, Cu, Eu, Fe, Gd, La, Lu, Mn, Pb, Yb, Zn                       | Preconcentration                                  | Offline                        |
| Benkhedda et al. (2001, 2002) | CASS-3  | Ce, Eu, Gd, La, Lu, Yb                                                  | Preconcentration-knotted reactor                  | Online                         |
| Abbasse et al. (2002)    | CASS-3    | Cd, Cu, Fe, Mn, Ni, Pb, V, Zn                                            | Preconcentration-chelating medium                  | Offline                        |
| Rahmi et al. (2007)      | CASS-3    | Cd, Co, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Sm, Tb, Tm, U, V, Yb, Zn | Preconcentration-chelating medium                  | Offline                        |
| Lee et al. (2002)        | CASS-4    | Cd, Co, Cu, Mn, Mo, Ni, U, V                                             | Preconcentration-chelating medium                  | Online                         |
| Hirata et al. (2003)     | CASS-4    | Cd, Co, Cu, Mo, Ni, U, V                                                | Preconcentration-chelating medium                  | Online                         |
| Kajiya et al. (2004)     | CASS-4    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb                | Preconcentration-chelating medium                  | online                         |
| Turetta et al. (2004, 2005) | CASS-4  | Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Pb, Sb, U, V, Zn                        | Dilution (10-fold)                                | -                              |
| Grinberg et al. (2005)   | CASS-4    | Pu, Th, U                                                                | Preconcentration-co-precipitation                 | Offline                        |
| Zhu et al. (2005a)       | CASS-4    | Al, Bi, Cd, Ce, Co, Cu, Dy, Er, Eu, Ga, Gd, Hf, Ho, Ho, La, Lu, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Sc, Sm, Sn, Tb, Th, Ti, Tm, U, V, W, Yb, Zn, Zr | Preconcentration-chelating medium                  | Offline                        |
| Grinberg et al. (2006)   | CASS-4    | Pu, Th, U                                                                | Preconcentration-co-precipitation                 | Offline                        |
| Lawrence and Kamber (2007) | CASS-4 | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb | Preconcentration-chelating medium | Offline |
| Point et al. (2007)      | CASS-4    | Cd, Cu, Mn, Ni, Pb, U, Zn                                               | Preconcentration-chelating medium                  | Offline                        |
| Sabarudin et al. (2007)  | CASS-4    | U                                                                         | Preconcentration-chelating medium                  | Offline                        |
| Beck et al. (2008)       | CASS-4    | Mo, U, V                                                                 | Dilution (25-fold)                                | -                              |
| Sohrin et al. (2008)     | CASS-4    | Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn                                      | Preconcentration-chelating medium                  | Offline                        |
| Staniszewski and Freimann (2008) | CASS-4 | As, Cu, Fe, Ni, Pb, U, V, Zn                                         | Preconcentration-column                            | Offline                        |
| Kim et al. (2010)        | CASS-4    | Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Tm, Yb                      | Preconcentration-chelating medium                  | Offline                        |
| Bayon et al. (2011)      | CASS-4    | Ce, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, V, Y, Yb, Zr | Preconcentration-co-precipitation                 | Offline                        |
| Freslon et al. (2011)    | CASS-4    | Co, Cr, Dy, Er, Eu, Gd, Ho, La, Mn, Nd, Pr, Sm, Tb, Y                    | Preconcentration-co-precipitation                 | Offline                        |
| Oliveira et al. (2011)   | CASS-4    | Co, V, Mn, Zn, Fe, Mo, U, Cd, Pb, Ni                                    | Preconcentration-chelating medium                  | Online                         |
| Preconcentration medium | Quatification method | Calibration technique | Range of detection limits a (ng l⁻¹) | Range of relative uncertainty equivalent [%] | Original unit | Measure of uncertainty |
|-------------------------|----------------------|-----------------------|--------------------------------------|---------------------------------------------|---------------|-----------------------|
| –                       | TXRF                 | Internal standard (Co) | 5–20                                 | 8–20                                        | µg l⁻¹        | s                     |
| Nobias Chelate-PA1 (Hitachi) | ICP-SFMS\(^g\)       | External              | 0.002–14.6                           | 6.3–25.0                                    | pmol l⁻¹ + nmol l⁻¹ | 2s                   |
| –                       | ICP-SFMS             | External              | n.s. (detailed discussion of blank levels) | 0.6–41                                      | ng ml⁻¹       | U(k = 2)              |
| Iminodiacetic functionalised beads | ICP-QMS\(^d\)      | External              | 0.01–7459                            | 1.0–47.8                                    | pg l⁻¹        | “accuracy”           |
| PMBP\(^m\)             | ICP-ToF-MS\(^d\)     | External              | 0.003–0.04                           | 1.0–10.2                                    | µg l⁻¹        | s                     |
| BHQ\(^a\) + C18\(^b\) | ICP-AES              | n.s.\(^i\)           | 60–6000                              | 0.2–7.0                                     | µg l⁻¹        | s                     |
| Chelex 100 (Bio-Rad)    | ICP-QMS              | External              | 0.06–1                               | 3.6–50.0                                    | ng ml⁻¹ + pg ml⁻¹ | s (n = 5)             |
| Iminodiacetic functionalised resin chelating disk | ICP-QMS             | External              | 7–400                                | 1.0–12.5                                    | ng ml⁻¹        | s (n = 5)             |
| MAF-BHQ\(^q\)          | ICP-QMS              | External              | 1–15                                 | 3.0–21.2                                    | ng ml⁻¹        | s                     |
| MAF-BHQ\(^q\)          | ICP-QMS              | n.s.\(^j\)           | 0.037–0.297                          | 3.1–37.4                                    | pg ml⁻¹        | s (n = 4)             |
| –                       | ICP-SFMS             | Standard addition     | 0.06–1.5                             | 5.0–24.5                                    | ng ml⁻¹        | U(k = 2)              |
| Ca\(_3\)(PO\(_4\))\(_2\) | ETV\(^k\)-ICP-CRC\(^c\)-QMS | External          | 0.013–0.029                          | 2.3–20.0                                    | pg ml⁻¹        | s (n = 5)             |
| Chelex 100 (Bio-Rad)    | ICP-QMS, ICP-AES     | External              | 0.03–20                              | 1.5–50.0                                    | µg l⁻¹        | s (n = 3)             |
| Ca\(_3\)(PO\(_4\))\(_2\) | ICP-CRC-QMS          | External              | 0.12–0.13                            | 1.0–28.6                                    | µg l⁻¹        | s (n = 3)             |
| HDEHP + H\(_2\)MEHP\(^m\) | ICP-QMS              | n.s.\(^j\)           | 0.05–4.33º                          | 0.4–24.2                                    | ng kg⁻¹        | s (n = 10)            |
| Metpac cc1 (Dionex)     | ICP-QMS              | External              | 0.6–33                               | 1–33                                        | ng l⁻¹        | s (n = 5)             |
| CCTS-DHBA\(^o\)        | ICP-MS               | n.s.\(^j\)           | 1                                    | 0.6                                         | ng ml⁻¹        | s                     |
| –                       | ICP-SFMS             | External              | n.s.\(^j\)                          | 4–7                                         | nmol l⁻¹       | s (n = 105)           |
| Nobias Chelate-PA1 (Hitachi) | ICP-CRC-QMS     | External              | 0.2–6.6                              | 0.8–15.9                                    | µg kg⁻¹       | s (n = 3)             |
| sodium dibenzylthiocarbamate + silica gel | TXRF                 | Internal standard (Co) | n.s.                                 | 3.7–11.8                                    | ng l⁻¹        | n.s.                  |
| Chelex 100 (Bio-Rad)    | ICP-QMS              | n.s.\(^j\)           | 0.02–0.55                            | 1.3–10.0                                    | ng l⁻¹        | s                     |
| FeO(OH)\(_2\)          | ICP-SFMS             | n.s.\(^j\)           | 0.2–37.6                             | ng l⁻¹                                        | s (n = 3)      |
| Mg(OH)\(_2\)          | ICP-SFMS             | Tm addition           | 0.001–0.50                           | 3.1–14                                       | ng kg⁻¹       | s                     |
| AF-Chelate-650 M + 8HQ + C18 | ICP-CRC-QMS     | ID\(^p\)             | 0.2–58                               | 0.6–8.3                                      | ng ml⁻¹       | s (n = 3)             |
| Authors                  | Water CRM | Analytes* | Direct/diluted/ preconcentration + matrix reduction | Online/offline preconcentration |
|--------------------------|-----------|-----------|---------------------------------------------------|---------------------------------|
| Matsumiya et al. (2012)  | CASS-4    | Bi, Cd, Cu, Ga, Ni, Pb | Preconcentration-chelating medium                  | Offline                         |
| Leme et al. (2018)       | CASS-4    | La, Nd    | Preconcentration-chelating medium                  | Offline                         |
| Rousseau et al. (2013)   | CASS-5    | Ba, Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb | Preconcentration-co-precipitation | Offline                         |
| Lemaitre et al. (2014)   | CASS-5    | Ce, Dy, Er, Eu, Fe, Gd, Ho, La, Lu, Mn, Nd, Pr, Sm, Tb, Y, Yb | Preconcentration-co-precipitation | Offline                         |
| Wang et al. (2014)       | CASS-5    | Cd, Ce, Co, Dy, Er, Eu, Fe, Gd, Ho, La, Lu, Mn, Nd, Ni, Pb, Pr, Sm, Tb, Tb, Tm, V, Y, Yb, Zn | Preconcentration-chelating medium | Offline                         |
| Minami et al. (2015)     | CASS-5    | Al, Cd, Co, Cu, Fe, Mn, Ni, Pb, Zn | Preconcentration-chelating medium                  | Offline                         |
| Wysocka and Vassileva (2017) | CASS-5 | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb | Preconcentration-chelating medium                  | Offline                         |
| Rodushkin and Ruth (1997) | NASS-4   | Al, Ba, Cd, Ca, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, U, V, Zn | Dilution (livefold) – | –                              |
| Kühn and Kriews (2000)   | NASS-4    | Bi, Cd, Ca, Cu, Dy, Eu, Fe, Gd, Ho, La, Mn, Pb, Yb, Zn | Preconcentration                   | Offline                         |
| Yabutani et al. (2001)   | NASS-4    | Al, As, Bi, Cd, Ce, Co, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Sb, Se, Sm, Sn, Tb, Ti, Tm, U, V, W, Y, Yb, Zn | Preconcentration-chelating medium + co-precipitation | Offline                         |
| Louie et al. (2002)      | NASS-4    | Cr, Cu, Mn, Ni, V | Dilution (10-fold) – | –                              |
| Shaw et al. (2003)       | NASS-4    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb | Preconcentration-co-precipitation | Offline                         |
| Rahmi et al. (2007)      | NASS-4    | Cd, Ce, Co, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Sm, Tb, Tm, U, V, Y, Yb, Zn | Preconcentration-chelating medium | Offline                         |
| Maltez et al. (2008)     | NASS-4    | Cd, Ca, Cu, Ni, Pb, V, Zn | Preconcentration-sorption medium                  | Online                          |
| Dressler et al. (2001)   | NASS-5    | Ag, Au, Te, U | Preconcentration-chelating medium                  | Online                          |
| Willie et al. (2001)     | NASS-5    | Cd, Ca, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn | Preconcentration-chelating medium                  | Online                          |
| Willie and Sturgeon (2001)| NASS-5  | Cd, Ce, Co, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Ni, Pb, Pr, Sm, Tb, Tm, Yb, Zn | Preconcentration-chelating medium | Online                          |
| Lee et al. (2002)        | NASS-5    | Cd, Ca, Cu, Mn, Mo, Ni, U, V | Preconcentration-chelating medium                  | Online                          |
| Leonhard et al. (2002)   | NASS-5    | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, (Se), U, V, Zn | dilution (10-fold) – | –                              |
| Hirata et al. (2003)     | NASS-5    | Cd, Ca, Cu, Mn, Mo, Ni, U, V, Zn | Preconcentration-chelating medium                  | Online                          |
| Shaw et al. (2003)       | NASS-5    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb | Preconcentration-co-precipitation | Offline                         |
| Preconcentration medium | Quatification method | Calibration technique | Range of detection limits[^a] (ng l[^-1]) | Range of relative uncertainty equivalent (%) | Original unit | Measure of uncertainty |
|-------------------------|----------------------|-----------------------|-------------------------------------------|---------------------------------------------|---------------|-----------------------|
| APDC[^3^] + CTAC-[covered silica] | ICP-MS | External | 0.7–4 | 0.9–12.5 | µg l[^-1] | none (s calculated from n = 2 runs) |
| 1-(2-pyridylazo)-2-naphthal | ICP-CRC-QMS | External | 3.9–4.0 | 8.9–13.2 | ng l[^-1] | 2s |
| Fe(OH)₃ | ICP-SFMS | ID | 0.001–0.030 | 0.7–4.7 | ppt[^b] | 2s (n = 11) |
| Mg(OH)₂ | ICP-SFMS | Tm addition for REE+Mn, ID for Fe | n.s. | 1.4–16.9 | ng kg[^-1] + µg kg[^-1] | s (n = 12) |
| Nobias Chelate-PA1 (Hitachi) | ICP-SFMS | External | 0.002–14.6 | 2.3–25.0 | pmol l[^-1] + nmol l[^-1] | 2s |
| Nobias Chelate-PA1 (Hitachi) | ICP-SFMS | External | 0.1–8.1 | 1.1–8.1 | nmol kg[^-1] + pmol kg[^-1] | s |
| Nobias Chelate-PA1 (Hitachi) | ICP-SFMS | External | 0.001–0.008 | 10.3–12.0 | ng l[^-1] | U(k = 2) |
| Iminodiacetic functionalised beads | ICP-QMS | External | 0.01–74.59 | 2.0–47.0 | pg l[^-1] | “accuracy” |
| Chelating resin: Chelex 100 (Bio-Rad); co-precipitation agent: La(NO₃)₃ | ICP-QMS | External | 0.006–600 | 2.9–60.0 | µg l[^-1] | s (n = 3) |
| - | ICP-CRC-QMS | Standard addition | 20–300 | 14.9–40.8 | µg l[^-1] | s (n = 10) |
| Mg(OH)₂ | ICP-SFMS | ID | 0.02–0.2 | 3.2–17.6 | ng l[^-1] | “error” |
| Chelex 100 (Bio-Rad) | ICP-QMS | External | 0.06–1 | 3.3–33.3 | ng ml[^-1] + pg ml[^-1] | s (n = 5) |
| Nb₂O₅-SiO₂ | ICP-QMS | External | 10–30 | 0.8–4.5 | µg l[^-1] | s (n = 6) |
| DDT/P + C18 | ICP-QMS | External | 0.05–2.24 | 3.3–17.9 | ng ml[^-1] | s (n = 5) |
| Toyopearl AF-Chelate-650 M (Tosohaas) | ICP-QMS | External | 0.1–12[^2] | 0.9–28.6 | ng l[^-1] | s (n = 3) |
| Toyopearl AF-Chelate-650 M (Tosohaas) | ICP-TOF-MS | External | 0.02–0.05 | 5–6 | ng l[^-1] | s (n = 3) |
| Iminodiacetic functionalised resin chelating disk | ICP-QMS | External | 7–400 | 3.3–17.9 | ng ml[^-1] | s (n = 5) |
| - | ICP-CRC-QMS | External | 0.25–100 | 7–50 | ng l[^-1] | s (n = 6) |
| MAF-8HQ | ICP-QMS | External | 1–15 | 3.2–46.6 | ng ml[^-1] | s |
| Mg(OH)₂ | ICP-SFMS | ID | 0.02–0.2 | 2.2–20.0 | ng l[^-1] | “error” |
| Authors                          | Water CRM | Analytes | Direct/diluted/preconcentration + matrix reduction | Online/offline preconcentration |
|---------------------------------|-----------|----------|---------------------------------------------------|---------------------------------|
| Kajiya et al. (2004)            | NASS-5    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb | Preconcentration-chelating medium | Online                          |
| Grinberg et al. (2005)          | NASS-5    | Pu, Tb, U | Preconcentration-co-precipitation                 | Offline                         |
| Zhu et al. (2005b)              | NASS-5    | Al, Bi, Cd, Co, Cs, Dy, Er, Eu, Ga, Gd, Hf, Ho, La, Lu, Mn, Mo, Nb, Nd, Ni, Pb, Pr, Sc, Sm, Sn, Tb, Ti, Tm, U, V, W, Y, Yb, Zn, Zr | Preconcentration-chelating medium | Offline                         |
| Shiller and Bairamadgi (2006)   | NASS-5    | Ga       | Preconcentration-co-precipitation                 | Offline                         |
| Field et al. (2007)             | NASS-5    | As, Ba, Mn, Mo, P, U, V                               | direct                           | –                               |
| Firdaus et al. (2007)           | NASS-5    | Hf, Nb, Ta, W, Zr                                    | Preconcentration-chelating medium | Offline                         |
| Lawrence and Kamber (2007)      | NASS-5    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb | Preconcentration-chelating medium | Offline                         |
| Rahmi et al. (2007)             | NASS-5    | Cd, Cs, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Sm, Tb, Tm, U, V, Y, Yb | Preconcentration-chelating medium | Offline                         |
| Sabarudin et al. (2007)         | NASS-5    | U        | Preconcentration-chelating medium                 | Offline                         |
| Maltez et al. (2008)            | NASS-5    | Cd, Ca, Cu, Ni, Pb, V, Zn                             | Preconcentration-sorption medium | Online                          |
| Murphy et al. (2008)            | NASS-5    | Ba, Mn, Mo, P, U, V                                  | dilution (10-fold)              | –                               |
| Sohrin et al. (2008)            | NASS-5    | Al, Cd, Ca, Cu, Fe, Mn, Ni, Pb, Zn                   | Preconcentration-chelating medium | Offline                         |
| Zhu et al. (2009)               | NASS-5    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Yb | Preconcentration-chelating medium | Online                          |
| Kim et al. (2010)               | NASS-5    | Ce, Dy, Er, Eu, Gd, Ho, La, Nd, Pr, Sm, Tb, Tm, Yb   | Preconcentration-chelating medium | Offline                         |
| Rahaman et al. (2010)           | NASS-5    | Mo, U                                             | dilution                        | –                               |
| Waseem et al. (2010)            | NASS-5    | V        | –                                                 | Online                          |
| Agatemor and Beauchemin (2011)  | NASS-5    | Mo, U                                             | Direct                           | –                               |
| Bayon et al. (2011)             | NASS-5    | Ce, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nd, Pr, Sm, (Sc), Tb, Tb, V, Y, Yb, Zr | Preconcentration-co-precipitation | Offline                         |
| Freslon et al. (2011)           | NASS-5    | Ce, Co, Cr, Dy, Er, Eu, Gd, Ho, La, Lu, Mn, Nd, Pr, Sm, Tb, Y, Yb | Preconcentration-co-precipitation | Offline                         |
| Matsumiya et al. (2012)         | NASS-5    | (Bi), Cd, Cu, (Ga), Ni, Pb                          | Preconcentration-chelating medium | Offline                         |
| Scholz et al. (2013)            | NASS-5    | Mo, U                                             | n.s.                             | –                               |
| Soyal-Erdene and Huh (2013)     | NASS-5    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb | Preconcentration-column         | Offline                         |
| Raso et al. (2013)              | NASS-6    | Ce, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nd, Pr, Sm, Tb, Tm, Y, Yb, Zr | Preconcentration-co-precipitation | Offline                         |
| Lemaître et al. (2014)          | NASS-6    | Ce, Dy, Er, Eu, Fe, Gd, Ho, La, Lu, Mn, Nd, Pr, Sm, Tb, Y, Yb | Preconcentration-co-precipitation | Offline                         |
| Wang et al. (2014)              | NASS-6    | Cd, Ce, Cu, Dy, Er, Eu, Fe, Gd, Ho, La, Lu, Mn, Nd, Ni, Pb, Pr, Sm, Tb, Tm, V, Y, Yb | Preconcentration-chelating medium | Offline                         |
| Clough et al. (2015)            | NASS-6    | Co, Fe, Pb, V                                      | Preconcentration-chelating medium | Online                         |
| Preconcentration medium | Quatification method | Calibration technique | Range of detection limits [ng l⁻¹] | Range of relative uncertainty equivalent [%] | Original unit | Measure of uncertainty |
|-------------------------|----------------------|-----------------------|--------------------------------------|-------------------------------------------|---------------|------------------------|
| MAF-8HQ                 | ICP-QMS              | n.s.                  | 0.037–0.297                          | 2.0–84.2                                  | pg ml⁻¹       | s (n = 4)              |
| Ca₃(PO₄)₂               | ETV-ICP-CRC-QMS      | External              | 0.013–0.029                          | 2.3–16.7                                  | pg ml⁻¹       | s (n = 5)              |
| Chelex 100 (Bio-Rad)    | ICP-QMS/ICP-AES      | External              | 0.07–20                              | 1.9–32.0                                  | µg l⁻¹        | s (n = 3)              |
| Mg(OH)₂                 | ICP-SFMS             | ID                    | n.s.                                 | 15                                        | pmol kg⁻¹     | s (n = 58)             |
|                         |                      |                       |                                      |                                            |               |                        |
| TSK-8HQ⁻                 | ICP-CRC-QMS          | Standard addition     | 0.15–0.23                            | 2–4                                       | pmol kg⁻¹     | s (n = 2)              |
| HDEHP+H₂MEHP             | ICP-QMS              | n.s.                  | 0.05–4.33                            | 7.2–31.6                                  | ng kg⁻¹       | s (n = 22)             |
| Chelex 100 (Bio-Rad)    | ICP-QMS              | External              | 0.06–1                               | 1.0–68.2                                  | ng ml⁻¹ + pg ml⁻¹ | s (n = 5) |
| CCTS-DHBA               | ICP-MS               | n.s.                  | 1                                    | 5.1                                       | ng ml⁻¹       | s                      |
| Nb₂O₅·SiO₂               | ICP-QMS              | External              | 10–30                                | 0.8–4.5                                   | µg l⁻¹        | s                      |
|                         |                      |                       |                                      |                                            |               |                        |
| Nobias Chelate-PA1 (Hitachi) | ICP-SFMS          | n.s.                  | 14–4200                              | 1.8–39.7                                  | µg l⁻¹        | RSD                    |
| Nobias chelate PB1 M (Hitachi) | ICP-CRC-QMS       | External              | 0.2–6.6                              | 2.7–9.1                                   | µg kg⁻¹       | s (n = 6)              |
| Chelex 100 (Bio-Rad)    | ICP-QMS              | n.s.                  | 0.02–0.55                            | 0.3–10.2                                  | ng l⁻¹        | s                      |
| HDEHP+H₂MEHP             | ICP-QMS              | n.s.                  | 3.5–3.7                              | 5.9                                       | µg l⁻¹        | s (n = 4)              |
|                         |                      | Flow injection        | 40                                   |                                            | µg l⁻¹        | s                      |
|                         |                      | chemiluminescence     |                                      |                                            |               |                        |
| FeO(OH)                 | ICP-SFMS             | n.s.                  | 0.9–7.1                              | ng l⁻¹                                    | s (n = 5)     |                        |
| Mg(OH)₂                 | ICP-SFMS             | Tm addition           | 0.001–0.50                           | 2.8–10                                    | ng kg⁻¹       | s                      |
| APDC + CTAC-covered silica | ICP-MS             | External              | 0.7–4                                | 4.2–16.7                                  | µg l⁻¹        | s                      |
|                         |                      |                       |                                      |                                            |               |                        |
| RE-Spec chromatographic extraction resin (Eichrom) | ICP-CRC-QMS  | ID                    | n.s.                                 | 0.8–0.9                                   | nmol l⁻¹      | s (n = 4)              |
| RE-Spec chromatographic extraction resin (Eichrom) | ICP-SFMS  | External              | 0.02–1.0                             | 3.6–10.5                                  | pg ml⁻¹       | s (n = 15)             |
| FeO(OH)                 | ICP-CRC-QMS          | External              | 2.1–408.3                            | 3.1–200.0                                  | pg ml⁻¹       | s                      |
| Mg(OH)₂                 | ICP-SFMS             | Tm addition for REE+Mn, ID for Fe | n.s.                                 | 2.4–18.9                                   | ng kg⁻¹ + µg kg⁻¹ | s (n = 11) |
| Nobias Chelate-PA1 (Hitachi) | ICP-SFMS          | External              | 0.002–14.6                           | 10.0–39.0                                  | pmol l⁻¹ + nmol l⁻¹ | 2s     |
| AF-Chelate-650          | ICP-QMS              | External              | 0.34–19                              | 5–9                                       | nmol l⁻¹      | 2s                     |
Table 1.
(continued)

| Authors                  | Water CRM | Analytes a | Direct/diluted/ preconcentration + matrix reduction | Online/offline preconcentration |
|--------------------------|-----------|------------|-----------------------------------------------------|--------------------------------|
| Censi et al. (2017)      | NASS-6    | Ce, Dy, Er, Eu, Gd, Hf, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Y, Yb, Zr | Preconcentration-co-precipitation | Offline |
| Wysoka and Vassileva (2017) | NASS-6    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Yb | Preconcentration-chelating medium | Offline |
| Crocket et al. (2018)    | NASS-6    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Yb | Preconcentration-chelating medium | Offline |
| Wuttig et al. (2019)     | NASS-6    | Cd, Co, Cu, Fe, Ga, Mn, Ni, Pb, Ti, Zn | Preconcentration-chelating medium dilution (10-fold) | – |
| Leonhardt et al. (2002)  | SLEW-3    | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, (Se), U, V, Zn | Preconcentration-co-precipitation | Offline |
| Lawrence and Kamber (2007) | SLEW-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Y, Yb | Preconcentration-chelating medium | Offline |
| Beck et al. (2008)       | SLEW-3    | Mo, U, V | Dilution (25-fold) | – |
| Rahaman et al. (2010)    | SLEW-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tb, V, Y, Yb, Zr | Dilution | – |
| Bayon et al. (2011)      | SLEW-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tb, V, Y, Yb, Zr | Preconcentration-co-precipitation | Offline |
| Wang et al. (2014)       | SLEW-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tb, V, Y, Yb, Zr | Preconcentration-chelating medium | Offline |
| Mohajerin et al. (2016)  | SLEW-3    | Fe, Mn, Mo, W | Dilution (1.5–10-fold) | – |
| Mohajerin et al. (2016)  | SLEW-3    | Mo, W | Dilution (1.5–10-fold) | – |
| Wysoka and Vassileva (2017) | SLEW-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Yb | Preconcentration-chelating medium | Offline |
| Peart et al. (1998)      | SIRS-1    | Al, As, Ba, Be, Bi, Br, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Gd, Ho, I, La, Li, (La), Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sr, Tb, Tb, (Tm), U, V, W, Y, Yb, Zn | Direct | – |
| Peart et al. (1998)      | SIRS-3    | Al, As, Ba, Be, Bi, Br, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Gd, Ho, I, La, Li, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Sm, Sr, Tb, Tb, (Tm), U, V, W, Y, Yb, Zn | Direct | – |
| Revel and Ayrault (2000) | SIRS-3    | As, Ba, Ce, Co, Cr, Cs, Eu, Fe, La, (Mo), Rb, Sb, Sc, Sm, Sr, Tb, Tb, (U), Zn | Direct | – |
| Revel and Ayrault (2000) | SIRS-3    | Al, As, Ba, Ce, (Cd), Co, Co, Cs, (Cs), Cu, (Eu), Fe, La, Li, Mg, Mo, Ni, Pb, Rb, Sr, (Sc), (Sm), Sr, (Tb), (Tm), U, V, W, Y, Zn | Direct | – |
| Dressler et al. (2001)   | SIRS-3    | Ag, Au, Te, U | Preconcentration-chelating medium Direct | Online |
| Veyssyere et al. (2001)  | SIRS-3    | Ag, Au, Ba, Bi, Cd, Co, Cu, Fe, Li, Mn, Mo, Pb, Pd, Pt, Sb, Sn, Tb, V, Y, Zn | Preconcentration-chelating medium Direct | – |
| Yan et al. (2001)        | SIRS-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Yb | Preconcentration-knotted reactor Direct | Online |
| Benkhedda et al. (2001)  | SIRS-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Yb | Preconcentration-knotted reactor Direct | Online |
| Aquilina et al. (2002)   | SIRS-3    | B, Ba, Ce, Cs, Dy, Er, Eu, Gd, Ho, La, Li, Lu, Mn, Mo, Nd, Pr, Rb, Sm, Sr, Tb, Tb, U, Yb | Preconcentration-chelating medium Dilute | Online |
| Mito et al. (2003)       | SIRS-3    | Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sm, Tb, Tb, Yb | Preconcentration-chelating medium Dilute | Online |
| Laborda et al. (2004)    | SIRS-3    | Al, Cd, Co, Cr, Cu, La, Mn, Mo, Nd, Ni, Pb, Pr, Sm, V | Preconcentration-chelating medium Dilute | Online |

CRM: Certified Reference Material

a. Analytes include Ag, Al, As, Au, Ba, Bi, Br, Cd, Ce, Co, Cr, Cu, Dy, Er, Eu, Gd, Ho, I, La, Li, Lu, Mn, Mo, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Sm, Sr, Tb, Tb, (Tm), U, V, W, Y, Yb, Zn
| Preconcentration medium | Quatification method | Calibration technique | Range of detection limits \[\text{ng l}^{-1}\] | Range of relative uncertainty equivalent \[\%\] | Original unit | Measure of uncertainty |
|-------------------------|----------------------|-----------------------|----------------|----------------|----------------|------------------|
| FeCl₃                   | ICP-QMS              | External              | n.s.           | 3.5–133.3       | pmol l\(^{-1}\) | s                |
| Nobias Chelate-PA1      | ICP-SFMS             | External              | 0.001–0.08     | 10.1–11.5       | ng l\(^{-1}\) | U\(k = 2\)          |
| Nobias Chelate-PA1      | ICP-QMS              | External              | n.s.           | 7–16            | pmol l\(^{-1}\) | 2s               |
| Nobias Chelate-PA1      | ICP-SFMS             | External              | 0.06–20.9      | 0.9–12.5        | nmol kg\(^{-1}\) | s                |
|                        | ICP-CRC-QMS          | External              | 0.25–101       | 6–36            | ng l\(^{-1}\) | s \(n = 6\)          |
| Ca₂(PO₄)₂               | ETV-ICP-CRC-QMS      | External              | 0.013–0.029    | 1.6–16.7        | pg ml\(^{-1}\) | s \(n = 5\)          |
| HDEHP+H₂MEHP            | ICP-QMS              | n.s.                  | 0.05–4.33      | 4.7–33.3        | ng kg\(^{-1}\) | s \(n = 11\)         |
|                        | ICP-SFMS             | External              | n.s.           | 5–8             | nmol l\(^{-1}\) | s \(n = 55\)          |
|                        | ICP-QMS              | n.s.                  | 0.5–1.7        | nmol kg\(^{-1}\) | s \(n = 12\)          |
| FeO(OH)                 | ICP-SFMS             | External              | n.s.           | 0.1–8.4         | ng l\(^{-1}\) | s \(n = 3\)          |
| Nobias Chelate-PA1      | ICP-SFMS             | External              | 0.002–14.6     | 0.7–55.6        | pmol l\(^{-1}\) | 2s               |
|                        | ICP-SFMS             | External              | 4.8–112        | 2.5–16.1        | nmol l\(^{-1}\) | s                |
|                        | ICP-SFMS             | ID                    | 4.8–112        | 18.5–29.8       | nmol l\(^{-1}\) | s                |
| Nobias Chelate-PA1      | ICP-SFMS             | External              | 0.001–0.08     | 10.3–11.5       | ng l\(^{-1}\) | U\(k = 2\)          |
|                        | ICP-QMS              | External              | n.s.           | 2.2–75.0        | µg l\(^{-1}\) | s \(n = 5\)          |
|                        | ICP-QMS              | n.s.                  | 0.9–50.0       | µg l\(^{-1}\) | s \(n = 5\)          |
|                        | INAA                 | n.s.                  | n.s.           | 1.7–11.8        | µg l\(^{-1}\) | s                |
|                        | ICP-MS               | n.s.                  | n.s.           | 7.7–250         | µg l\(^{-1}\) | s                |
| DDTP + C18              | ICP-QMS              | External calibration  | 0.05–2.24      | ng l\(^{-1}\) | s \(n = 6\)          |
|                        | ICP-SFMS             | n.s.                  | n.s.           | no measure of uncertainty given | pg g\(^{-1}\) | none            |
|                        | ICP-MS               | External + ID for Nd+Yb | n.s.          | 4.0–18.8        | µg l\(^{-1}\) | s                |
| PMBP                    | ICP-TOF-MS           | External              | 0.003–0.04     | 1.6–37.5        | µg l\(^{-1}\) | s \(n = 3\)          |
| HDEHP+H₂MEHP on C18     | ICP-QMS              | n.s.                  | 0.1–2.3 (REE)  | 3–12            | ng l\(^{-1}\) + µg l\(^{-1}\) | none |
| Iminodiacetate chelate resin | ICP-QMS    | n.s.                  | 0.002–0.09     | 0.4–15.0        | pg g\(^{-1}\) | s                |
|                        | ICP-QMS              | External (multi-point | 1–201          | 1.2–18.8        | ng ml\(^{-1}\) | u                |
As of the REE, the so-called technology-critical elements (TCEs), which include Te, Ge, Ga, In, Nb, Ta, platinum-group elements and the REE, gain more and more attention and will eventually find their way into the aquatic environment (Nuss and Blengini 2018, Romero-Freire et al. 2019). A potential new contamination source of Ga and In are offshore wind farms, as Ga and In are used in corrosion protection systems (Kirchgeorg et al. 2018, Reese et al. 2020). Moreover, Ga is also of interest as a biogeochemical tracer, for example monitoring dust inputs into the ocean (Shiller and Bairamadgi 2006). However, literature values of these elements in (sea) water CRMs are extremely scarce. As shown in Table 1, currently only five publications provide values for Ga in four of the seventeen studied CRMs (Zhu et al. 2005, Shiller and Bairamadgi 2006, Matsumya et al. 2012, Wuttig et al. 2019, Yeghicheyan et al. 2019) without providing any values for In. To the best of our knowledge, no certified values are available for Ga or In in any water CRMs.

Due to this lack of information, the scientific community depends on quality literature values of non-certified analytes, and profits from advancing and complementary analytical methods providing these literature values. In addition, CRMs are costly due to the complex and demanding certification process. Therefore, it is profitable for the community to be able to choose from a wide variety of literature values not only of recent but also of out-of-stock CRMs that might be still available in laboratories and ready-to-use.

Table 1 gives an overview of studies providing concentration data for CRMs used in this study, together with details of the analytical methods used. The main research tool for the compilation of this overview was the geochemical database GeoReM (Jochum et al. 2005, http://georem.mpch-mainz.gwdg.de/sample_query_pref.asp). However, non-listed literature is also included in Table 1. Literature for this table and for statistical treatment of compiled and measured data was collected until May 2021. No literature data for elements of interest were found for the water CRMs AQUA-1, BCR-403, CASS-2, CASS-6, NASS-7 and ERM-CA-403 until then. Analytical methods for element quantification in water matrices are mainly ICP-MS-based; however, TXRF, INAA and chemiluminescence were also applied.

| Authors                     | Water CRM | Analytes | Direct/diluted/ preconcentration + matrix reduction | Online/offline preconcentration |
|-----------------------------|-----------|----------|-----------------------------------------------------|--------------------------------|
| Laborda et al. (2004)       | SIRS-3    | Al, Co, La, Nd, Pb, Pr, Sm, V                | Direct                              |                                |
| Bowie et al. (2010)         | SIRS-3    | Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, U, V, Zn | Dilution (10-fold)                  |                                |
| Yeghicheyan et al. (2019)†  | SIRS-6    | Al, As, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cu, Ca, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, Re, Rh, Sb, Sc, Se, Si, Sn, Sr, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr | Direct/diluted/ preconcentration through evaporation | Offline |

The table lists only publications that contain at least one analyte that was not present in the respective CRM Certificate of Analysis. Types of ICP-MS setups are specified when given in the source publication and otherwise stated as 'ICP-MS'.

*Analytes of interest for this study are printed in bold. Analytes set in parentheses were below LOD or LOQ; † reproduced as provided in original publication; ‡ ICP-SFMS: Sector field ICP-MS; † ICP-QMS: Quadrupole ICP-MS; § PMBP: 1-phenyl-3-methyl-4-benzoylpyrazol-5-one; ‡ ICP-TOFMS: Time-of-flight ICP-MS; ‡ BHQ: B-hydroxyquinoline; ‡ C18: octyldecylsilane; ‡ n.s.: not stated; ‡ MAF-BHQ: fluorinated metal alkoxide glass-immobilised B-hydroxyquinoline; ‡ ETV: electrothermal vapourisation; ‡ CRC: Collision reaction cell; ‡ HDEHP/HY2MEHP: mixture of bis(2-ethylhexyl) hydrogen phosphate and 2-ethylhexyl diphenylphosphate; ‡ Not stated in publication, in retrospect calculated from blank values and s of blanks as LOD; ‡ + 3(blank); ‡ CTS-DHBA: cross-linked chitosan 3,4-dihydroxybenzoic acid; ‡ ID: isotope dilution; ‡ APDC: ammonium pyrrolidinedithiocarbamate; ‡ CTAC: cetyltrimethylammonium chloride; ‡ Assumed to be ng l; ‡ DI: DDTP: dithiophosphoric acid O,O-diethyl ester; ‡ For solutions of otolith samples; ‡ TSK-BHQ: vinyl polymer resin-immobilised B-hydroxyquinoline; ‡ Paper written in Japanese; ‡ Interlaboratory comparison.

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In particular, ICP-MS has matured to the method of choice for environmental analysis due to its sensitivity, multi-element capabilities and flexibility in terms of sample introduction methods (Pröfrock and Prange 2012, Wysocka 2021). However, despite the availability of highly sensitive ICP-MS instrumentation, water analysis remains challenging. The combination of a complex sample matrix and low analyte concentrations (ng l$^{-1}$ or even pg l$^{-1}$ levels) may be another reason for the limited data availability. The formation of matrix-related spectral interferences (e.g., polyatomic ions) within the plasma requires the application of high-resolution sector field ICP-MS (ICP-SFMS) or recently introduced tandem ICP-MS setups (ICP-MS/MS). Nevertheless, sample preparation such as preconcentration and matrix removal is crucial for a successful quantification of trace elements. In particular, the dissolved salt matrix has to be reduced in order to minimise interferences, but also to maintain long-term stability of the instrument. Therefore, the majority of studies listed in Table 1 relied on both preconcentration and matrix removal either by chelating (e.g., Sohrin et al. 2008) or co-precipitation protocols (e.g., Shaw et al. 2003). Both methods allow the enrichment of analytes of interest and matrix reduction. Depending on the analysed elements and sample matrix, a direct measurement (e.g., Peart et al. 1998 for river water or Field et al. 2007 for bulk elements in seawater) or simple dilution (e.g., Leonhard et al. 2002) can also be applied.

Chelating media allow both online preconcentration and matrix removal (Sohrin et al. 2008), which has led to the development of sample introduction systems such as the seaFAST by Elemental Scientific (Hathorne et al. 2012, Rapp et al. 2017, Wuttig et al. 2019). Online setups have the advantage of minimising blank values through fewer sample handling steps compared with offline procedures, while also enabling the possibility to continuously monitor blanks during online measurements. Moreover, evaporation of the separated and preconcentrated sample is prevented.

Although the increasing number of published values for non-certified elements in water CRMs is beneficial for the scientific community and data quality, the sheer amount of studies on similar analytes in the same CRM (e.g., eleven studies providing concentrations of REE in NASS-5, cf. Table 1) can be overwhelming. Aside from common databases, a comprehensive compilation allowing for the development of consensus values is currently missing.

As a consequence, the aim of this study was (a) to develop a method for the reliable quantification of thirty-four elements including classical heavy metals, as well as non-certified elements (e.g., REE, Ga, In, Sn, W and Th) in different natural water matrices, (b) to determine values for non-certified elements in seventeen water CRMs and (c) to compile and evaluate available literature values of non-certified elements for these seventeen water CRMs in order

| Preconcentration medium | Quatification method | Calibration technique | Range of detection limits$^a$ [ng l$^{-1}$] | Range of relative uncertainty equivalent [%] | Original unit | Measure of uncertainty |
|------------------------|----------------------|-----------------------|-------------------------------------------|------------------------------------------|---------------|-----------------------|
| –                      | ICP-QMS              | External (double-point calibration) | 1–201                                      | 1.4–21.4                                 | ng ml$^{-1}$ | u                     |
| –                      | ICP-SFMS             | External               | 1–400                                      | 0.003–22                                 | µg l$^{-1}$  | s ($n = 5$)          |
| –                      | ICP-MS/ ICP-OES      | External / ID          | n.s.                                       | 0.5–80.0                                 | µg l$^{-1}$ + ng l$^{-1}$ | U($k = 2$) |

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In particular, ICP-MS has matured to the method of choice for environmental analysis due to its sensitivity, multi-element capabilities and flexibility in terms of sample introduction methods (Pröfrock and Prange 2012, Wysocka 2021). However, despite the availability of highly sensitive ICP-MS instrumentation, water analysis remains challenging. The combination of a complex sample matrix and low analyte concentrations (ng l$^{-1}$ or even pg l$^{-1}$ levels) may be another reason for the limited data availability. The formation of matrix-related spectral interferences (e.g., polyatomic ions) within the plasma requires the application of high-resolution sector field ICP-MS (ICP-SFMS) or recently introduced tandem ICP-MS setups (ICP-MS/MS). Nevertheless, sample preparation such as preconcentration and matrix removal is crucial for a successful quantification of trace elements. In particular, the dissolved salt matrix has to be reduced in order to minimise interferences, but also to maintain long-term stability of the instrument. Therefore, the majority of studies listed in Table 1 relied on both preconcentration and matrix removal either by chelating (e.g., Sohrin et al. 2008) or co-precipitation protocols (e.g., Shaw et al. 2003). Both methods allow the enrichment of analytes of interest and matrix reduction. Depending on the analysed elements and sample matrix, a direct measurement (e.g., Peart et al. 1998 for river water or Field et al. 2007 for bulk elements in seawater) or simple dilution (e.g., Leonhard et al. 2002) can also be applied.

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Although the increasing number of published values for non-certified elements in water CRMs is beneficial for the scientific community and data quality, the sheer amount of studies on similar analytes in the same CRM (e.g., eleven studies providing concentrations of REE in NASS-5, cf. Table 1) can be overwhelming. Aside from common databases, a comprehensive compilation allowing for the development of consensus values is currently missing.

As a consequence, the aim of this study was (a) to develop a method for the reliable quantification of thirty-four elements including classical heavy metals, as well as non-certified elements (e.g., REE, Ga, In, Sn, W and Th) in different natural water matrices, (b) to determine values for non-certified elements in seventeen water CRMs and (c) to compile and evaluate available literature values of non-certified elements for these seventeen water CRMs in order
to propose new consensus values. Within this study, the term consensus value is used in its broadest definition, from Paule and Mandel (1982), as “best” estimates from a series of experimental results’.

Materials and methods

Water CRMs

Seventeen water reference materials were analysed to determine their (trace) element concentrations. Drinking water AQUA-1, riverine waters SLRS-1, SLRS-3 and SLRS-6, estuarine water SLEW-3, near shore seawaters CASS-2, CASS-3, CASS-4, CASS-5 and CASS-6 and (open ocean) seawaters NASS-4, NASS-5, NASS-6 and NASS-7 were purchased from the NRC (Ottawa, Canada). Seawaters BCR-403 and ERM-CA-403 and estuarine water BCR-505 were purchased from the Joint Research Centre (Geel, Belgium). Table 2 provides an overview of the studied water CRMs, their certification year, commercial availability and the certified elements. The matrices comprise of drinking water, fresh- and brackish water from rivers and estuaries, and salt water ranging from nearshore to open ocean seawater. All CRMs were acidified in the process of preparation (to a pH value between 1 and 2 after filtration of the original natural water) and were measured within this study without further pH adjustment. CRMs were selected according to availability in the research group’s CRM collection. Measurement aliquots of the reference materials were stored in acid cleaned 50 ml DigiTUBEs (SCP Science; Quebec, Canada). The reference materials were exclusively handled in a class 10000 cleanroom environment. All manipulation (e.g., preparation of aliquots, packing and unpacking) has been conducted inside a class 100 metal-free clean bench. All CRMs were packed in two LDPE bags to minimise contamination and evaporation during their transportation and storage at 4 °C.

Reagents

Preparatory laboratory work was performed in a class 10000 clean room inside a class 100 clean bench. Type I reagent-grade water (resistivity: 18.2 MΩ cm) was obtained from a Milli-Q Integral water purification system equipped with a QPod-Element polishing system (Merck Millipore; Darmstadt, Germany). Nitric acid (HNO₃, suprapur®, w = 65%, Merck KGaA or ROTIPURAN® Supra, w = 69%, Carl Roth GmbH + Co. KG; Karlsruhe, Germany) was further purified by double sub-boiling in quartz stills (AHF Analysentechnik; Tübingen, Germany) or using PFA acid purification systems (Savillex; Eden Prairie, USA) operated under clean room conditions. Optima grade glacial acetic acid and optima grade ammonia solution (w = 20–22%; Fisher Scientific; Schwerte, Germany) were used without further purification.

All plastic consumables were pre-cleaned by established protocols in solutions of HNO₃ (w = 1–2%) for a minimum of 1 week. Before usage, the material was flushed several times with Milli-Q water and dried inside a metal-free class 100 clean bench operated inside a clean room.

Instrumentation

Online preconcentration: Throughout this work, a seaFAST pico and, after its installation in 2018, a seaFAST SP2 (both Elemental Scientific; Omaha, USA), equipped with two columns filled with Nobias chelate-PA1 (HITACHI High-Tech Fielding Corporation; Tokyo, Japan) resin, were used. The instruments perform the sample loading, washing and elution of the analytes by a syringe driven system. All valves and tubes in contact with the different reagents, as well as the column, consist of high-purity PFA. Both systems consist of an autosampler as well as a hood equipped with an ULPA filter, to protect the samples against airborne contamination during their storage inside the autosampler (for schematics see Rapp et al. 2017).

For measurements using the seaFAST pico, external calibration standard solutions were prepared manually, whereas for measurements using the seaFAST SP2, the automated dilution of two multi-element stock solutions (20 and 1000 ng l⁻¹, respectively) via the integrated SP module was used.

The seaFAST systems were operated following supplier recommendations with a 4 mol l⁻¹ ammonia acetate buffer (pH = 6.0 ± 0.2) and 1.5 mol l⁻¹ HNO₃ as eluent. Samples were preconcentrated by a factor of 20.

ICP-MS/MS: The seaFAST systems were coupled online to an ICP-MS/MS system (Agilent 8800 or, after its installation in 2018, Agilent 8900 with similar settings, cf.
| CRM     | Matrix       | Supplier | Certified elements                                                                 | Elements with reference value | Elements with indicative value | Elements with information value | Year of certification | Commercial availability* |
|---------|--------------|----------|------------------------------------------------------------------------------------|-------------------------------|-------------------------------|--------------------------------|------------------------|--------------------------|
| AQUA-1  | Drinking water | NRC      | Al, As, Ba, Cd, Ca, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, U, V, Zn             |                               |                               |                                | 2017                   | Yes                      |
| BCR-403 | Seawater     | BCR      | Cd, Cu, Mo, Ni, Pb, Zn                                                            |                               |                               |                                | 1992                   | No                       |
| BCR-505 | Estuarine water | BCR     | Cd, Cu, Ni, Zn                                                                    |                               |                               |                                | 1994                   | No                       |
| CASS-2  | Nearshore Seawater | NRC | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn                                       |                               |                               |                                | 1989                   | No                       |
| CASS-3  | Nearshore Seawater | NRC | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn                                       |                               |                               |                                | 1989                   | No                       |
| CASS-4  | Nearshore Seawater | NRC | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Zn                                       |                               |                               |                                | 1989                   | No                       |
| CASS-5  | Nearshore Seawater | NRC | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn                                    |                               |                               |                                | 1999                   | No                       |
| CASS-6  | Nearshore Seawater | NRC | B, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, U, V, Zn                                      | As, Cs, V                     |                               |                                | 2016                   | Yes                      |
| NASS-4  | Open Ocean Seawater | NRC | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, U, Zn                                    |                               |                               |                                | 1992                   | No                       |
| NASS-5  | Seawater     | NRC      | As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, U, Zn                                    |                               |                               |                                | 1998                   | No                       |
| NASS-6  | Seawater     | NRC      | As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn                                        |                               |                               |                                | 2010                   | No                       |
| NASS-7  | Seawater     | NRC      | B, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, U, V, Zn                                      | As, Cs, V                     |                               |                                | 2016                   | Yes                      |
| ERM-CA-403 | Seawater | ERM | As, Cd, Co, Cu, Mn, Mo, Ni, Pb                                                    |                               |                               |                                | 1992                   | No                       |
| SLEW-3  | Estuarine water | NRC | As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, Zn                                       |                               |                               |                                | 2000                   | No                       |
| SLRS-1  | River water  | NRC      | Al, As, Ba, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, U, V, Zn           |                               |                               |                                | 1986                   | No                       |
| SLRS-3  | River water  | NRC      | Al, As, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, U, V, Zn  |                               |                               |                                | 1994                   | No                       |
| SLRS-6  | River water  | NRC      | Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sb, Sr, U, V, Zn           |                               |                               |                                | 2015                   | Yes                      |

Included are CRMs that are no longer commercially available but might still be in stock in research facilities for method quantification and development.

* At the time of the preparation of the manuscript (May 2021).
Element quantification: An external calibration, stabilised in diluted HNO₃ with \( w = 0.14\% \), ranging from 0.1 to 100 ng l⁻¹ for In, 10 to 10000 ng l⁻¹ for Al and 1 to 1000 ng l⁻¹ for all other analytes (REE, Co, Cu, Zn, Ga, Ma, Cs, In, Sn, W, Pb, Th and U. The ICP-MS/MS was equipped with x-lenses for measurements in O₂ mode and with either x- or s-lenses in He mode. Detailed operating instrument parameters and configurations are given in Table S1.

Standard addition was performed for the determination of Ga and In in the CRMs BCR-403, BCR-505 and NASS-4 according to DIN 32633:2013-05 procedure E (DIN e.V. 2013) in order to check for potential matrix effects on the quantification of In and Ga in natural waters. Aliquots of a 1000 ng l⁻¹ Ga stock solution and of a 50 ng l⁻¹ In stock solution (both stabilised in HNO₃ with \( w = 0.14\% \)) were added to aliquots of 45 ml CRM. For Ga, the stock solution was added in steps of 25 µl (0, 25, 50, 75, 100, 125, 150 and 175 µl) and for In in steps of 10 µl (0, 10, 20, 30, 40, 50, 60 and 70 µl). The solutions were diluted to 50 ml with high-purity (Milli-Q) water before measurement.

The CRMs were repeatedly measured via external calibration between 2017 and 2020. Therefore, measurement replicates differ for different CRMs (between \( n = 4 \) for REE in AQUA-1 and \( n = 62 \) for REE in CASS-3).

Evaluation strategy

Multi-elemental data were pre-processed using MassHunter version 4.4 (Agilent Technologies; Tokyo, Japan) in time-resolved mode and a custom written Excel® spreadsheet. The isobaric interference of \(^{115}\text{Sn} \) on \(^{115}\text{In} \) was corrected for by peak stripping as implemented in MassHunter using the signal of \(^{116}\text{Sn} \) and the isotopic abundances provided by the Commission on Isotopic Abundances and Atomic Weights (de Laeter et al. 2003).

Limits of detection (LOD) and limits of quantification (LOQ) were calculated in accordance with the blank value method described in DIN 32645:2008-11 (DIN e.V. 2008) based on calibration blanks (\( n = 3 \) per batch). The calibration blanks of all samples were combined to an average blank after outlier elimination.

Combined uncertainties were propagated according to GUM (BIPM 2008) considering overall reproducibility of the general element quantification and measurement precision of the element in a specific CRM. Uncertainties are reported with a coverage factor \( k = 2 \). For concentrations determined by standard addition, expanded uncertainties were calculated according to DIN 32633:2013-05 procedure E.

Statistical treatment of compiled and measured data

Consensus values were calculated without any weighting from the values determined in this study and the available literature values (including information values from CRM certificates where available). When values from external calibration and standard addition were determined, both values were included in the calculation of the consensus values. No consensus value was derived when no literature values were available. The consensus values were calculated following the procedure described in ISO 13528:2015 7.7 Annex C3 Robust analysis Algorithm A/ISO 5725-5 Algorithm A (ISO. 2015). A median \( x^* \) was calculated from \( p \) studies. A standard deviation \( s^* \) was calculated according to Equation (1).

\[
s^* = 1.483 \text{ median of } |x_i - x^*| \text{ with } (i = 1, 2, \ldots, p) \quad (1)
\]

Updated values of \( x^* \) and \( s^* \) were then calculated following Equations (2–5):

\[
\delta = 1.5s^* \quad (2)
\]

\[
\text{For each } x_i \text{ (} i = 1, 2, \ldots, p), \text{ an } x^*_i \text{ was calculated according to Equation (3)}:
\]

\[
x^*_i = \begin{cases} 
  x^* - \delta & \text{when } x_i < x^* - \delta \\
  x^* + \delta & \text{when } x_i > x^* + \delta \\
  x_i & \text{otherwise}
\end{cases} \quad (3)
\]

With that, the updated values for \( x^* \) and \( s^* \) were calculated following Equations (4) and (5):

\[
\text{Table S1, Agilent Technologies; Tokyo, Japan. Both instruments were optimised in a daily routine using a tuning solution containing Li, Co, Y, Ce and Tl to maintain a reliable day-to-day performance. The ICP-MS/MS instruments were operated in O₂ mode for the quantification of Sc, Ti, Y and REE and in He mode for the quantification of Al, V, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ma, Cs, In, Sn, W, Pb, Th and U. The ICP-MS/MS was equipped with x-lenses for measurements in O₂ mode and with either x- or s-lenses in He mode. Detailed operating instrument parameters and configurations are given in Table S1.}

\[
\text{Limits of detection (LOD) and limits of quantification (LOQ) were calculated in accordance with the blank value method described in DIN 32645:2008-11 (DIN e.V. 2008) based on calibration blanks (} n = 3 \text{ per batch). The calibration blanks of all samples were combined to an average blank after outlier elimination.}
\]

\[
\text{Combined uncertainties were propagated according to GUM (BIPM 2008) considering overall reproducibility of the general element quantification and measurement precision of the element in a specific CRM. Uncertainties are reported with a coverage factor } k = 2. \text{ For concentrations determined by standard addition, expanded uncertainties were calculated according to DIN 32633:2013-05 procedure E.}
\]

\[
\text{Statistical treatment of compiled and measured data}
\]

\[
\text{Consensus values were calculated without any weighting from the values determined in this study and the available literature values (including information values from CRM certificates where available). When values from external calibration and standard addition were determined, both values were included in the calculation of the consensus values. No consensus value was derived when no literature values were available. The consensus values were calculated following the procedure described in ISO 13528:2015 7.7 Annex C3 Robust analysis Algorithm A/ISO 5725-5 Algorithm A (ISO. 2015). A median } x^* \text{ was calculated from } p \text{ studies. A standard deviation } s^* \text{ was calculated according to Equation (1).}
\]

\[
s^* = 1.483 \text{ median of } |x_i - x^*| \text{ with } (i = 1, 2, \ldots, p) \quad (1)
\]

\[
\text{Updated values of } x^* \text{ and } s^* \text{ were then calculated following Equations (2–5):}
\]

\[
\delta = 1.5s^* \quad (2)
\]

\[
\text{For each } x_i \text{ (} i = 1, 2, \ldots, p), \text{ an } x^*_i \text{ was calculated according to Equation (3)}:
\]

\[
x^*_i = \begin{cases} 
  x^* - \delta & \text{when } x_i < x^* - \delta \\
  x^* + \delta & \text{when } x_i > x^* + \delta \\
  x_i & \text{otherwise}
\end{cases} \quad (3)
\]

\[
\text{With that, the updated values for } x^* \text{ and } s^* \text{ were calculated following Equations (4) and (5):}
\]

\[
\text{Updated values of } x^* \text{ and } s^* \text{ were then calculated following Equations (2–5):}
\]

\[
\delta = 1.5s^* \quad (2)
\]

\[
\text{For each } x_i \text{ (} i = 1, 2, \ldots, p), \text{ an } x^*_i \text{ was calculated according to Equation (3)}:
\]

\[
x^*_i = \begin{cases} 
  x^* - \delta & \text{when } x_i < x^* - \delta \\
  x^* + \delta & \text{when } x_i > x^* + \delta \\
  x_i & \text{otherwise}
\end{cases} \quad (3)
\]

\[
\text{With that, the updated values for } x^* \text{ and } s^* \text{ were calculated following Equations (4) and (5):}
\]
Online analysis yielded blank levels that were below the detection limits for most analytes. The multi-element seaFAST-ICP-MS/MS method measured REE, Sc, Ti and Y in O\textsubscript{2} mode and seventeen (trace) metals (Al, Cd, Co, Cu, Fe, Ga, In, Mn, Mo, Ni, Pb, Sn, Th, U, V, W, Zn) in He mode. Each run required 7.5 ml of sample and 12 min for the measurement of one sample. The setup with s-lenses were generally lower than those measured with the x-lenses, with the exception of Fe, Ga, Th and V. The LOD and LOQ of all analytes are given in Table S2. For analytes measured in He mode, values are available for both x- and s-lenses. X-lenses are the standard extraction lenses for robust, high-sensitivity measurements, the more robust x-lenses are preferable due to lower maintenance requirements.

\[ x^* = \frac{1}{p} \sum_{i=1}^{p} x_i^* \quad (4) \]

\[ s^* = \frac{1.134}{(p-1)} \left( \sum_{i=1}^{p} (x_i^* - x^*)^2 \right)^{1/2} \quad (5) \]

Robust \( x^* \) and \( s^* \) were derived by the iteration of the calculations until the process converges. Convergence was assumed when there was no change in the third significant digit of \( x^* \) and \( s^* \). No consensus value is provided in cases where convergence did not occur.

The expanded uncertainty of the consensus value was calculated according to Equation (6):

\[ U(k = 2) = ku = 2 \times 1.25s^*/\sqrt{p} \quad (6) \]

**Results and discussion**

**Method performance**

The multi-element seaFAST-ICP-MS/MS method measured REE, Sc, Ti and Y in O\textsubscript{2} mode and seventeen (trace) metals (Al, Cd, Co, Cu, Fe, Ga, In, Mn, Mo, Ni, Pb, Sn, Th, U, V, W, Zn) in He mode. Each run required 7.5 ml of sample and 12 min for the measurement of one sample. Thus, the quantification of thirty-four elements was completed within 24 min with a required 1.5 ml of sample. The combination of matrix removal, preconcentration and online analysis yielded blank levels that were below the detection limits for most analytes, which is vital for the analysis of environmental water samples. The LOD and LOQ of all analytes are given in Table S2. For analytes measured in He mode, values are available for both x- and s-lenses. X-lenses are the standard extraction lenses for robust, high-sensitivity applications, while s-lenses enable higher sensitivities under similar conditions (Agilent 2016). The results of an F-test showed that the blank measurements of x- and s-lenses could not be combined to one LOD or LOQ, with the exception of Fe, Ga, Th and V. The LOD and LOQ of the setup with s-lenses were generally lower than those measured with the x-lenses, with the exception of Fe, Ga and V. Hence, with the application of s-lenses instead of x-lenses, lower LODs and LOQs and higher sensitivities could be obtained with the Agilent ICP-MS/MS system. The application of s-lenses is advised for the quantification of challenging elements (such as Ga and In) in seawater. However, for the quantification of higher abundant elements, the more robust x-lenses are preferable due to lower maintenance requirements.

No significant difference was found between manually prepared calibrations and calibrations prepared by the seaFAST system. The method proved to be very robust against variations in the pH value in preliminary tests (pH range: 5.2–7.0) for the majority of elements. A pH of 6.0 ± 0.2 was adopted as a compromise.

**Certified elements**

A summarising matrix of the determined elements for all CRMs is provided in Figure 1. Analysis data for certified elements were generally in good accordance with the certificate. The multi-element method is viable for Al in fresh water, Cd, Co, Cu, Fe, Mn, Mo, Ni, Pb, V and Zn in fresh, brackish and seawater, and U in fresh and seawater. Exceptions are Cd in ERM-CA-403 and in SLRS-1, Co in SLRS-1, Mo in CASS-5, NASS-5 and NASS-6, Ni in BCR-403 and ERM-CA-403, U in CASS-5 and Zn in BCR-403. However, a re-evaluation of values for SLRS-1 by the USGS (Peart et al. 1998) found different values for Co and Cd, which agree with the analysed data of this study. It is suspected that the measured aliquot of BCR-403 might have been contaminated with Ni and Zn due to the long-term storage and usage. BCR-403 was prepared in 1989 and certified in 1992 (Quevauviller et al. 1992). The deviation of Mo and U concentrations of CASS-5, NASS-5 and NASS-6 might be due to the fact that the concentrations in these CRMs were above the working range of the calibration (1000 ng l\textsuperscript{-1} for Mo and U).

The determination of Al was challenging and is reflected in relative uncertainties > 40%. This is mainly due to a lower affinity of Al to the NOBIAS chelate-PA1 resin at pH 6 (Sohrin et al. 2008). Low Al concentrations (< 200 ng l\textsuperscript{-1}) in seawater can lead to relative uncertainties of > 90%. However, this was only observed for two of the twelve analysed seawater CRMs. In general, the method provides reliable results for Al in water samples, especially for brackish and freshwater. Additionally, the results for Al measured in seawater CRMs agree with respective literature values (seven references for CASS-4, CASS-5, NASS-4 and NASS-5).

Although the quantification of Fe yielded accurate results, precision can be compromised by relative uncertainties of > 70% for some brackish and seawater CRMs with concentrations < 780 ng l\textsuperscript{-1}. This may be again explained by the lower affinity of Fe to the NOBIAS chelate-PA1 resin at pH 6 (Sohrin et al. 2008), as well as interferences of various Ar species (mainly \(^{40}\text{Ar}^{16}\text{O}^4\)) on m/\(z = 56\). Initial experiments also included the measurement of \(^{54}\text{Fe}\) and \(^{56}\text{Fe}\). However, results showed that the achievable LOD using \(^{54}\text{Fe}\) were poorer than for \(^{56}\text{Fe}\), mainly caused by the lower abundance of the
In addition to the certified elements, numerous non-certified elements were analysed and literature values were collected, and consensus values were suggested. Figure 1 shows all analysed CRMs and gives the number of studies from which a consensus value was calculated. For AQUA-1, BCR-403, CASS-6 and NASS-7, no literature values were found, for the remaining thirteen CRMs at least one other study was found and considered. The following sections will give further details for the determination of Ga, In, Sc, Sn, Th, Ti and W – a selection of elements for which only a limited number of literature values are available.

**Non-certified elements**

For Ga, seven literature values were found for four water CRMs. The values measured in CASS-4, NASS-6 and SLRS-6 agree within uncertainty (53–77%) with the literature values. For NASS-5, the measured value does not agree with the available literature. The measurement of NASS-6 agrees with the concentration range measured by Wütig et al. (2019). However, the calculated consensus value for Ga (1.9 ± 1.9 ng l⁻¹) has a relative uncertainty of 100% due to the absolute difference in concentration. Relative uncertainties > 70% were obtained for four of the CRMs. This is especially true for very low concentrations (sub ng l⁻¹ range) close to the LOD, which was also described by Yeghichyan et al. (2019). Data obtained by external calibration agrees with the data obtained by standard addition.

**Indium:** Out of the seventeen analysed CRMs, no literature values were found for In. For BCR-403, BCR-505...
and NASS-4, In was also quantified via standard addition. The results were in good agreement with external calibration. Therefore, we propose external calibration as a suitable and simple way for ultra-trace quantification of In in natural waters. Relative uncertainties around 100% were obtained for three of the CRMs. This is especially true for very low concentrations (sub ng l\(^{-1}\)) range close to the LOQ. The use of s-lenses was especially important for In in terms of lowering LOD and LOQ and allowed for the more precise determination of sub ng l\(^{-1}\) concentrations in seawater.

**Scandium:** One literature value of Sc was each found for SLEV-3, SLRS-3 and SLRS-6. For SLEV-3, concentrations of REE, as well as Sc, agree with at least one value from the literature. For SLRS-3, no consensus value was determined as the large difference in reported values meant that the iteration process did not lead to convergence. The measured Sc concentration of SLRS-6 (this study 9.3 ± 8.3 ng l\(^{-1}\)) does not agree with data given by Yeghicheyan et al. (2019, 333 ± 15 ng l\(^{-1}\)). Therefore, Sc values provided within this study should only be considered indicative until additional studies confirm the results.

**Tin:** One literature value of Sn was each found for five of the seventeen water CRMs. The measured data agreed with the values provided for CASS-4, NASS-5 and SLRS-6, but was higher than the literature value for NASS-4 and lower for SLRS-3. However, the literature values given for NASS-4 and SLRS-3 do not provide any measurement uncertainty, making a statistically sound comparison difficult. The quantification of Sn is critically affected by its behaviour on the column. The elution of Sn is characterised by tailing of the elution profile and hence increased uncertainty of the quantification (Sohrin et al. 2008). This could be overcome by the addition of HCl to the eluent reagent. However, it will compromise the quantification of other elements as unpublished preliminary tests showed. Therefore, Sn values provided within this study should only be considered indicative until additional studies confirm the results.

**Thorium:** Literature values of Th were found for the CRMs CASS-4, NASS-4, NASS-6, SLRS-3 and SLRS-6. While the values determined for CASS-4, NASS-4, SLRS-3 and SLRS-6 do not agree with the literature values, which is partly reflected in high uncertainties for the suggested consensus value (e.g., \(U_{rel}(k = 2) = 260\%\) for NASS-4), the value for NASS-6 agrees with the value provided by Wuttig et al. (2019). Ti values provided within this study should therefore only be considered indicative until additional studies confirm the results.

**Tungsten:** Literature values of W were found for the CRMs CASS-4, NASS-4, NASS-5, SLEV-3, SLRS-1, SLRS-3 and SLRS-6. Zhu et al. (2003) reported higher W concentrations in CASS-4 than this study, which is also reflected in the relative uncertainty \((U_{rel}(k = 2) = 190\%)\) of the consensus value. The concentration of W for SLEV-3, given by Mohajerin et al. (2016) \((57.0 ± 9.2\text{ ng l}^{-1}\text{ via external calibration and 49.6 ± 9.2 ng l}^{-1}\text{ via ID})\), does not agree with this study \((27.6 ± 7.7\text{ ng l}^{-1})\). Tungsten values provided within this study should therefore only be considered indicative until additional studies confirm the results.

**Reference materials**

The following sections briefly describe results of all analysed CRMs. A summarising matrix of the determined elements for all CRMs can be found in Figure 1. Measurement results of the analyses of the CRMs that are still commercially available (AQUA-1, CASS-4, NASS-4, NASS-5, SLRS-6) are reported in the manuscript, whereas results for all other CRMs are reported in the Supporting Information.

**AQUA-1:** The results for thirty-four metals in AQUA-1 are given in Table 3, including certified values. Results for the certified elements are in good agreement with the certified values, although agreement between AI values is due to a high relative uncertainty of \(U_{rel}(k = 2) = 46\%\). No literature values were found for determination of consensus values for non-certified elements before the completion of data analysis. However, data from the recent publication of Yeghicheyan et al. (2021) for the determination of trace element concentrations in AQUA-1 agrees with the values found in this study, with the exception of Ti, which was reported as indicative only in both studies. No literature values were provided for In and W.

**BCR-403:** The results for thirty-four metals in BCR-403 are given in Table S3, including results for standard addition of Ga and In. The analytical results for the certified elements are in agreement with the certified values, with exception of...
Ni and Zn. No literature values were found for analysed non-certified elements.

**BCR-505:** The results for thirty-four metals in BCR-505 are given in Table S4, including results for standard addition of Ga and In. The analytical results for the certified elements are in agreement with the certified values. Measured and literature values were combined to suggested consensus values for non-certified elements.

**CASS-2:** The results for thirty-four metals in CASS-2 are given in Table S5, including certified values. The analytical results for the certified elements are in agreement with the certified values. Measured and literature values were combined to suggested consensus values for non-certified elements.

**CASS-3:** The results for thirty-four metals in CASS-3 are given in Table S6, including certified and literature values. The analytical results for the certified elements are in agreement with the certified values. Measured data agree within uncertainty with at least one of the provided literature values for each element.

**CASS-4:** Results for thirty-four metals in CASS-4 are given in Table S7, including certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. Analytical results for the certified elements are in agreement with the certified values. Measured data agree within uncertainty with at least one of the provided literature values for each element.

**Table 3. Measurement results and certified values for AQUA-1**

| Element | This study–external calibration | | Certified | |
|---------|-------------------------------|---|---|---|
| | c (ng l⁻¹) | U(k = 2) (%) | n | c (ng l⁻¹) | U(k = 2) (%) |
| Al | 43000 | 20000 | 46 | 6 | 54600 | 1600 |
| Cd | 6.1 | 1.8 | 29 | 5 | 4.3 | 1.4 |
| Ce | 63 | 12 | 18 | 4 | | |
| Co | 26.3 | 5.4 | 20 | 6 | 27.1 | 2.8 |
| Cu | 7800 | 1700 | 22 | 6 | 7460 | 120 |
| Dy | 3.67 | 0.54 | 15 | 4 | | |
| Er | 2.6 | 0.41 | 16 | 4 | | |
| Eu | 1.15 | 0.30 | 26 | 4 | | |
| Fe | 36500 | 8800 | 24 | 5 | 38000 | 1200 |
| Ga | 7.9 | 4.6 | 58 | 6 | | |
| Gd | 5.6 | 1.1 | 19 | 4 | | |
| Ho | 0.83 | 0.14 | 17 | 4 | | |
| In | 0.128 | 0.059 | 46 | 4 | | |
| La | 66 | 12 | 19 | 4 | | |
| Lu | 0.41 | 0.055 | 13 | 4 | | |
| Mn | 2620 | 540 | 21 | 6 | 2420 | 80 |
| Mo | 209 | 80 | 38 | 6 | 189 | 8 |
| Nd | 51.2 | 8.5 | 17 | 4 | | |
| Ni | 490 | 160 | 32 | 6 | 447 | 30 |
| Pb | 1420 | 370 | 26 | 6 | 1364 | 34 |
| Pr | 12.8 | 2.2 | 17 | 4 | | |
| Sc | 2.1 | 1.1 | 55 | 3 | | |
| Sm | 7.1 | 1.0 | 14 | 4 | | |
| Sn | 24 | 13 | 56 | 6 | | |
| Tb | 0.60 | 0.11 | 18 | 4 | | |
| Th | 1.15 | 0.64 | 56 | 5 | | |
| Ti | 37.7 | 9.8 | 26 | 4 | | |
| Tm | 0.372 | 0.048 | 13 | 4 | | |
| U | 6.65 | 0.98 | 15 | 4 | 6.95 | 0.52 |
| V | 165 | 38 | 23 | 6 | 152 | 8 |
| W | 5.7 | 1.5 | 26 | 6 | | |
| Y | 29 | 9 | 31 | 4 | | |
| Yb | 2.48 | 0.48 | 19 | 4 | | |
| Zn | 1050 | 270 | 26 | 6 | 970 | 80 |

The analytical results for the certified elements are in agreement with the certified values. Measured and literature values were combined to suggested consensus values for non-certified elements. Measured data agree within uncertainty with at least one of the provided literature values for each element.
REEs in CASS-4. The data are quite homogeneous, with the exception of data published by Kajiya et al. (2004) whose values are generally lower compared with other studies.

CASS-5: The results for thirty-four metals in CASS-5 are given in Table S8, including certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. The analytical results for the certified elements are in agreement with the certified values, with the exception of Mo and U. Measured data agree within uncertainty with at least one of the provided literature values for each element.

CASS-6: The results for thirty-four metals in CASS-6 are given in Table 4, including certified values. The analytical results for the certified elements are in agreement with the certified values. No literature values were found for the analysis of non-certified elements.

NASS-4: The results for thirty-four metals in NASS-4 are given in Table S9, including results from standard addition for Ga and In, as well as certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. The analytical results for the certified elements are in agreement with the certified values. The measured concentration of Ti is lower than the concentration published by Yabutani et al. (2001), which leads to a high uncertainty of the suggested consensus value ($U_r(\kappa = 2) = 260\%$).

NASS-5: The results for thirty-four metals in NASS-5 are given in Table S10, including certified and literature values. Measured and literature values were combined to

### Table 4.
Measurement results for CASS-6 from measurements with 'external' calibration

| Element | $c$ (ng l$^{-1}$) | $U(k = 2)$ (%) | $n$ | $c$ (ng l$^{-1}$) | $U(k = 2)$ |
|---------|------------------|----------------|----|------------------|------------|
| Al      | 2500             | 1100           | 46 | 11               | 21.7       |
| Cd      | 28               | 12             | 43 | 12               | 1.8        |
| Ce      | 5.5              | 1.1            | 20 | 5                | 5          |
| Co      | 75               | 15             | 20 | 12               | 67.2       |
| Cu      | 620              | 160            | 26 | 12               | 530        |
| Dy      | 1.41             | 0.24           | 17 | 5                | 1.4        |
| Er      | 1.19             | 0.21           | 18 | 5                | 1.4        |
| Eu      | 0.292            | 0.064          | 22 | 5                | 2          |
| Fe      | 1920             | 920            | 48 | 12               | 1560       |
| Ga      | 3.8              | 1.7            | 46 | 10               | 2          |
| Gd      | 1.85             | 0.4            | 21 | 5                | 2          |
| Ho      | 0.35             | 0.068          | 19 | 5                | 2          |
| In      | 0.47             | 0.14           | 30 | 11               | 2          |
| La      | 1.02             | 1.9            | 19 | 5                | 7          |
| Lu      | 0.211            | 0.048          | 23 | 5                | 0.4        |
| Mn      | 2330             | 480            | 20 | 12               | 2220       |
| Mo      | 7600             | 2800           | 37 | 12               | 9150       |
| Nd      | 6.4              | 1.2            | 18 | 5                | 4          |
| Ni      | 463              | 94             | 20 | 12               | 418        |
| Pb      | 12.5             | 3.4            | 27 | 12               | 10.6       |
| Pr      | 1.15             | 0.27           | 19 | 5                | 2          |
| Sc      | < 0.97 (LOQ)     |                |    | 5                | 4          |
| Sm      | 1.14             | 0.22           | 19 | 5                | 4          |
| Sn      | 6.7              | 5.8            | 86 | 12               | 2          |
| Tb      | 0.199            | 0.040          | 20 | 5                | 0.3        |
| Th      | 1.6              | 2.8            | 170| 12               | 0.2        |
| Ti      | 10.5             | 3.8            | 36 | 5                | 120        |
| Tm      | 0.169            | 0.038          | 22 | 5                | 0.2        |
| U       | 2360             | 810            | 34 | 12               | 2920       |
| V       | 550              | 220            | 41 | 12               | 500        |
| W       | 11.1             | 2.6            | 24 | 12               | 120        |
| Y       | 15.6             | 4.6            | 30 | 5                | 120        |
| Yb      | 1.24             | 0.31           | 25 | 5                | 1.6        |
| Zn      | 1380             | 280            | 20 | 12               | 1270       |

Additionally, the certified values are given (reference value for V and information values REE).
suggested consensus values for non-certified elements. The analytical results for the certified elements are in agreement with the certified values, with the exception of Mo, which is slightly below the certified range.

Measured values overlap with at least one of the literature values with the exception of Ti, Ga and Th, for which only one other value was found in literature (Zhu et al. 2005b, Shiller and Bairoamodji, 2006, Bayon et al. 2011). No consensus value is provided for Ti and Th, as the difference between reported values meant that convergence was not achieved following the iteration process. The measured values for each non-certified element overlap with at least one of the existing literature values.

**Table 5. Measurement results for NASS-7 from measurements with external calibration**

| Element | This study–external calibration | Certified |
|---------|--------------------------------|-----------|
|         | $c$ (ng l$^{-1}$) | $U(k = 2)$ | $U_{rel}(k = 2)$ (%) | $n$ | $c$ (ng l$^{-1}$) | $U(k = 2)$ |
| Al      | 340 | 170 | 48 | 20 |
| Cd      | 21.3 | 9.4 | 44 | 22 |
| Ce      | 3.48 | 0.62 | 18 | 8 |
| Co      | 16.3 | 2.5 | 16 | 22 |
| Cu      | 233 | 65 | 28 | 21 |
| Dy      | 1.51 | 0.22 | 15 | 8 |
| Er      | 1.3 | 0.2 | 15 | 8 |
| Eu      | 0.230 | 0.047 | 20 | 8 |
| Fe      | 570 | 400 | 71 | 21 |
| Ga      | 1.71 | 0.94 | 55 | 11 |
| Gd      | 1.39 | 0.27 | 19 | 8 |
| Ho      | 0.394 | 0.056 | 14 | 8 |
| In      | 0.0099 | 0.0078 | 79 | 13 |
| La      | 9.8 | 1.7 | 17 | 8 |
| Lu      | 0.203 | 0.036 | 18 | 8 |
| Mn      | 820 | 130 | 16 | 22 |
| Mo      | 8600 | 1500 | 17 | 19 |
| Nd      | 609 | 0.85 | 14 | 8 |
| Ni      | 265 | 44 | 17 | 22 |
| Pb      | 2.7 | 1.2 | 42 | 21 |
| Pr      | 1.38 | 0.25 | 18 | 8 |
| Sc      | < 0.97 (LOQ) | 7 |
| Sm      | 1.06 | 0.14 | 13 | 8 |
| Sn      | 5.4 | 3.7 | 69 | 22 |
| Tb      | 0.202 | 0.028 | 14 | 8 |
| Tm      | 0.9 | 1.7 | 200 | 22 |
| U       | 2250 | 680 | 30 | 19 |
| V       | 1330 | 220 | 16 | 22 |
| W       | 9.1 | 2.1 | 21 | 22 |
| Y       | 18.0 | 5.2 | 29 | 8 |
| Yb      | 1.23 | 0.34 | 27 | 8 |
| Zn      | 500 | 110 | 22 | 22 |

Additionally, the certified values are given (reference value for V and information values for REE).

were excluded as outliers from the calculation of the consensus value, as the values are generally higher or lower by a factor of two compared with the mean of the other values published for NASS-5.

**NASS-6:** The results for thirty-four metals in NASS-6 are given in Table S11, including certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. The analytical results for the certified elements are in agreement with the certified values, with the exception of Mo, for which the measured concentration range ($7500 \pm 1600$ ng l$^{-1}$) was slightly below the certified range ($9890 \pm 720$ ng l$^{-1}$). The measured values for each non-certified element overlap with at least one of the existing literature values.

**NASS-7:** The results for thirty-four metals in NASS-7 are given in Table 5, including certified values. The analytical
The results for the certified elements are in agreement with the certified values. However, the measured concentrations for some REE vary from the stated information values, with recoveries between 49% (Nd) and 260% (Eu). No literature values were found for determined non-certified elements.

ERM-CA-403: The results for thirty-four metals in ERM-CA-403 are given in Table 6, including certified values. The analytical results for the certified elements are in agreement with the certified values, with the exception of Ni and Cd. For Ni, the measured concentration in this study of 1370 \(\pm\) 160 ng l\(^{-1}\) was slightly above the certified value of 1040 \(\pm\) 160 ng l\(^{-1}\). For Cd, the measured concentration range (130 \(\pm\) 16 ng l\(^{-1}\)) was above the certified value (94 \(\pm\) 11 ng l\(^{-1}\)). No literature values were found for determined non-certified elements.

SLEW-3: The results for thirty-four metals in SLEW-3 are given in Table S12, including certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. The analytical results for the certified elements are in agreement with the certified values. For REE, Sc, Mo, U and Th, the measured concentrations overlap with at least one literature value. For W, the concentration given by Mohajerin et al. (2016, 57.0 \(\pm\) 9.2 ng l\(^{-1}\) via external calibration and 49.6 \(\pm\) 9.2 ng l\(^{-1}\) via ID) is different to the value determined in this study (27.6 \(\pm\) 7.7 ng l\(^{-1}\)).

SLRS-1: Results for thirty-four metals in SLRS-1 are given in Table S13, including certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. The analytical results for the certified elements are in agreement with the certified values, with the exception of Co and Cd. The measured concentration of Co (28.3 \(\pm\) 2.4 ng l\(^{-1}\)) is slightly below the certified value of

| Element | This study-external calibration | Certified |
|---------|---------------------------------|-----------|
|         | \(c\) (ng l\(^{-1}\)) | \(U(k = 2)\) | \(U_{rel}(k = 2)\) (%) | \(n\) | \(c\) (ng l\(^{-1}\)) | \(U(k = 2)\) |
| Al      | 2500   | 1000   | 40   | 7    |                    |          |
| Cd      | 130    | 16     | 12   | 7    |                    |          |
| Ce      | 6.05   | 0.88   | 15   | 8    | 94                 | 11       |
| Co      | 85.7   | 10.0   | 12   | 7    | 74                 | 11       |
| Cu      | 1120   | 160    | 14   | 7    | 870                | 130      |
| Dy      | 1.56   | 0.21   | 13   | 8    |                    |          |
| Er      | 1.20   | 0.15   | 13   | 8    |                    |          |
| Eu      | 0.306  | 0.057  | 19   | 8    |                    |          |
| Fe      | 4900   | 1300   | 27   | 7    |                    |          |
| Ga      | 6.3    | 1.6    | 26   | 7    |                    |          |
| Gd      | 3.52   | 0.55   | 16   | 8    |                    |          |
| Ho      | 0.370  | 0.054  | 15   | 8    |                    |          |
| In      | 0.057  | 0.010  | 18   | 7    |                    |          |
| La      | 6.48   | 0.94   | 15   | 8    |                    |          |
| Lu      | 0.198  | 0.026  | 13   | 8    |                    |          |
| Mn      | 2890   | 330    | 12   | 7    | 2470               | 110      |
| Mo      | 11900  | 1800   | 15   | 7    | 12000              | 600      |
| Nd      | 5.21   | 0.71   | 14   | 8    |                    |          |
| Ni      | 1370   | 160    | 11   | 7    | 1040               | 160      |
| Pb      | 112    | 15     | 14   | 7    | 98                 | 10       |
| Pr      | 1.15   | 0.17   | 15   | 8    |                    |          |
| Sc      | < 0.97 (LOQ) | 6       |
| Sm      | 1.17   | 0.19   | 17   | 8    |                    |          |
| Sn      | 145    | 18     | 12   | 7    |                    |          |
| Tb      | 0.220  | 0.033  | 15   | 8    |                    |          |
| Th      | 1.97   | 0.79   | 40   | 7    |                    |          |
| Ti      | 51     | 11     | 22   | 8    |                    |          |
| Tm      | 0.176  | 0.027  | 16   | 8    |                    |          |
| U       | 2880   | 500    | 17   | 5    |                    |          |
| V       | 1100   | 190    | 17   | 7    |                    |          |
| W       | 34.4   | 3.3    | 9.6  | 7    |                    |          |
| Y       | 15.6   | 3.1    | 20   | 8    |                    |          |
| Yb      | 1.20   | 0.17   | 14   | 7    |                    |          |
| Zn      | 5480   | 620    | 11   | 7    | 4600               | 600      |

Additionally, the certified values are given.
However, a re-evaluation of this CRM by the US Geological Survey (Peart et al. 1998) reported Co < 12 ng l\(^{-1}\), indicating discrepancies in the determination of Co in SLRS-1. A Cd concentration of 19.6 ± 2.2 ng l\(^{-1}\) was measured in this study compared with the certified value of 15 ± 2 ng l\(^{-1}\), while Peart et al. (1998) reported 34 ± 20 ng l\(^{-1}\).

**SLRS-3:** The results for thirty-four metals in SLRS-3 are given in Table S14, including certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. Results of the certified elements are in agreement with the certified values. Literature values and measured values are in good agreement for most non-certified elements, except Sc, Ti and Sn. It was not possible to completely compare the Sn concentration published by Veysseyre et al. (2001, 282 ng l\(^{-1}\)) with this study (198 ± 55 ng l\(^{-1}\)) as no uncertainty was given. For Sc and Th, the large difference between reported values meant that convergence was not achieved following the iteration process.

**SLRS-6:** The results for thirty-four metals in SLRS-6 are given in Table 7, including certified and literature values. Measured and literature values were combined to suggested consensus values for non-certified elements. The analytical results for the certified elements are in agreement with the certified values. The measured data for non-certified elements agrees with the data published by Yeghicheyan et al. (2019), with the exception of Sc. The Sc concentration measured in this study was 9.3 ± 8.3 ng l\(^{-1}\), while Yeghicheyan et al. (2019) report 333 ± 15 ng l\(^{-1}\). This is reflected in the high relative uncertainty (270%) of the calculated consensus value for Sc.

**Table 7.** Measurement results for SLRS-6 from measurements with external calibration

| Element | c (ng l\(^{-1}\)) | U (k = 2) | U\(_{rel}\) (k = 2) | p | U\(_{rel}\) (k = 2) |
|---------|-----------------|-----------|---------------------|---|---------------------|
| Al      | 31000           | 16000     | 51                  | 6 | 33800               |
| Cd      | 7.9             | 1.3       | 6                   | 5 | 6.3                 |
| Ce      | 314             | 67        | 21                  | 4 | 33800               |
| Co      | 58.8            | 6.5       | 11                  | 6 | 53                  |
| Cu      | 25600           | 2600      | 10                  | 6 | 23900               |
| Dy      | 23.3            | 4.2       | 18                  | 4 | 21.9                |
| Er      | 13              | 2.3       | 18                  | 4 | 12.4                |
| Eu      | 7.3             | 1.5       | 21                  | 4 | 7.26                |
| Fe      | 80000           | 19000     | 24                  | 6 | 84300               |
| Ga      | 7.3             | 3.9       | 53                  | 6 | 11                  |
| Gd      | 33.4            | 6.6       | 20                  | 4 | 31.6                |
| Ho      | 4.55            | 0.80      | 18                  | 4 | 4.3                 |
| In      | 0.23            | 0.11      | 46                  | 6 | 248.3               |
| La      | 267             | 57        | 21                  | 4 | 248.3               |
| Lu      | 1.85            | 0.32      | 17                  | 4 | 1.91                |
| Mn      | 2290            | 440       | 19                  | 7 | 2120                |
| Mo      | 188             | 79        | 42                  | 7 | 215                 |
| Nd      | 251             | 48        | 19                  | 4 | 227.8               |
| Ni      | 610             | 62        | 10                  | 6 | 616                 |
| Pb      | 174             | 41        | 23                  | 7 | 170                 |
| Pr      | 63              | 13        | 20                  | 4 | 59.1                |
| Sc      | 9.3             | 8.3       | 19                  | 4 | 525                 |
| Sm      | 420             | 7.8       | 19                  | 4 | 39.5                |
| Sn      | 108             | 6.6       | 11                  | 7 | 10                  |
| Tb      | 401             | 0.75      | 19                  | 4 | 4.07                |
| Th      | 224             | 41        | 18                  | 6 | 16                  |
| Ti      | 499             | 99        | 20                  | 4 | 333                 |
| Tm      | 1.82            | 0.35      | 19                  | 4 | 1.79                |
| U       | 666             | 8.5       | 13                  | 5 | 69.8                |
| V       | 364             | 76        | 21                  | 7 | 1200                |
| W       | 9.9             | 2.2       | 22                  | 7 | 16.5                |
| Y       | 124             | 39        | 31                  | 4 | 128                 |
| Yb      | 121             | 2.8       | 23                  | 4 | 11.2                |
| Zn      | 1870            | 420       | 22                  | 7 | 1760                |

Additionally, the certified values are given (reference value for Co) and available literature values. Consensus values are suggested combining measured and literature data.
Conclusions

The reported online preconcentration ICP-MS/MS method enabled the quantification of thirty-four elements in seventeen different water CRMs ranging from fresh water to seawater. The method proved to be robust and time efficient. The focus of this study was the development of a quick and versatile multi-element method including as many elements as possible. Due to this broad focus, including a variety of water matrices, certain limitations for the quantification of individual elements cannot be ruled out. Nevertheless, this study also showed that ‘old’ and out-of-stock CRMs are generally still suitable for use and of great benefit to the scientific community.

The measured data were combined with a comprehensive literature review of sixty-one references, reporting values for various non-certified elements of the studied water CRMs, and suggestions for consensus values were derived from an iteration process. The literature review and the suggestion of consensus values summarise the existing literature values for REE that are available within the community. Moreover, the suggested consensus values allow the use of the different available water CRMs for method validation of other elements, such as the emerging TCEs Ga and In, which to date have not been within the focus of the scientific community, nor measured routinely. This clearly highlights the need of new reference materials, taking into account the changing requirements of the scientific community.

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Data availability statement

The data that support the findings of this study are available in the Supplementary Material of this article.

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Supporting information

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

Table S1. Representative instrument settings for the ICP-MS/MS systems.
Table S2. LOD and LOQ of the measured analytes. Table S3. Element results for BCR-403 from measurements with external calibration and results for Ga and In of measurements using standard addition.
Table S4. Element results for BCR-505 from measurements with external calibration and results for Ga and In of measurements using standard addition.
Table S5. Element results for CASS-2 from measurements with external calibration.
Table S6. Element results for CASS-3 from measurements with external calibration.
Table S7. Element results for CASS-4 from measurements with external calibration.
Table S8. Element results for CASS-5 from measurements with external calibration.

Table S9. Element results for NASS-4 from measurements with external calibration and results for Ga and In of measurements using standard addition.

Table S10. Element results for NASS-5 from measurements with external calibration.

Table S11. Element results for NASS-6 from measurements with external calibration.

Table S12. Element results for SLEW-3 from measurements with external calibration.

Table S13. Element results for SLRS-1 from measurements with external calibration.

Table S14. Element results for SLRS-3 from measurements with external calibration.

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