



Quantification of 68 elements in river water monitoring samples in single-run measurements

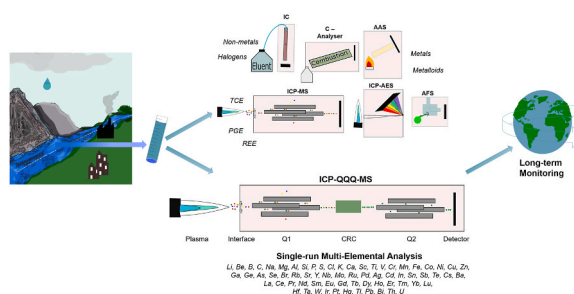
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HIGHLIGHTS

- First best-practice advice for a single-run quantification of 68 elements.
- Best-practice advice for multi-element analysis of surface waters via ICP-QQQ-MS.
- Readers can simply derive own methods from the method developed and validated.
- Addresses multi-element challenges from analyte-analyte- to analyte-matrix-effects.
- Opens the door to a better monitoring and understanding of global element dynamics.

GRAPHICAL ABSTRACT



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ABSTRACT

Triple-quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ-MS) is a unique analytical technique which is, next to speciation analyses, applied for the determination of total element concentrations in several matrices. Due to its wide linear range, short analysis times, and the collision-reaction gas technology, it is capable of addressing a high number of analytes in a single run with sufficient low limits of quantification for river water monitoring. Over the last decades, the focus of the environmental monitoring changed from “traditional” and regulated analytes to elements of possibly rising concern from new applications such as the so-called technology-critical elements (TCE). By widening the analytical window of this method for applications in networks of future river water monitoring, a better understanding of natural transport processes and global biogeochemical element cycles will be established and the total number of methods can be reduced. During method development and validation, certified reference materials, calibration check solutions, and spiked river water samples from 12 major German rivers covering different catchment areas were measured and evaluated with the three cell gases He, H₂ and O₂. The method delivers a best as possible undisturbed simultaneous determination for 68 out of 71 target analytes with recoveries in an accepted range of 80–120% for river water samples (dissolved fraction; <0.45 µm). After comprehensive evaluation, we offer a novel best-practice multi-element method for river water monitoring with the goal of fostering the exchange and discussion between practitioners in long-term river monitoring. It enables the readers to create their own methods based on the scientific needs to monitor elemental “fingerprints” of rivers and their catchments.

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1. Introduction

A modern and comprehensive monitoring of the chemical river water status includes the analysis of a wide spectrum of inorganic analytes (Arndt et al., 2022). Full quantification of major, minor, and trace elements improves the assessment of riverine fluxes as well as the identification of anthropogenic or natural element cycles. Accordingly, routine analyses are performed on potentially toxic trace elements (e.g., Cr, Ni, Cu, Zn, As, Cd, Hg, Pb), radionuclides (e.g., ^3H , ^{90}Sr , ^{137}Cs), nutrients (e.g., NO_2^- , NO_3^- , PO_4^{3-}) as well as major anions (e.g., CO_3^{2-} , SO_4^{2-} , Cl^-) and cations (e.g., Na^+ , Mg^{2+} , K^+ , Ca^{2+}) with different analytical techniques in river water monitoring concepts (Arle et al., 2016). Many of these analytes are part of the regulative requirements in Europe and worldwide. Chemical monitoring of river water has to be continuously adapted to changing requirements and changing societal demands. An example of these requirements is the inclusion of emerging contaminants such as the technology-critical elements (TCE) (Filella and Rodriguez-Murillo, 2017; Romero-Freire et al., 2019). Details on the importance and potential motivation for the analyses of major, minor, and trace elements in environmental river water monitoring is provided in the Supporting Information (S1section 1 and Table S1). Table S1 provides an extensive list about the individual elements, their environmental relevance in river water, possible regulatory limits, as well as references to specific studies about analytical methods as well as biogeochemical cycling of the element in river systems.

Quadrupole based inductively coupled plasma mass spectrometry (ICP-Q-MS) is established as the analytical method of choice for multi-element approaches in environmental samples. It delivers low detection limits, a high sensitivity, a large dynamic range and a high sample throughput (Nelms, 2005; Thomas, 2013). However, the analyses of certain elements require thorough method development and the consideration of existing spectroscopic interferences including isobaric, doubly charged, polyatomic, and tailing interferences within the respective matrix (Wilschefske and Baxter, 2019). Therefore, the benefits from ICP-Q-MS were significantly expanded by the introduction of techniques that further support the elimination of spectroscopic interferences, such as the collision-reaction-cells (CRC) and the introduction of a second scanning quadrupole in ICP-QQQ-MS analyses (Tanner et al., 2002; Pröfrock and Prange, 2012; Balcaen et al., 2015; Wilschefske and Baxter, 2019).

From our perspective, many published applications do not cover the full instrumental capabilities for multi-element analyses, by focusing only on a narrow element window such as potentially toxic trace metals (e.g., Makishima et al. (2010); O'Sullivan et al. (2013)) rare earth elements (REE; e.g., Palmieri et al. (2011)) or platinum group elements (PGE; e.g., Machado et al. (2017)). In order to fulfil the long-term monitoring needs of surface water and rising societal demands (Arndt et al., 2022), the analytical spectrum should be widened and integrated into standard operation procedures by exploiting the full ICP-QQQ-MS capabilities.

The overall challenge in multi-element approaches consists of adding each individual analyte to a single run measurement. Thereby, optimising the operation conditions becomes significantly more complex. Next to known spectroscopic interferences, the non-spectroscopic interferences must be addressed in detail with regard to matrix-effects reaching from sample and standard preparation to the detection. As an example, Wilschefske and Baxter (2019) stated that there are several complicated mechanisms that appear in all parts of the process including enhancement or suppression of analytes by further analytes or matrix constituents. From our perspective, the two major challenges are i) potential contamination sources for a multitude of elements and ii) a balance and “best as possible” analytical compromise between the multitude of single element analytical demands in multi-element analyses.

As an improvement for the future river water monitoring, we here present a novel best-practice advice. It aims to simultaneously quantify

an as large as possible number of elements in filtered river water samples (dissolved fraction, $<0.45\ \mu\text{m}$) in a single analytical run. At the beginning 71 elements were considered within method development which are naturally occurring stable isotopes or long-lived radionuclides: Li, Be, B, C, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Sb, Te, I, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, U.

We addressed the following main research questions regarding potential spectroscopic and non-spectroscopic interferences during method development of our multi-element method: I. Spectroscopic interferences: To which degree can spectroscopic interferences, as previously documented by others, be avoided in multi-element analysis of river water? II. Non-spectroscopic interferences: i) Internal standards: Which elements can be used as internal standards (ISTD) to respond to matrix effects and to cover the whole range of analytes? ii) Analyte-to-matrix interaction: Which analyte-to-matrix reactions and thus analytical artefacts such as precipitation or complex-formation have to be considered? iii) Analyte-to-analyte interaction: How can we calibrate all analyte elements without analyte-to-analyte disturbances for the concentration range needed in river water monitoring in as few as possible parallel approaches? iv) Stabilisation: How can we reach sufficient stabilisation of all analyte elements in samples and standards by as few as possible parallel steps? v) Memory effects: Which memory effects can be expected from the full range of analytes and which rinsing procedures are required to achieve sufficiently low limit of quantifications (LOQs) in routine river water monitoring?

By addressing these questions, we created a best-practice advice considering the three cell gases He, H₂ and O₂ in on-mass and mass-shift modes. Decision criteria for the potential best-practice were based on the LOQ, the sensitivity (as counts per seconds (cps) per $\mu\text{g/l}$), the background equivalent concentration (BEC), the instrument detection limit (IDL), as well as the recovery of certified reference materials (CRM), calibration check solutions, and spiked river water samples. Spectroscopic interferences were assessed by preparing and testing worst-case-matrices containing elements known to interfere with the target analytes in river water. A calibration strategy was developed that enables the simultaneous quantification of major, minor, and trace elements. Therefore, each element was examined and calibrated in concentration ranges from ng/l to mg/l . A set of ISTDs was selected from the remaining elements. They were chosen from light to heavy masses for matrix corrections. As a result, a first best-practice method is offered, enabling the simultaneous detection of 68 out of 71 elements in river water samples. The aim of this method is i) to provide a best-practice advice which is tailor-made for adaptation by ICP-QQQ-MS operators according to their monitoring needs in different catchment areas, ii) to foster the discussion between practitioners from the global surface water monitoring community in order to iii) contribute to a better understanding of riverine fluxes and transport budgets within biogeochemical element cycles and consequently to assess elemental “fingerprints” within the long-term monitoring.

2. Materials and methods

2.1. Instrumentation

The method was developed using an Agilent 8900 series ICP-QQQ-MS (Agilent Technologies, Japan) equipped with an autosampler (ESI SC4 DX, ESI Elemental Service & Instruments GmbH, Germany), x-lenses and a standard sample introduction kit consisting of a MicroMist glass concentric nebulizer, a Peltier-cooled quartz spray chamber and a quartz torch with 2.5 mm injector. Due to elevated HCl concentrations during some of the measurements, the instrument was equipped with a nickel-plated sampler cone and nickel skimmer cone. The instrument settings are listed in Table 1.

Additionally, measurements were carried out with an Agilent 8800

Table 1

Instrument settings of the 8900 Agilent ICP-QQQ-MS.

Parameter	H ₂	He	O ₂
Mode	MS/MS	MS/MS	MS/MS
RF power/W	1550	1550	1550
Sampling depth/mm	1.40	6.00	6.00
Plasma gas flow rate/(l/min)	15.0	15.0	15.0
Nebulizer gas flow rate/(l/min)	1.07	1.07	1.07
Auxiliary gas flow rate/(l/min)	0.90	0.90	0.90
Cell gas flow rate/(ml/min)	7.00	4.60	0.30
Energy Discrimination/V	0.00	4.60	−7.00

(Agilent Technologies, Japan) for method cross validation purposes. It was equipped with an autosampler (Agilent SPS-4, Agilent Technologies, Japan) and the standard sample introduction kit as described for the 8900 series.

The ICP-QQQ-MS instruments were tuned with a tuning solution containing Li, Co, Y, Ce and Tl (10 µg/l). The sensitivity, the relative standard deviation (<3%) during tuning which reflects the stability of the signal, the doubly charged ion ratio ($^{140}\text{Ce}^{++}/^{140}\text{Ce}^{+} < 3\%$), and the oxide formation rate ($^{140}\text{Ce}^{16}\text{O}^{+}/^{140}\text{Ce}^{+} < 2\%$) were checked before each measurement. The instrument was tuned daily in all gas modes (cf. Table 1).

2.2. Reagents, standard solutions and reference materials

Stock solutions and calibration standards were prepared by dilution of single element ICP standards purchased from Merck (Merck GmbH, Germany). A ^6Li standard (94.66%, SPEX CertiPrep™, USA) was used as an ISTD in addition to ^{103}Rh and ^{185}Re . For the carbon calibration, single element standards prepared from tartaric acid (Spetec GmbH, Germany) and oxalic acid (PerkinElmer, USA) were both tested. Calibration standards for ion chromatography (IC; Merck, Germany) were used to calibrate the halogens (Cl, Br, and I).

Ultrapure water ($\leq 0.055 \mu\text{S}/\text{cm}$) was produced with an Arium mini water purification system (Sartorius, Germany). HNO_3 (65% w/w) and HCl (37% w/w) were purchased from Merck (EMSURE®, Merck GmbH, Germany) and were further purified using sub-boiling distillation systems (dst-4000 and dst-1000, Savillex, USA). All further dilutions were done volumetrically, but use the percentage of the concentrated acid as reference (e.g., 1.3% HNO_3 corresponds to a volumetric 1:50 dilution of the concentrated 65% HNO_3).

All samples and calibration standards were prepared in 15 mL or 50 mL centrifuge vials (VWR catalyst Laboratory Services, USA and SCP Science, Canada), which were cleaned with HNO_3 (1.3%) for >24 h and rinsed with ultrapure water prior to utilisation. All preparation steps were conducted under clean room conditions in a laminar flow box (SPETEC GmbH, Germany).

The following CRMs were used as quality check controls and for method development: SPS-SW1, SPS-SW2 (Spectrapure Standards AS, Norway), NW-TM-15.3, NW-TM-24.4, NW-TM-35, NW-TMDA-51.5 (Environment and Climate Change Canada, CRM Sales, Canada) and NIST SRM 1640a (National Institute of Standards and Technology, USA). For the method validation, SPS-SW1, SPS-SW2 and NW-TMDA-51.5 were used. However, no appropriate surface water CRM for dissolved species was available for the following elements: C, Cl, Ge, Br, Zr, Nb, Ru, Pd, In, Te, I, Hf, Ta, W, Ir, Pt, Au, Hg. The CRMs, the calibration check solutions, and the spike solutions were prepared daily from multi-element stock solutions containing all analytes in three different concentration ranges. The detailed composition of all quality standards (CRMs, calibration check, spikes) is listed in Table S2. Details on the composition of the stock solutions is given in section 2.5.

2.3. Cell gas and measurement mode

ICP-QQQ-MS offers an octupole CRC which is positioned between

two quadrupole mass filters Q1 and Q2. This configuration allows different strategies to address the different potentially occurring spectroscopic interferences (isobaric, doubly charged, polyatomic, tailing; Wilschefske and Baxter (2019)). In this study, it was examined which combination of analytical modes provides the most reliable results in the analysis of river water samples, with the goal of using as few modes as possible for routine analytical procedures. For this purpose, all elements under consideration were examined in different analytical modes using on-mass and mass-shift methods and the different cell gases He, H₂, and O₂ that appeared potentially applicable based on available reaction data (Sugiyama and Nakano, 2014). An overview of the considered modes for the individual elements is given in Table S3.

2.4. Isotopes detected

If possible, elements were analysed on a mass not shared with another element to prevent isobaric interferences. If several isotopes without isobaric overlap were available for one element, the most abundant among those was chosen for analyses. An exception of the latter mentioned is Ga. It consists of two isotopes: ^{71}Ga and ^{69}Ga . ^{69}Ga was not chosen, as ^{138}Ba can easily form doubly charged ions due to its lower 2nd ionisation potential of 10 eV compared with the 1st ionisation potential of Ar (15.76 eV). Indium, which possesses no isotopes free from isobaric overlaps, was analysed on mass 115 and a mathematical correction by Sn, which is measured on mass 118 and which also occurs as an isotope with mass 115, was applied. Pb consists of three abundant radiogenic isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) and the less abundant ^{204}Pb . Depending on the geological conditions (type and age of rock formations in the area) and anthropogenic influences, these isotopes can occur in strongly varying ratios in the environment (Bird, 2011; Bridgestock et al., 2018). Therefore, Pb concentrations were calculated from the sum of the three abundant isotopes, similar to previous studies (Delves and Campbell, 1988). For all other investigated elements, potentially occurring small variations in the relative distribution of stable isotopes in environmental samples (Wiederhold, 2015) were deemed to be negligible for the purposes of this study.

2.5. Calibration strategy

In single element standards, most elements are stabilised by HNO_3 (2–3%) with some exceptions. Si standards contain HF traces. Zr, Ru, Sn, Sb, Hf, Ir, Pt and Au are stabilised in HCl (7%). B, P, S, Mo, Nb, Re as well as the halogens (Cl, Br, I) are stable in H_2O without additives. Hence, mixing of single element calibration standards for parallel external calibration stabilised in different matrices requires careful considerations to avoid artefacts. First, the halogen IC standards are usually prepared from sodium salts which prevents the calibration of Na and halogens from the same stock solution or calibration series. The same limitation exists with Cl and standards containing HCl . Second, further issues arise from these HCl stabilised standards. Low HCl concentrations are known to cause precipitation of some of the dissolved elements, e.g., Ag as AgCl (Fritz, 1985; Walkner et al., 2017), which makes the mixing of the corresponding standards impractical. In contrast, the use of calibration series in different matrices (e.g., one series prepared with diluted HNO_3 and one series prepared with diluted HCl) creates difficulties with regard to the stability of the ISTD during ICP-MS measurements. Therefore, the calibration solutions have to be matrix-matched in the best possible way. The term “matrix-matched” means in this case that the acid composition of all solutions measured in one analytical run should be as similar as possible. Due to practical and economic reasons such as time requirements during standard preparation and analyses, a limited number of calibration series and stock solutions, stable for several weeks, is desirable.

2.6. River water samples

To estimate the expected concentration ranges of the different elements and to examine spike recoveries during method development and validation, river water samples (grab samples, $<0.45\ \mu\text{m}$, acidified to 1.3% HNO_3) from 12 sampling locations, covering different German rivers and their respective catchment area characteristics were included (cf. Fig. 3). Filtration and acidification were conducted immediately after sample delivery (within 1–3 days). All samples were stored at $4\ ^\circ\text{C}$ prior to analysis.

2.7. Method development and validation

The most suitable measurement mode for each of the target analytes was selected based on recoveries of CRMs, calibration check solutions, and spiked river water samples as well as on the LOQ calculated for each analytical run from the measurement of a minimum of ten replicates of blank measurements (1.3% HNO_3) per day. Moreover, criteria from the external calibration, namely, the instrument detection limit (IDL), the background equivalent concentration (BEC), and the sensitivity (as cps per $\mu\text{g/l}$) were assessed (Tables S4–S7). Additionally, interference check solutions were analysed. They contained low concentrations of different analytes (0.1 $\mu\text{g/l}$ and 1 $\mu\text{g/l}$) and high concentrations of potentially interfering elements (10 $\mu\text{g/l}$ to 10 mg/l) to simulate potential matrix effects. Hence, a successful elimination of polyatomic and doubly charged ion interferences in the different analytical modes was evaluated. Details on potentially occurring interferences and calculated recoveries for each standard are given in Tables S8A–S8F. Relevant spectroscopic interferences in the concentration ranges of the selected analytes for river water are shown in Tables S8A–S8F. They were based on the Agilent MassHunter Software (MassHunter 4.5, Workingstation, Version C01.05) and on existing literature (May and Wiedmeyer, 1998; Sugiyama and Shikamori, 2015; Machado et al., 2017; Flores et al., 2020).

To elaborate strategies regarding HCl stabilisation, the elements Zr, Ru, Sn, Sb, Hf, Ir, Pt, Au - all available in single-element solutions stabilised with HCl - were measured in matrices containing HNO_3 (1.3%), aqua regia (1 HNO_3 : 3 HCl diluted 1:50 with ultrapure water) and HCl (3%). All solutions (samples, multi-element stock solutions, calibrations, calibration check solutions, spikes) were prepared with the respective acid or acid mixture.

Different solutions to rinse the sample loop were assessed during method development. They covered alkaline solutions using NH_3 , complexing agents such as EDTA, stronger acid concentrations of up to 6.5% HNO_3 , HCl in different concentrations of up to 3% and diluted mixtures of HNO_3 and HCl.

For all analytes suitable analytical modes were defined. The final multi-element method was validated in 12 measurement sessions by two different operators on the same instrument (Agilent 8900 ICP-QQQ-MS). The analyses included CRMs, calibration check solutions and (spiked) river water samples. Additionally, one measurement session was performed on a different instrument (Agilent 8800 ICP-QQQ-MS) for method cross validation in a second laboratory (cf. Fig. S1).

2.8. Statistics and graphs

Figures were prepared with the R software (R version 4.0.1, 2020 The R Foundation for Statistical Computing) using the function “boxplot” and the package “ggplot2”.

The LOQ was calculated as blank $+10\ \sigma$. For recovery calculations, concentrations below the respective LOQ and/or a relative standard deviation (RSD) above 10% were not included. An exception is Fig. 3, where values below LOQ were included for better comparability.

Regarding the calculation of spike recoveries and for Fig. 2, only spikes $>10\%$ in relation to the element concentration of the respective river water sample were considered. Since multi-element spike solutions

were prepared by covering a wide range of concentrations, it became apparent that for some elements the lowest spike concentration was not high enough in relation to the concentrations present in the river water samples, e.g. for Na, Mg, Ca.

All analytes of the final method were quantified via external calibration with $R^2 > 0.999$ by a 10-point calibration.

3. Results and discussion

The knowledge and experiences gained from our comprehensive method development are described in this section along with the summary of the final analytical procedure. Subsequently, the results of the method validation are presented.

3.1. Identification of the most suitable analytical modes

Based on the evaluated decision criteria (cf. section 2.7) at least one analysis mode per analyte was identified for the quantification of the elements considered in river water samples. The final set-up for the multi-element measurement by ICP-QQQ-MS is presented in Table 2. Alternative analytical modes are given when comparably good results were achieved for the respective analyte. This alternative option may potentially deliver better results in catchment areas chemically different to those included in this study. These options have to be evaluated by each operator for the respective catchment.

Details on the decision criteria regarding LOQs and the external calibration parameters (BEC, IDL, sensitivity), which were also used for the selection of the analytical mode for each element next to the recoveries of several standards, are given in Tables S4–S7. Additionally, all analytical modes considered during method development were tested for their ability to eliminate spectroscopic interferences that are likely to influence the analyses of river water samples. A list of the tested spectroscopic interferences is presented in the SI including a summary of the results obtained (Tables S8A–S8F and S9). Examples of V, As, Cd, and Gd are shown in Fig. 1. Good recoveries for As were only achieved in mass-shift mode using O_2 , while Cd was measurable in all on-mass modes but due to a poor reactivity with O_2 not as MO^+ which is also supported by Sugiyama and Nakano (2014). The spectroscopic interferences checked for V led to the conclusion that not all on-mass modes were suitable, but only He or MO^+ . Good Gd recoveries were achieved in all depicted modes except for O_2 due to its high reaction ability with O_2 and the formation of MO^+ (Sugiyama and Nakano, 2014). All further results of the standards containing “worst-case” matrices for selected analytes are given in Tables S8A–S8F.

3.2. Selection of the internal standards

The aim of quantifying that large number of elements in surface waters limits the elements/isotopes that can be used as ISTD. In this study, ^{103}Rh and ^{185}Re proved to be suitable ISTD for the applied mass range. ^6Li was added as an option for the correction of lighter elements, while detecting ^7Li as an analyte. However, the standard purchased was only 95% ^6Li enriched and therefore the $<5\%$ ^7Li interfered in the Li measurements close to the LOQ. A higher enriched standard was not available at the time when measurements started. Moreover, the ^6Li standard is prepared from a carbonate salt which could potentially interfere with the carbon measurement, but only to a minor degree due to the comparatively high carbon concentration range (mg/l). The impact of ^6Li as ISTD needs to be taken into consideration for the Li quantification. Hence, we suggest that ^6Li is only a convenient option as an ISTD in quadrupole-based analyses at higher degrees of enrichment to minimise the need for the implementation of correction calculations.

3.3. Calibration strategy

Challenges with regard to the composition of stock solutions and

Table 2

Selected isotopes, analytical modes and integration times for all elements included in the final method. The 1st option which was applied during method validation and the 2nd option as alternative are shown. Q1 and Q2 indicate the m/z settings of the first and second quadrupole mass filter, respectively.

Element	Q1	1st option		2nd option		Integration time/s	Element	Q1	1st option		2nd option		Integration time/s
		Cell gas	Q2	Cell gas	Q2				Cell gas	Q2	Cell gas	Q2	
Li	7	He	7	H ₂	7	0.5	Pd	105	O ₂	105	–	–	2.0
Be	9	O ₂	9	He	9	0.5	Ag	107	He	107	H ₂	107	1.0
B	11	O ₂	11	He	11	0.5	Cd	111	He	111	H ₂	111	0.3
C	12	O ₂	28	–	–	0.2	In	115	He	115	H ₂	115	1.0
Na	23	He	23	O ₂	23	0.01	Sn	118	He	118	O ₂	118	0.3
Mg	24	He	24	O ₂	24	0.05	Sb	121	He	121	H ₂	121	0.3
Al	27	H ₂	27	He	27	0.5	Te	125	He	125	H ₂	125	0.1
Si	28	O ₂	34	H ₂	28	0.2	Cs	133	He	133	H ₂	133	0.5
P	31	O ₂	47	–	–	0.2	Ba	137	He	137	H ₂	137	0.3
S	32	O ₂	48	–	–	0.1	La	139	He	139	O ₂	155	0.5
Cl	35	H ₂	37	O ₂	51	0.05	Ce	140	He	140	O ₂	156	0.5
K	39	He	39	O ₂	39	0.05	Pr	141	He	141	–	–	0.5
Ca	44	O ₂	60	He	44	0.05	Nd	146	O ₂	162	He	146	0.5
Sc	45	O ₂	61	He	45	0.3	Sm	147	O ₂	163	He	147	0.5
Ti	47	O ₂	63	–	–	0.3	Eu	153	He	153	O ₂	169	0.5
V	51	O ₂	67	He	51	0.3	Gd	157	O ₂	173	He	157	0.5
Cr	52	O ₂	68	He	52	0.3	Tb	159	O ₂	175	He	159	0.5
Mn	55	He	55	H ₂	55	0.3	Dy	163	O ₂	179	He	163	0.5
Fe	56	He	56	H ₂	56	0.1	Ho	165	O ₂	181	He	165	0.5
Co	59	He	59	H ₂	59	0.3	Er	166	O ₂	182	He	166	0.5
Ni	60	He	60	H ₂	60	0.3	Tm	169	He	169	O ₂	185	0.5
Cu	63	He	63	H ₂	63	0.3	Yb	172	He	172	O ₂	188	0.5
Zn	66	He	66	O ₂	66	0.3	Lu	175	O ₂	191	He	175	0.5
Ga	71	H ₂	71	He	71	0.5	Hf	178	O ₂	194	–	–	2.0
Ge	72	He	72	H ₂	72	0.5	Ta	181	O ₂	197	–	–	0.5
As	75	O ₂	91	–	–	0.5	W	182	He	182	–	–	1.0
Se	78	O ₂	94	–	–	2.0	Ir	193	He	193	H ₂	193	0.5
Br	79	O ₂	95	He	79	0.2	Pt	195	O ₂	195	He	195	3.0
Rb	85	O ₂	85	H ₂	85	0.1	Hg	202	O ₂	202	He	202	1.0
Sr	88	O ₂	104	–	–	0.5	Tl	205	He	205	H ₂	205	0.3
Y	89	O ₂	105	–	–	0.3	Pb	208	He	208	O ₂	208	0.3
Nb	93	O ₂	109	–	–	1.0	Bi	209	He	209	O ₂	209	1.0
Mo	95	He	95	O ₂	111	0.3	Th	232	He	232	H ₂	232	2.0
Ru	101	He	101	H ₂	101	0.5	U	238	He	238	O ₂	270	0.5

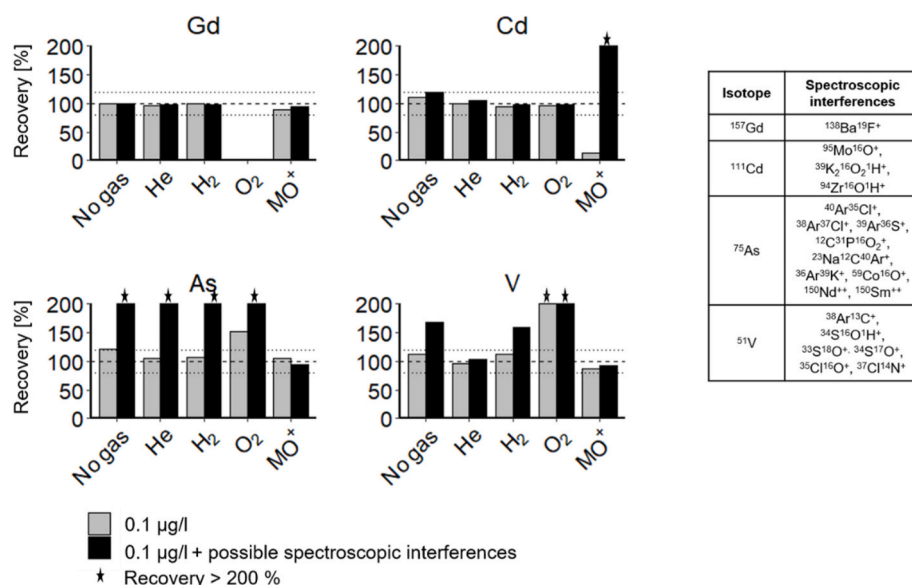


Fig. 1. Recoveries of Gd, Cd, As, and V are depicted in different analytical modes in standards containing the analytes in concentrations of 0.1 µg/l and possibly interfering elements in concentrations ≥ 10 µg/l as given in Tables S8A-S8F and S9. The table shown above lists selected potentially occurring polyatomic interferences based on existing literature (May and Wiedmeyer, 1998; D'Illo et al., 2011).

calibration series are highlighted in section 2.5. To find an optimal approach for the accurate calibration of all 71 elements considered, four stock solutions were prepared depending on the stabilisation and concentration range covering i) trace elements in 1.3% HNO₃ (Li, Be, B, Al,

Si, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Rb, Sr, Y, Nb, Mo, Pd, Ag, Cd, In, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Ta, W, Tl, Pb, Bi, Th, U), ii) major elements (Na, Mg, K, Ca) in 1.3% HNO₃, iii) elements requiring HCl stabilisation in 3% HCl (Zr, Ru,

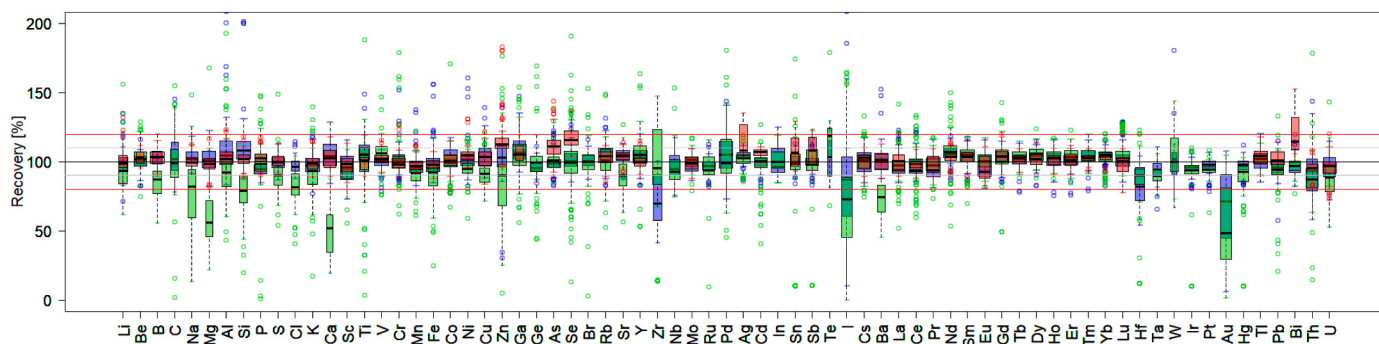


Fig. 2. Recoveries of all elements quantified in the reference materials SPS-SW1, SPS-SW2 and TMDA-51.5 (red; please note that some elements are not present in the reference materials) as well as the calibration check solutions (blue) and the spiked river water samples (green) for 12 measurement sessions. The compositions of all measured standards are listed in Table S2. Grey and red horizontal lines represent recovery rates of $\pm 10\%$ and $\pm 20\%$.

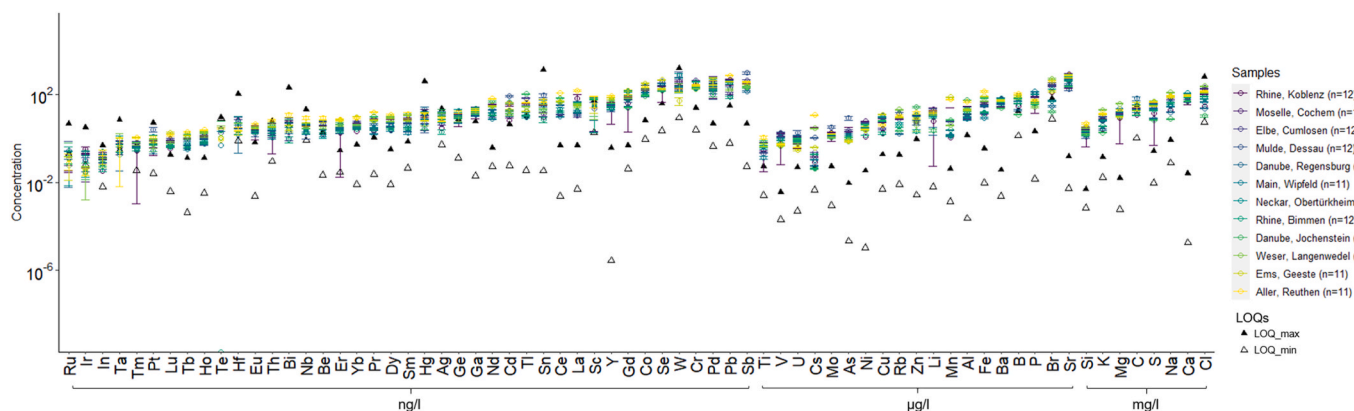


Fig. 3. Measured concentrations in 12 river water samples ordered by increasing values in the unit ranges ng/l, $\mu\text{g/l}$, and mg/l, as well as the minimum and maximum values of the lower LOQ during method validation ($n = 140$). The LOQ was measured in 12 subsequent measurements, thus “LOQ_max” is defined as the obtained maximum value and “LOQ_min” reflects the minimum value of all 12 measurements. Not all 12 samples were analysed in all 12 measurements, therefore a total number of 140 samples is given. Au, Zr, and I are not depicted since no reliable results were achieved.

Sn, Sb, Hf, Ir, Pt, Au, Hg), and iv) the non-metals C, S, P, Cl, Br, and I in 1.3% HNO_3 . Hg, although supplied as a 1000 mg/l standard stabilised in HNO_3 (10%), was added to the stock solution containing HCl (3%). This way, a stable chloro-complex is formed as described, for example, by Pappas (2012).

Out of the four stock solutions, a set of three calibration series in a 1.3% HNO_3 matrix was compiled: i) HNO_3 stabilised major and trace elements, ii) HCl stabilised elements and iii) non-metals. For each calibration series, a ten-point calibration was prepared by the stepwise dilution of the respective stock solution with 1.3% HNO_3 . The major and trace element stock solutions were both included into one calibration series. The multi-element calibration solutions of the HCl stabilised elements were diluted from the stock solution (3% HCl) with 1.3% HNO_3 to match the matrix of the samples analysed. Calibration standards of HCl stabilised elements were prepared from the stock solution on a daily basis and of HNO_3 stabilised elements on a weekly basis before measurements during method validation to avoid any calibration artefacts. Information about the concentration levels of all calibration and stock solutions are shown in Table S10.

3.4. HCl stabilisation

As already mentioned, elements such as Zr, Hf, Au or Hg are preferably stabilised in solution by HCl. Especially for Zr and Au, poor recoveries were found when analysing spiked river water samples acidified with HNO_3 . In order to overcome this issue and to integrate these elements into the analytical procedure, different approaches for sample preparation were tested (cf. section 2.7).

Table 3 shows the results regarding HCl stabilisation for Zr and Au as two challenging examples. The results indicated that a complete HCl matrix as well as an aqua regia matrix enable acceptable recoveries for Au in the range of 106–108% and 104 to 105%, respectively (on-mass mode O_2). The same was observed for Zr in the complete HCl matrix for standards containing 1 $\mu\text{g/l}$. However, high background concentrations and therefore LOQs in the 1 $\mu\text{g/l}$ range led to problems in quantifying Zr. Interference check solutions which contained Zr as interfering element with an amount of 10 $\mu\text{g/l}$ were accurately quantified with recoveries ranging between 97 and 113% for He mode and 83 to 102% in measurement as MO^+ .

3.5. Rinsing procedure

To overcome elevated background concentrations for elements such as B, I, W, Au or Hg (Clausen et al., 2010; Pappas, 2012; Kmiecik et al., 2016; Flores et al., 2020; Tang et al., 2020) the use of different rinsing solutions was tested according to section 2.7. Results for boron, as one example, are presented in Fig. S2.

Challenges regarding memory effects and impurities in the introduction system of the instrument were addressed by measuring a series of ten blanks (1.3% HNO_3) prior to and after each daily analysis run consisting of the calibration sequence and the subsequent quality control and sample sequences. Cones were cleaned when necessary, but mostly before each second measurement day. One rinsing blank (1.3% HNO_3) was measured after each calibration series and after each set of CRMs. During method validation only 1.3% HNO_3 was used for rinsing to avoid any contamination with C and Cl.

Table 3

Overview of Zr and Au recoveries in the interference check solutions in different matrices (HNO₃, aqua regia and HCl) as described in section 2.7. STD 6.1 and STD 6.2 contain only the analytes (0.1 and 1 µg/l, respectively), whereas STD 6.3 and 6.4 contain analytes and interfering elements (10 µg/l). All values are given in %. Values between 80 and 120% are marked in bold.

Nominal analyte concentrations in µg/l			Zr	Zr	Au	Au
			90	90	197	197
			On-mass: He	Mass-shift: MO ⁺	On-mass: He	On-mass: O ₂
			Spectroscopic interferences: ¹⁸⁰ Hf ⁺⁺ , ⁵⁵ Mn ³⁵ Cl ⁺		Spectroscopic interferences: ¹⁶² Dy ³⁵ Cl ⁺ , ¹⁸¹ Ta ¹⁶ O ⁺	
HNO ₃ , 1.3%	STD	0.1	46	37	68	71
	6.1					
	STD	1	33	23	90	97
	6.2					
	STD	0.1	630	636	142	49
	6.3					
aqua regia, diluted 1:50	STD	1	111	99	97	92
	6.4					
	STD	0.1	66	48	93	105
	6.1					
	STD	1	43	31	95	104
	6.2					
HCl, 3%	STD	0.1	527	508	169	104
	6.3					
	STD	1	107	93	104	105
	6.4					
	STD	0.1	251	236	93	106
	6.1					
HCl, 3%	STD	1	93	70	97	107
	6.2					
	STD	0.1	393	449	186	108
	6.3					
	STD	1	117	100	106	106
	6.4					

3.6. Method validation

Out of the 71 elements which were considered in this study, 68 elements were successfully quantified simultaneously in a single analytical run. For Zr, I, and Au, no satisfactory results could be achieved in the HNO₃ matrix as stated in section 3.4 for Zr, and Au as well as in section 3.7.6.2 for I. Briefly, Zr and Au require stabilisation with HCl while for I analyte loss was observed which may occur due to volatilisation or adsorption (Mesko et al., 2010).

Recoveries of all considered 71 elements in 12 measurements during method validation covering the CRMs, the calibration check solutions, and the spiked river water samples are depicted in Fig. 2. Major elements such as Na, Mg, or Ca showed poor recoveries in spiked samples. The reason for this is that the spiked amounts of these elements were too low in relation to the background concentrations in the river water samples (refer to Table S2). This is a good example for one of the many challenges in multi-element analyses. However, an accurate determination of these elements was validated by CRMs and the calibration check solutions. As no surface water CRMs for C, Cl, Ge, Br, Zr, Nb, Ru, Pd, In, Te, I, Hf, Ta, W, Ir, Pt, Au and Hg were available, only calibration check solutions and spiked river water samples could be considered. This emphasises the urgent need for more multi-element surface water CRMs for ICP-MS analyses.

Fig. 3 presents the measured concentrations of all 68 elements in the various river water samples as well as the respective minimum and maximum values of the lower LOQ during method validation. 65 out of the 68 elements, which are possible to be quantified with our method, were detected > LOQ in at least one of the river water samples during method validation. For the elements Ru, Te, and Ta, the concentrations were below LOQ in all river water samples although the LOQ range was 0.19–4.7 ng/l, 8.5 to 9.2 ng/l, and 0.31 to 7.2 ng/l, respectively.

Moreover, the quantification frequencies defined as the number of measurements above the respective LOQ per total number of measurements were below 10% in all freshwater samples (n = 140) for Nb, In, Ir, and Bi. Thus, in 90% of all measured samples (n = 140), 61 elements were quantified above the respective LOQ in German river water samples. One option to address the analytes below LOQ are enrichment methods, such as solid-phase extraction which can be used offline (Jackson et al., 2018) as well as online (O'Sullivan et al., 2013). However, multi-element capabilities are restricted when using enrichment methods due to the different retention abilities of each element. For the analytes Li, Be, Th and U, depending on the catchment and therefore on the surface water composition, the no gas mode can be an option to additionally lower the LOQs if needed. However, adding the no gas mode means that the time for emptying the collision-reaction-cell is added to each sample run and therefore, the measurement is significantly prolonged.

3.7. Detailed results for each element group

This section delivers an overview sorted by the element groups. More information is provided in the SI section 6.

3.7.1. Alkali metals

From the group 1 elements of the periodic table, Li, Na, K, Rb, and Cs were included into the analytical method by on-mass measurements. In the river water samples analysed during method validation, the concentrations of Na and K were in the mg/l range, while the concentrations of Li and Rb were in the one-to two-digit µg/l range. Cs concentrations in some samples were even lower (ng/l to two-digit µg/l). With the exception of Li and Cs, the LOQs achieved during all analyses were sufficiently low to achieve results above the respective LOQs (refer to Fig. 3). For ⁷Li, the LOQs were negatively affected by the use of ⁶Li as an internal standard as stated in section 3.2. Despite the increased background while using ⁶Li as an ISTD, Li quantification was possible in most samples measured above the LOQ with a quantification frequency of 92% (n = 140).

3.7.2. Alkaline earth metals

Best results for Be, Mg, and Ba were obtained in on-mass measurements with different cell gases and for Ca and Sr by detection as MO⁺. In the analysed river water samples, with the exception of Be, concentrations in the two- or three-digit µg/l (Sr and Ba) or even in the mg/l (Mg and Ca) range were detected. LOQs of Mg, Ca, Sr and Ba were low enough for achieving quantification frequencies of 100% (n = 140) during all river water measurements (refer to Fig. 3). The measured Be concentrations were in the one-digit ng/l range, therefore only a low quantification frequency of 12% (n = 140) was achieved.

3.7.3. Transition and post-transition metals

The transition and post-transition metals covered by the presented method (Al, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Y, Zr, Nb, Mo, Ru, Pd, Ag, Cd, In, Sn, Hf, Ta, W, Ir, Pt, Au, Hg, Tl, Pb, Bi) include elements which are routine analytes in numerous laboratories such as Cr, Fe, Ni, Cu, Zn (Roje, 2010; Fiket et al., 2017; Walkner et al., 2017) as well as less frequently analysed elements such as the PGE (e.g., Ru, Pd, Ir, Pt) or the "less-studied technology-critical elements" (e.g., Nb, Ta, Ga, In) (Sugiyama and Shikamori, 2015; Filella and Rodriguez-Murillo, 2017; Machado et al., 2017; Romero-Freire et al., 2019; Klein et al., 2021). The detailed description on the decision process for the optimal measuring mode is given in paragraph SI 6.3.

In all river water samples measured in this study, the concentrations of the group 3 to 6 elements were below 3 µg/l. Despite concentrations in the ng/l or low µg/l range (cf. Fig. 3), all elements except Ta were quantified above LOQ in at least one river water sample during method validation. Moreover, for Nb and Hf, despite of a low LOQ in the one- or two-digit ng/l range, their quantification frequencies were 9% and 2%

($n = 140$), respectively. Nevertheless, recoveries in calibration check solutions and spiked samples indicate the suitability of the proposed method for their quantification in other environments. An exception was Zr as mentioned in section 3.4.

For the group 7 to 12 elements of the periodic table, best results were obtained by analyses in on-mass modes (cf. Table 2). On-mass analysis delivered superior results in our experiments with regard to the elimination of possible spectroscopic interferences (refer to Tables S8A–S8F). Limitations in Ag analyses are mainly caused by the poor analyte stability in contact with Cl^- as detailed in SI section 6.3. Best results in all addressed modes were obtained in no gas mode which was however not included to minimise the analysis time. Therefore, as a compromise, He was applied in the final method for Ag.

High LOQs, mostly in the two-to three-digit ng/l range, in relation to the expected low concentrations of the same range were achieved for Au and Hg which are both known to be challenging analytes in ICP-MS analysis due to memory effects (Pappas, 2012; Tang et al., 2020). The same applies for W which is also known to suffer from carry-over effects within the sample introduction system (Clausen et al., 2010) and therefore causing wash-out problems and high LOQs ranging from 8.8 to 1600 ng/l in this study. Hg analysis can be additionally biased due to volatilisation. During method development, problems regarding the calibration of Hg occurred when preparing Hg calibration standards from HNO_3 stock solutions. A clear improvement was achieved by adding Hg to the HCl stabilised stock solution which can be explained by better stability of the standards due to the formation of soluble $[\text{HgCl}_4]^{2-}$ species (Pappas, 2012). During method validation, recoveries for calibration check and spike recoveries were in the acceptable range of 80–120% (cf. Fig. 2). Nevertheless, due to its outstanding environmental relevance and the typically very low concentrations in river waters (cf. River Rhine concentration $<0.01 \mu\text{g/l}$, Table S1), it is strongly recommended to measure Hg by highly sensitive single-elemental approaches such as cold vapor atomic absorption/fluorescence spectrometry (CV-AAS or CV-AFS) or by single analyte ICP-MS, taking the respective cleaning and calibration measures into account and to consider Hg results from multi-element analyses only as indicative values.

Pd, Ag, Cd, Pt were detected in the river water samples of this study with quantification frequencies of 100%, 81%, 49% and 38% ($n = 140$), respectively. Ru, Ir, and Hg were not (Ru) or rarely detected (Ir, Hg) in trace concentrations of 2.2–3.8 ng/l for Ir and 9.0 to 27 ng/l for Hg. Mn, Fe, Co, Ni, Cu, and Zn were all quantified above LOQ in 99%–100% of all river water samples during method validation (cf. Fig. 3).

For the group 13 to 14 metals - Al, Ga, In, Sn, Tl, Pb and Bi - on-mass approaches using He, H_2 or O_2 as cell gases were selected for the final method as detailed in SI section 6.3. Except for Al, which was detected in concentrations between 10 and $50 \mu\text{g/l}$ in the river water samples, the other elements were quantified in the low ng/l range (refer to Fig. 3).

3.7.4. Lanthanides and actinides

All lanthanides (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) as well as the two long-lived radioactive actinides Th and U were included in the proposed method. An exception is the radioactive and short-lived Pm.

Thanks to their generally low ionisation potentials and the low background signals on these masses, LOQs in the ng/l range were achieved for all considered lanthanides. Therefore, quantification frequencies of between 41% (Tm) and 99% (Gd) were obtained in the river water samples used during method validation ($n = 140$) measuring in He mode or as MO^+ species as shown in Table 2 and as detailed in SI section 6.4. Especially Gd is of high importance in river water due to the extensive use of Gd-based MRI (magnetic resonance imaging) contrasting agents, which also explains the high quantification frequency of the river water samples measured in this study (Kulaksiz and Bau, 2013).

3.7.5. Metalloids

According to the results obtained in this study and detailed in SI

section 6.5, the metalloids B, Si, Ge, As, Se, Sb, and Te can be mainly measured on-mass, except for Si, As, and Se which are preferably quantified as MO^+ . While Si concentrations were between 1.2 and 5.0 mg/l in the analysed river water samples, all further elements were in the ng/l (Ge, Se, Sb, Te) or $\mu\text{g/l}$ range (B, As) according to Fig. 3. Boron is a good example for elements that show comparably high LOQs in the $\mu\text{g/l}$ range, but for which a satisfying quantification frequency (e.g., 99%, $n = 140$) was achieved for German river water samples with B concentrations between 11.2 and $121 \mu\text{g/l}$ (cf. Fig. 3). Reasons for the high LOQs are described in section SI 6.5.

3.7.6. Non-metals

3.7.6.1. Polyatomic non-metals. The quantification of the polyatomic non-metals C, P, and S was hindered in classical ICP-Q-MS by nitrogen- and oxygen-based polyatomic interferences. Thanks to the improved options for interference elimination, the analysis of P and S with triple quadrupole devices is mostly achieved by O_2 as cell gas and measurement with mass-shift (Diez Fernandez et al., 2012; Gong et al., 2015; Zhu et al., 2015; Möller et al., 2016; Kroepfl et al., 2017). Low LOQs and best recoveries as MO^+ compared to other analytical modes were also observed for both elements in this study. The obtained LOQs for P and S were in the range of 0.014–2.09 and 9.40 to $265 \mu\text{g/l}$, respectively. This appears to be sufficient for the river water analysis in major German rivers with all concentrations measured above LOQs in the 10 to 100 (P) and 10,000 to $50,000 \mu\text{g/l}$ (S) range.

The quantification of ^{12}C with ICP-MS is a niche application. It has been shown in individual studies that a common quantification of C with metal (loid)s in the same analytical run is possible (Amaral et al., 2015; Schroeder et al., 2019). Due to the poor ionisability and the high background, only significantly poorer LOQs in the range of 1–30 mg/l, compared to many other analytes, can be achieved so far for C. Due to the high concentrations in many river water samples, in our case in the range of 12–80 mg/l, 95% of all samples ($n = 140$) were measured above LOQ. Hence, the integration of C in the multi-element methods is an option, but we also suggest to proceed with caution in the interpretation of the measured total C values due to the fact that, in contrast to other specialised analytical techniques such as combustion analysers using photometric measurements or chromatographic methods, it is not possible to assign the C atoms detected in ICP-MS to the multitude of possible organic and inorganic C species.

3.7.6.2. Halogens. Chlorine, bromine, and iodine were considered as potential analytes for this multi-element approach. The lightest halogen fluorine is one of the few elements whose direct quantification by Ar-based ICP-MS is excluded due to its high ionisation energy ($>\text{Ar}$). All halogens are considered to be challenging analytes in ICP-MS analyses due to their high ionisation energies, potential volatility, and severe plasma or matrix derived interferences (e.g., $^{16}\text{O}^{18}\text{O}^+\text{H}^+$ or $^{17}\text{O}^{18}\text{O}^+$ on $^{35}\text{Cl}^+$, $^{1}\text{H}^{36}\text{Ar}^+$ on $^{37}\text{Cl}^+$, $^{38}\text{Ar}^{40}\text{Ar}^+\text{H}^+$ on $^{79}\text{Br}^+$, $^{40}\text{Ar}^{40}\text{Ar}^+\text{H}^+$ on $^{81}\text{Br}^+$) (Flores et al., 2020). Additionally, they suffer from high background signals. It has been shown that the use of a CRC with H_2 or O_2 and analyses with mass-shift can significantly improve the LOQs (Romarís-Hortas et al., 2009; Romarís-Hortas et al., 2011; Ohata and Wada, 2017; Nelson et al., 2019). Comparatively low sensitivities in the determination of Cl and Br appear acceptable for the analysis of river water samples due to the high concentrations in which these elements typically occur.

In this study, almost equally good results for the quantification of Cl were obtained using O_2 or H_2 and analysis as MO^+ and MH_2^+ while Br quantification was possible in He and MO^+ modes. In the relevant concentration ranges, good recoveries were achieved and LOQs were obtained which are significantly below the concentrations measured in the river water samples with minimum observed values of 5.54 mg/l (Cl) and $7.87 \mu\text{g/l}$ (Br).

In contrast, iodine could not be successfully included into the multi-element method. Even though several authors report the quantification of iodine in trace concentrations by ICP-MS in different matrices (e.g., Reid et al. (2008); Xu et al. (2018)) recoveries of below 80% and widely varying results were obtained in this multi-element study. Reasons can be assumed to be signal suppression and analyte losses, which can arise particularly for iodine from volatilisation and adsorption of the analyte during sample introduction and especially in the nebulisation process (Mesko et al., 2010; Badocco et al., 2016). One option for improvement might be to prepare all solutions in alkaline medium for trace analyses of iodine according to Flores et al. (2020). Hence, iodine was not included in this best-practice advice.

4. Conclusions

Our best-practice method has the potential to become a valuable tool in the long-term monitoring of rivers, especially if the online or atline capacities can be improved in future monitoring efforts (Arndt et al., 2022). It allows the simultaneous quantification of 68 out of 71 tested elements with very different chemical properties and strongly varying concentrations in river waters. Hence, the method is capable to close gaps within our knowledge of the geochemical cycle of the elements addressed. As discussed before, elements which are now measured below LOQ may be of higher concern in the future. Therefore, a rapid response to element shifts within our waters is crucial.

In total, for 61 of 68 elements (i.e. Li, Be, B, C, Na, Mg, Al, Si, P, S, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Mo, Pd, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Pt, Hg, Tl, Pb, Th, U), quantification frequencies over 10% ($n = 140$) and therefore low LOQs in relation to the measured concentrations were achieved for their direct analysis in 12 different German rivers without the need of an additional sample preparation or analyte enrichment. For the elements Nb, Ru, In, Te, Ta, Ir, Bi, preconcentration steps in multi-element approaches should be evaluated in future studies, considering that preconcentration steps need to be adapted to multi-element analyses. For the elements I, Zr, and Au, it was not possible or economically reasonable to integrate them into the best-practice advice as discussed above. For the analytical quality control, a better availability of multi-element CRMs for a larger number of analytes in surface waters was identified as an urgent necessity to support future multi-element efforts.

The best-practice advice presented in this study aims to ignite further discussions and improvements in multi-element analyses with ICP-QQQ-MS. Most of all it is a blueprint, to be adapted to the monitoring needs within a certain catchment area with its specific regional conditions and set of analytes. Consequently, this study delivers a versatile tool regarding elemental “fingerprints” in long-term river monitoring programs which is easily adjustable to the questions and requirements of scientists from different disciplines.

Credit author statement

Nadine Belkouteb: Methodology, Laboratory work, Investigation, Data curation, Validation, Calculations, Formal analysis, Visualization, Writing – Original Draft & Editing, **Lars Duester:** Conceptualization, Project administration, Methodology, Supervision, Writing - Review & Editing, **Henning Schroeder:** Methodology, Laboratory work, Data curation, Validation, Calculations, Writing - Review & Editing, **Julia Arndt:** Methodology, Laboratory work, Review & Editing, **Jan G. Wiederhold:** Methodology, Review & Editing, **Thomas A. Ternes:** Supervision, Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.138053>.

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Supporting Information

Quantification of 68 elements in river water monitoring samples in single-run measurements

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1. Choice of analytes and their environmental relevance in river water

In order to narrow down the range of analytes, condensation steps were carried out in this study, starting from the periodic table of the elements. First of all, it was checked which elements are measurable at all by ICP-QQQ-MS within the framework given by river water monitoring networks (e.g., conservation of sample by acidification with HNO_3 , masses which cannot be considered, stable or long-lived isotopes). Subsequently, it was categorised which elements in different watersheds are of higher or lower priority today and most likely in the near future. Elements regulated by law in Europe were given the highest priority. The final question was whether anthropogenic sources, or known research questions, are already found in the scientific literature. As a result, 71 target analytes were assessed in the method development approach and Table S1 was created. Since it was not possible in the scope of this study to provide a worldwide overview, the table focuses mostly on Europe. Besides information on the legal background and research questions, the columns also provide already existing information on concentrations along the river Rhine or in other European rivers, if available, as well as references to studies about the biogeochemical cycling of the respective element in river systems.

While some analytes might be less significant regarding their environmental impact, other analytes, are of rising concern. As an example, for changing societal demands, current efforts have become known to exploit lithium deposits in the “Upper Rhine Valley” and thereby, Li monitoring may become of increasing importance in the future (Frey, 2020). Moreover, especially the lanthanides are considered to be of growing environmental concern due to their use in various modern technologies such as cell phones, televisions, LED light bulbs, or wind turbines (Balaram, 2019). Although there is not much data available on the bioaccumulation and health effects, concerns about their environmental toxicity were raised (Gonzalez et al., 2015; Malhotra et al., 2020). Besides the resulting need to include these elements in environmental monitoring efforts, a significant interest exists in the context of closing knowledge gaps with regard to global geochemical element cycles for which the riverine flux from terrestrial to aquatic systems is an essential and often poorly known component.

Table S1: Background information, existing data as well as international and national regulations regarding all elements considered in this study.

Grouping and sub grouping ^I	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ^{II}	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ^{III})	Examples for ICP-Q-MS based analyses in environmental samples
alkali metals	Li	Apart from Li extraction processes in several countries and its use in batteries, Li is used in various other mass products such as alloys, plastics and concrete (Schaefer, 2004a).	none	Li was used for oil source tracking in the environment (Guo et al., 2014; Harkness et al., 2018).	The FOREGS ^V geochemical baseline mapping delivered values based on ICP-QMS analysis. The median across Europe in <0.45 µm filtered stream water (n=807) was 2.1 µg/l. ^V
	Na	NaCl is an omnipresent cultural good and almost universal is also the industrial sodium use (Anke, 2004c).	none	A very significant release pathways into surface water is the use as road salt (Kelly et al., 2019) and mine drainages (Turunen et al., 2020). The long-term data from river Rhine varies from <10 mg/l in Switzerland to >1400 mg/l in the Delta in the Netherlands. Within the dense populated areas from Lauterbourg (France) to the German/Dutch border the river water concentrations show a declining trend from the 70th and 90th until today.	none
	K	"Potassium constitutes about 2.4% of the earth crust, and is the seventh most abundant element." (Anke, 2004b)	none	Mining may cause significant impact on potassium concentration in rivers (Schulz and Canedo-Arguelles, 2019) and is a relevant measure in salinization studies (Haq et al., 2018). The long-term data from river Rhine varies from <2 mg/l in Switzerland to >50 mg/l in the Delta in the Netherlands. Within the dense populated areas from Lauterbourg (France) to the German/Dutch border the river water concentrations show a declining trend from the 70th and 90th until today, but it is much less pronounced than for Na.	Becker et al. (2008) measured Mg, Ca and K isotope ratios using ICP-QMS.
	Rb	The rubidium abundance within the earth crust is between nitrogen and fluorine. An essential supply for higher organisms is discussed. Significant industrial sources into the environment are not described (Anke and Angelov, 2004).	none	Rb can be used as an element which is not significantly impacted from anthropogenic sources in the environment (Rinklebe et al., 2019).	Zhu (2018) describes next to other elements Rb reactions in ICP-QMS analyses. Kilic (2019) shows the concentration in natural mineral waters. The FOREGS geochemical baseline mapping delivered values based on ICP-QMS. The media across Europe in <0.45 µm filtered stream water (n=807) was 1.3 µg/l. ^V
	Cs	The non-essential element caesium owns a low earth crust abundance. Most commonly known are the radioactive isotopes from nuclear power plant accidents and bomb tests (Hecht, 2004).	none	The Cs-134/137 ratio is used as a tracer (Avery, 1996; Guzman et al., 2013; Igarashi et al., 2019).	The FOREGS geochemical baseline mapping delivered values based on ICP-QMS. The media across Europe in <0.45 µm filtered stream water (n=807) was 0.006 µg/l. ^V

Table S1 continued.

Grouping and sub grouping ^I	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ^{II}	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ^{III})	Examples for ICP-Q-MS based analyses in environmental samples
alkaline earth metals	Be	The earth crust abundance of beryllium is low and it is used in various applications (Rossman, 2004).	none	Different radioactive Be isotopes are used in various environmental studies (Suhrhoff et al., 2019; Benoit et al., 2020; Eyrolle et al., 2020).	Tazoe et al. (2014) determined low level Be concentrations in seawater and the FOREGS geochemical baseline mapping delivered values based on ICP-QMS. The media across Europe in <0.45 µm filtered stream water (n=807) was 0.009 µg/l. ^V
	Mg	The essential element magnesium is the eighth most abundant element of the earth's crust. It is used in several different large-scale industries (Vormann, 2004).	none	The long-term data from river Rhine varies from 8 mg/l in Switzerland to 160 mg/l in the Delta in the Netherlands. No significant concentration changes and trends are visible in the data base. Land degradation and salinization effects make Mg an interesting monitoring parameter (e.g., (Qadir et al., 2018)).	Roman et al. (2019) delivered an automated method to determine the Mg/Ca ratio.
	Ca	Calcium is the fifth most abundant element in the environment and the human body (Peterlik and Stoeppeler, 2004).	none	The long-term data from river Rhine varies from 50 mg/l in Switzerland to 70-100 mg/l in the Delta in the Netherlands. Calcium decline in soft waters (lakes) is a known threat for food webs (Jeziorski et al., 2008). It is one of the elements used in salt water/groundwater interaction studies (e.g., (Charef et al., 2012)).	Shen et al. (2007) describe the high precision measurements of Mg/Ca- and Sr/Ca-ratios in carbonates by cold plasma ICP-QMS.
	Sr	The earth crust abundance is comparable to Cl, S and C. Due to its affinity to be deposited in bones, radioactive Sr isotopes remain to be of concern (Seifert, 2004).	none	Sr Isotope ratios and Sr ratios with other elements (e.g., Ca) are from significant interest (e.g., (Engstedt et al., 2012; Gunn et al., 2019)).	Dronov et al. (2018) published a method to determine Sr in gypsum by ICP-QMS and (Takagai et al., 2014) addressed radioactive Sr-90. Zhu et al. (2017) confirmed the formation of $\text{SrF}(\text{CH}_3\text{F})_{(0.4)}^{(+)}$ and $\text{SrF}(\text{H}_2\text{O})(\text{CH}_3\text{F})_{(0.3)}^{(+)}$ cluster ions generated in the reaction-cell of ICP-MS/MS systems.
	Ba	Barium is used in a wide range of industrial applications and the range of concentration may vary from µg/l to mg/l. In the transition from freshwater to the marine environment, Ba is precipitated as sulphate (Jaritz, 2004).	none	Ba can be used as a tracer for different water sources (e.g., (Richards et al., 2016; Ho et al., 2019))	The FOREGS geochemical baseline mapping delivered values based on ICP-QMS. The media across Europe in <0.45 µm filtered stream water (n=807) was 24.9 µg/l. ^V

Table S1 continued.

Grouping and sub grouping ⁱ	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ⁱⁱ	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ⁱⁱⁱ)	Examples for ICP-Q-MS based analyses in environmental samples
transition metals	Sc	The occurrence and potential release into the environment are described by Chaim (Horovitz, 1999).	none	"Scandium has a dispersed lithophile behaviour and rarely forms minerals in which it is a major constituent. The relatively large Sc ³⁺ ionic radius (75 pm) often precludes favourable substitution for Al and Fe in rocks, although most of the Sc in the lithosphere is held in ferromagnesian minerals, especially Fe-rich pyroxenes in which Sc ³⁺ does substitute for Fe ³⁺ . ^{iv}	Liu et al. (2013) delivered a method to detect Sc in environmental samples and the detection limit for scandium was 0.013 ng/l in water.
first d-block	Ti	Ti is almost omnipresent in its anthropogenic applications. Most common is the use as whitening pigment. Lately the use as nanoparticle in several applications as well as the release from sunscreen gained more attention in the scientific community, (e.g., Phalyvong et al. (2020).	none	"Titanium values in stream water range over three orders of magnitude, from <0.01 to 16.8 µg/l, with a median value of 0.9 µg/l. Titanium values tend to correlate with Ge and Pb data, especially in Fennoscandian countries and Britain. ^v	Fabricius et al. (2014) gave advice on how to analyse nanoparticles in different matrices including TiO ₂ by ICP-MS.
	V	Huang et al. and Shaheen et al. gathered pathways and speciation of V in the environment (Huang et al., 2015; Shaheen et al., 2019). Additionally, several industrial residues and tailings release significant amounts of V, (e.g., Misik et al. (2014); Ettler et al. (2020)).	none	"Vanadium values range over three orders of magnitude, from <0.05 to 19.5 µg/l, with a median value of 0.460 µg/l. Vanadium distribution resembles that of As, Mo, Sb, Se, U and W. ^{vi}	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.46 µg/l. ^v
	Cr	The potential natural and industrial sources were lately updated by Tumolo et al. (2020). Based on several potential anthropogenic pathways into surface water chromium is regulated via the water framework directive and a Rhine specific threshold is given. ⁱⁱ	German surface water ordinance (OGewV): 640 mg/kg suspended solids; ICPR: <0.45 µm AA-EQS 3.9 µg/l, target value suspended solids 100 mg/kg. ⁱⁱ	Long-term Cr data along river Rhine is available for the total and dissolved water phase. Taking the monitoring station Koblenz as an example the total water phase content declines from the 70s to 90s and now stabilised around 2 µg/l. The <0.45 µm (dissolved) concentration is about ten times lower. ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.38 µg/l. ^v
	Mn	The use of Mn is detailed by Schaefer 2004 and still most of the Mn mined is used in heavy industry products (Schaefer, 2004b).	none	Total water content of Mn varied from Lauterbourg/Karlsruhe (France/Germany) to Maasluis (Netherlands) from around 20 to 40 µg/l in 2018. ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 15.9 µg/l. ^v
	Fe	With an earth crust abundance of 4.7%, iron is almost omnipresent in surface water and the same holds true for its industrial use (Schümann and Elsenhans, 2004).	none	Yearly mean total water content Fe values were always <1 mg/l from Lauterbourg/Karlsruhe (France/Germany) to Maasluis (Netherlands) during the last years. ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 67 µg/l. ^v
	Co	Co is essential to animals and humans as well as known to pose potential danger due to excessive exposures. Examples for known pathways to surface waters are mining activities, as well as industrial and domestic waste water (Schrauzer, 2004).	none	A comprehensive review on the terrestrial speciation and chemistry is given by Collins and Kinsela (2010).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.16 µg/l. ^v

Table S1 continued.

Grouping and sub grouping ⁱ	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ⁱⁱ	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ⁱⁱⁱ)	Examples for ICP-Q-MS based analyses in environmental samples
	Ni	Sundermann 2004 names the following anthropogenic sources into the environment: fossil fuel consumption, industrial production, disposal of nickel containing materials and alloys. The anthropogenic release is higher than the one from natural processes (Sundermann, 2004). Based on several potential anthropogenic pathways into surface water, nickel and its compounds is regulated via the water frame work directive and a Rhine specific target value is available. ⁱⁱ	WFD: AA-EQS <0.45 µm bio available 4 µg/l, MAC-EQS <0.45 µm 34 µg/l; ICPR 90percentile suspended solids 50 mg/kg. ⁱⁱ	The total Ni water concentration between Switzerland and the Netherlands varied between <1 and 4 µg/l during the last years. The <0.45 µm filtered concentrations were <1 µg/l in the upper and middle and <2 µg/l in the lower and delta Rhine. ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 1.91 µg/l. ^v
	Cu	Copper belongs to the transition metals and is a common element in the earth's crust. Copper is a vital trace element for humans, animals and plants in small quantities. It occurs naturally in water, depending on geology and water chemistry. Until the 1980s, the discharge of municipal and industrial wastewater was an important cause of water pollution with Cu (Hillenbrand et al., 2005). Based on several potential anthropogenic pathways into surface water, copper and its compounds are regulated via the water frame work directive and a Rhine specific threshold value is available. ⁱⁱ	OGewV: suspended solids 160 mg/kg; ICPR < 0.45 µm 3.3 µg/l, suspended solids 50 mg/kg	The total Cu water concentration between Switzerland and the Netherlands varied between <1 and 9 µg/l the last years. The <0.45 µm filtered concentrations were between 1 and 2 µg/l. ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.88 µg/l. ^v
	Zn	The European Union Risk Assessment Report on Zn metal delivers an overview on use patterns (Aschberger et al., 2010). Next to galvanising industry, Zn in brass containing chemicals are important for the release into surface water. It is regulated via the German surface water ordinance. ⁱⁱ	OGewV: suspended solids 800 mg/kg; ICPR < 0.45 µm 10.8 µg/l, suspended solids 200 mg/kg. ⁱⁱ	The total Zn water concentration between Switzerland and the Netherlands varied between 2 and 20 µg/l the last years. The <0.45 µm filtered concentrations were between <1 and 8 µg/l. ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 2.68 µg/l. ^v
second d-block	Y	Yttrium compounds and alloys are widely used in engineering (glasses, fluorescent tubes, TV sets superconductors (Dobrowolski, 2004).	none	According to Dobrowolski 2004 the yttrium content of European rivers is between 0.4 to 0.7 µg/l (Dobrowolski, 2004).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.064 µg/l. ^v
	Zr	A wide range of applications is named by making use of its heat, corrosion and resistant properties, as well as the use in dyes and pigments or in personal care products (Schaller, 2004).	none	The fate of Zr (from anthropogenic sources) in estuaries was examined by (Godfrey et al., 2008; Schneider et al., 2016).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.053 µg/l. ^v
	Nb	Niobium is considered as "less-studied technological critical element" with a rising application in new technology sectors. Niobium is used in the aerospace or medical industry in structural steel, superalloys or capacitors (Filella and Rodriguez-Murillo, 2017).	none	According to Romero-Freire et al. (2019), the Nb/Ta ratio and fractionation is from interest in the aquatic environment and hence, in several studies the ratio is used as a tracer, e.g., (Sutliff-Johansson et al., 2021).	Usually the detection of Nb trace concentrations is based on high resolution ICP analyses. However, also Q-type based examples are available (Lu et al., 2007).
	Mo	According to Anke, 2004 Mo is comparably omnipresent in industrial applications. Most noteworthy are maybe iron and steel industries, fertilisers and the use as catalyst (Anke, 2004a).	none	The distribution of dissolved Mo concentrations along the salinity gradient was found to be highly variable by Strady et al. (2009) at the Gironde and an overview for the Yangtze is given by Wang et al. (2021a).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.22 µg/l. ^v

Table S1 continued.

Grouping and sub grouping ⁱ	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ⁱⁱ	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ⁱⁱⁱ)	Examples for ICP-Q-MS based analyses in environmental samples
	Ru	Together with Pt, the element is released from automotive catalysators (Ravindra et al., 2004).	none	More information is needed on the contribution of rivers to the global Ru budget and evidence on biomagnification was stated by Campbell et al. (2005).	The median across Europe in <0.45 µm filtered stream water (n=807) was 1.3 µg/l. ^v
	Rh (used as internal standard)	Rh is also released from automotive catalysators (Ravindra et al., 2004).	none	Insufficient information is available on the Rh concentration in freshwater and its fate in the environment, e.g., (Zimmermann and Sures, 2018).	Several studies addressing Rh analyses by ICP-MS are available, e.g., (Krushevska et al., 2006).
	Pd	Next to Pt, the element is released from automotive catalysators (Ravindra et al., 2004).	none	cf. Rh	The detection of three PGE by laser ablation ICP-MS is described by Motelica-Heino et al. (2001).
	Ag	Silver was often addressed with respect to the potential release as nanoparticles from several applications (Duester et al., 2014). In addition, it is regulated via the water framework directive. ⁱⁱ	OGewV: <0.45 µm AA-EQS 0.02 µg/l. ⁱⁱ	Since Ag is a factor of concern in several countries, studies on the environmental fate are available, e.g., (Zhang et al., 2008; Ayrault et al., 2010).	Wimmer et al. described an improved cloud-point-extraction method hyphenated to single particle ICP-MS for silver-based nanoparticles (Wimmer et al., 2021).
	Cd	Based on several potential anthropogenic pathways into surface water, cadmium and its compounds are regulated via the water framework directive. ⁱⁱ In addition a Rhine specific threshold for suspended solids is given.	WFD: AA-EQS <0.45 µm depending on water hardness <0.08 - 0.25 µg/l, MAC-EQS <0.45 µm <0.45-1.5 µg/l; ICPR 90percentile suspended solids 1 mg/kg. ⁱⁱ	The total Cd water concentration between Switzerland and the Netherlands varied between 0.02 and 0.25 µg/l the last years. The <0.45 µm filtered concentrations were between 0.01 and 0.08 µg/l. ⁱⁱⁱ Based on a bibliometric analysis, Ifan et al. (2021) describe emerging Cd concentrations to be a global problem.	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.01 µg/l. ^v
third d-block	Hf	According to the FOREGS, the predominant source of Hf into the environment is weathering. ^v	none	Rahlf et al. (2021) used Hf to trace the Kongo river plume in the Atlantic Ocean based on isotope analyses.	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.004 µg/l. ^v
	Ta	Tantalum is considered as "less-studied technological critical element" with a rising application in new technology sectors. Ta is used in the aerospace or medical industry in structural steel, superalloys or capacitors (Divine and Goering, 2004; Filella and Rodriguez-Murillo, 2017; Romero-Freire et al., 2019).	none	Divine and Goering (2004) deliver the following numbers: seawater <4 ng/kg, total water content 0.8 µg/kg and dissolved <1 ng/kg.	The median across Europe in <0.45 µm filtered stream water (n=807) was <0.002 µg/l. ^v
	W	The use of Tungsten is summarised by Krauss (2004) and varies from alloys, filaments of bulbs, to pigments and as catalysts in automobiles.	none	Steenstra et al. (2020) found aqueous tungsten concentrations in Washington State surface waters spanning two orders of magnitude (10.3 ng/l - 2.05 µg/l) with average tungsten concentrations in both water and sediments more than two-fold higher in watersheds with tungsten-bearing underlying rock types than in watersheds without such underlying geology.	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.007 µg/l. ^v

Table S1 continued.

Grouping and sub grouping ⁱ	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ⁱⁱ	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ⁱⁱⁱ)	Examples for ICP-Q-MS based analyses in environmental samples
	Re (used as internal standard)	Rhenium is used almost exclusively for alloys and thus serves two major application areas in particular: Turbine blades for aircraft engines and catalysts for the petrochemical industry. It is also used in thermocouples for high-temperature measurements and as a glow wire in mass spectrometers (https://www.rhenium.de).	none	Gooday et al. (2009) used the Re redox chemistry as one of the proxys for hypoxia phenomena in sediment cores. The vertical distribution of rhenium in seawater was examined by Tagami et al. (2006).	Sproson et al. (2018) used, next to high resolution MS analyses, ICP-QMS analyses to detect the dissolved content of Re in Icelandic river samples. Tagami and Uchida (2004) published a simple QMS method for the detection of Re in sea water.
	Ir	Several exemplary uses of Ir are listed at https://www.metalary.com/2018/05/21/the-many-uses-of-iridium/ , like in LEDs or in corrosion resistant products.	none	Anbar et al. (1996) state, that "Rivers contain from $17.4 (+/-0.9) \times 10^8$ to $92.9 (+/-2.2) \times 10^8$ atoms per kilogram and supply more dissolved iridium to the oceans than do extra-terrestrial sources."	Sugiyama and Shikamori (2015) describe, next to other noble metals, the analyses of Ir by ICP-QQQ-MS.
	Pt	Catalytic converters are considered to be the main sources of Pt into the environment and many studies and reviews are available (e.g., (Ravindra et al., 2004)).	none	Not the release from road traffic, but the natural background of the Rhine was investigated using sediment particles by (Oberthur et al., 2016).	As an example, Machado et al. (2017) delivered a MS/MS method for Cd, Sn, Pd, Rh and Pt.
	Au	Beside mining, Au can be released from e.g., processing, or its use as catalyst (Ishida, 2004).	none	Next to Pt, Oberthur et al. (2016) addressed also Au.	Sugiyama and Shikamori (2015) describe, next to other noble metals, the analyses of Au by ICP-QQQ-MS.
	Hg	Based on several potential anthropogenic pathways into surface water, mercury and its compounds are regulated via the water frame work directive. ⁱⁱ	WFD: MAC-EQS <0.45 µm 0.07 µg/l, EQS biota 20 µg/kg (wet weight); ICPR 90percentile suspended solids 0,5 mg/kg. ⁱⁱ	The total Hg water concentration between Switzerland and the Netherlands was <0.02 µg/l the last years. The <0.45 µm filtered concentrations was <0.01 µg/l. ⁱⁱⁱ	Siepacki et al. (2020) studied the Hg concentration in a lake by ICP-MS/MS analyses.
lanthanides	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	The group of lanthanides are not known to be nutritionally essential in animals and humans and so is lanthanum not (Goering, 2004).	none	These elements are often addressed as rare earth elements (REE). Promising new technologies include these elements. Therefore, they are one of the critical raw materials in the EU (https://ec.europa.eu/growth/sectors/raw-materials/specific-interest/critical_en). Taking this into account, rising environmental concentrations are foreseen, apart from geochemical anomalies (Pignotti et al., 2017), or point sources (Hissler et al., 2015; Song et al., 2017). Special attention must be given to the river Rhine (Moermond et al., 2001; Kulaksiz and Bau, 2011; Klaver et al., 2014; Zhao and Liu, 2018). As an example, for trace functions Neodymium was used for several reasons as a tracer in ocean sciences and gains more and more attention also in freshwater and transition zone sciences (e.g., (Laukert et al., 2017; Rahlf et al., 2021)).	The FOREGS geochemical baseline mapping delivered values based on ICP-QMS. The median across Europe in <0.45 µm filtered stream water (n=807) was 0.034 La, 0.055 Ce, 0.009 Pr, 0.04 Nd, 0.009 Sm, 0.005 Eu, 0.01 Gd, 0.002 Tb, 0.008 Dy, 0.002 Ho, 0.006 Er, <0.002 Tm, 0.006 Yb, <0.002 Lu all values in µg/l. ^v

Table S1 continued.

Grouping and sub grouping ^I	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ^{II}	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ^{III})	Examples for ICP-Q-MS based analyses in environmental samples
actinides	Th	With a half-life time of 14 billion years, ²³² Th is the most stable isotope of an element owning only radioactive isotopes and it finally decays into ²⁰⁸ Pb (Melo and Burkart, 2004).	none	Th has the potential, next to other elements, to enter fresh water environments from different source e.g., nuclear fuel, power stations, ore processing or waste treatment, e.g., (Lofts et al., 2015).	Besides alpha-spectrometry or neutron activation analysis, ICP-MS is advised to analyse Th (Melo and Burkart, 2004). Mas et al. (2020) used ID ICP-MS/MS to analyse Th in kaolinitic samples. An online solid-phase-extraction method is available (Avivar et al., 2012). "Th-234/U-238 activity ratios have been used for decades in marine and freshwater systems as a tracer for particle flux-where disequilibrium between particle-reactive Th-234 (half-life: 24.1 d) and its conservative parent U-238 measures particle removal rates on a time scale of days to weeks." (Waples and Orlandini, 2010). The median across Europe in <0.45 µm filtered stream water (n=807) was 0.009 µg/l. ^V
	U	Its upper earth crust abundance is high and all isotopes undergo a chain of radioactive decays. Phosphate and Uranium mining, nuclear fuel recycling and military uses are well known potential sources to the environment (D. and W., 2004).	none	According to ICP based analyses from Birke and Rauch (2008), the stream water background in Germany is assumed to be 0.3 µg/l. They stated also: "Whereas the distribution of uranium in stream sediments is governed for the most part by geogenic factors related to mineralization, the distribution in stream water is determined mainly by lithological and anthropogenic (e.g. old mines, ore treatment plants, agricultural practices) factors."	The suitability of ICP-MS to analyse several radio-isotopes, including U isotopes was described before (Diez-Fernández et al., 2020). The median across Europe in <0.45 µm filtered stream water (n=807) was 0.32 µg/l. ^V
post-transition-metals	Al	Al is used in building and construction, transportation, packaging and as sacrificial anode in marine constructions (Yokel, 2004).	none	Newman and Watling (2007) found aluminium and iron to be suitable for normalising the concentrations of copper, cobalt, chromium, manganese, nickel, lead and zinc in sediments to differentiate between natural and anthropogenic sources in coastal regions.	The median across Europe in <0.45 µm filtered stream water (n=807) was 17 µg/l. ^V
	Ga	Gallium is considered as "less-studied technological critical element" and is mainly applied in semiconductors as GaAs (Filella and Rodriguez-Murillo, 2017; Romero-Freire et al., 2019).	none	As an example, McAlister and Orians (2012) found Ga suitable to identify the aged Colombian river plume in the coastal Pacific Ocean.	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.001 µg/l. ^V
	In	Indium is considered as "less-studied technological critical element" coming into application in the LCD production for screens as indium tin oxide (Filella and Rodriguez-Murillo, 2017; Romero-Freire et al., 2019).	none	Beside the work of Romero-Freire et al. (2019) and of Filella and Rodriguez (2017), White and Hemond (2012) reviewed the anthropo-biogeochemical cycle of In.	The median across Europe in <0.45 µm filtered stream water (n=807) was <0.002 µg/l. ^V

Table S1 continued.

Grouping and sub grouping ⁱ	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ⁱⁱ	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ⁱⁱⁱ)	Examples for ICP-Q-MS based analyses in environmental samples
	Sn	Besides its use as organo-tin species in several applications (Anger, 2004), the release from brake pads is observed in various countries (Yun et al., 2010).	none	The total Sn water concentration in the lower and delta Rhine were <0.06 µg/l during the last years. ⁱⁱⁱ	For decades QMS based speciation and total content analyses of environmental samples are available, e.g., (Krupp et al., 1996; Anger, 2004)
	Tl	Tl is also regulated via the German ordinance on the protection of surface waters. ⁱⁱ	OGewV: <0.45 µm AA-EQS 0.2 µg/l. ⁱⁱ	In a review, Zhuang and Song (2021) provide basic information on Tl in the aquatic environment and wider perspective was delivered by (Belzile and Chen, 2017).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.005 µg/l. ^v
	Pb	Based on several potential anthropogenic pathways into surface water, lead and its compounds are regulated via the water frame work directive. ⁱⁱ	WFD: AA-EQS <0.45 µm bio available 1,2 µg/l, AA-EQS, MAC-EQS <0.45 µm 14 µg/l; ICPR suspended solids 100 mg/kg. ⁱⁱ	The total Pb water concentration between Switzerland and the Netherlands was during the last years <6 µg/l. The <0.45 µm filtered concentrations were < 0.2 µg/l . ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.09 µg/l. ^v
	Bi	Neagoe (2004) describes several uses of Bi which may cause a release into the environment (e.g., electronic, use as catalyst or paints and cosmetics).	none	The biomethylation of bismuth and its impact on the biogeochemical cycle was examined in several studies, e.g., (Bentley and Chasteen, 2002) or (Michalke et al., 2002).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.002 µg/l. ^v
metalloids	B	Boron has a long history of human use and common actual uses are, fire retardants, fertilizers, personal care products and pharmaceuticals (Nielsen, 2004).	none	Boron is often used as a conservative wastewater tracer, e.g., (Guinoiseau et al., 2018).	The median across Europe in <0.45 µm filtered stream water (n=807) was 15.6 µg/l. ^v
	Si	Silicon is one of the most common elements of the earth crust and many different applications making use of Si are available impacting the global Si cycle, e.g. construction, coatings, food industries, silicon rubbers, personal care products and pharma (D'Haese et al., 2004).	none	Apart from the fact that the global Si cycle (nutrient aspect) is from general relevance (Laruelle et al., 2009) or (Street-Perrott and Barker, 2008), from special interest are silicic acid and the use of Si isotopes as tracers (e.g., (Varela et al., 2016)).	ICP-QQQ-MS was already used to examine the Si isotope ratio in nuclear waste glasses (Gourgiotis et al., 2017).
	Ge	Germanium is considered as "less-studied technological critical element" and is mainly used in fibre-optic systems. Germanium is found to be a by-product in Zn mining (Filella and Rodriguez-Murillo, 2017; Romero-Freire et al., 2019).	none	Next to pollution and speciation questions, Ge is from interest with respect to isotope signatures (Baronas et al., 2018).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.009 µg/l (V) and recently Garcia-Figueroa et al. (2021) published a derivatisation technique coupled to a MS/MS for Ge speciation.
	As	Based on several potential anthropogenic pathways into surface water, arsenic is regulated via the German ordinance on the protection of surface waters. In addition a Rhine specific threshold is available. ⁱⁱ	OGewV: AA-EQS suspended solids 40 mg/kg; ICPR AA-EQS <0.45 µm 1.5 µg/l, 90th percentile of suspended solids: 40 mg/kg. ⁱⁱ	The total As water concentration between Switzerland and the Netherlands was <2 µg/l during the last years. The <0.45 µm filtered concentrations < 1.4 µg/l. ⁱⁱⁱ	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.63 µg/l. ^v
	Se	Even though selenium is one of the essential elements to man, based on several potential anthropogenic pathways into surface water, selenium is regulated via the German ordinance on the protection of surface waters. In addition a Rhine specific threshold is available. ⁱⁱ	OGewV: <0.45 µm AA-EQS 3 µg/l. ⁱⁱ	Many reviews on the environmental behaviour and potential Se impact are available. As an example, He et al. (2018) delivered a review focusing on soils and water.	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.34 µg/l. ^v

Table S1 continued.

Grouping and sub grouping ⁱ	Element	Examples for potential anthropogenic sources/uses	European or German environmental quality standard or Rhine specific quality standard ⁱⁱ	Particular examples with respect to environmental aspects (e.g., exceptional species, applications or long-term trend at river Rhine ⁱⁱⁱ)	Examples for ICP-Q-MS based analyses in environmental samples
	Sb	Many uses of Sb are known e.g., brake linings, flame retardants, or PET incineration and munitions hardening (Duester et al., 2008). Studies are available from a regional character, (e.g., (He et al., 2012)) to specific global release scenarios (e.g., (Filella, 2020)).	none	The biogeochemical cycle of Sb in the environment incl. the aquatic environment is addressed by many studies within the last decades (e.g., (Filella et al., 2003)).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.07 µg/l. ^v
	Te	Tellurium is considered as "less-studied technological critical element" due to its application in the new technology sector for solar cell production as CdTe (Filella and Rodríguez-Murillo, 2017; Romero-Freire et al., 2019).	none	The Tellurium behaviour in the Gironde estuary is described by Gil-Diaz et al. (2019) and within the GEOTRACES project in Changjiang (Yangtze) river by (Wu et al., 2014).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.003 µg/l. ^v
reactive non-metals	C	The natural release and the release from wastewater treatment plants dominate the budget of many rivers (e.g., (Barrenha et al., 2018)). The evaluation of the detailed speciation of organic pollutants is an important task, e.g., with respect to emerging contaminants.	OGewV: whole water sample AA-EQS 5 µg/l as total organic C. ⁱⁱ	Total dissolved carbon (TDC) is an important parameter in the surface water quality evaluation (Jarvie et al., 2017).	Schroeder et al. (2020) studied the dissolved C concentrations in sediment pore water profiles.
	P	Most important to mention is the release from agricultural runoff and wastewater (Gulati and van Donk, 2002).	OGewV: Whole water sample total P AA-EQS 0.05 µg/l, ortho-PO ₄ -P whole water sample AA-EQS 0.02 µg/l. ⁱⁱ	The total P water concentration between Switzerland and the Netherlands was <0.2 µg/l during the last years. The ortho-P concentrations < 0.1 µg/l. ⁱⁱⁱ	P is a limiting factor in surface water (Gulati and van Donk, 2002).
	S	Agrochemicals/fertilisers, fossil fuel burning and anthropogenic induced weathering (mining) are very significant emission scenarios (e.g., (Li et al., 2008; Devendar and Yang, 2017)).	none	The biogeochemistry of S was addressed, next to other elements, by Harris (1999). From rising interest in aquatic research are S isotope ratios (e.g., (Li et al., 2008)) and Norici et al. (2005) described the interplay between sulphur and the primary production in aquatic environments.	S analyses by ICP-MS was reviewed by Martinez-Sierra et al. (2015).
	Cl	Chlorine is often released in significant quantities to freshwater environments. Examples for the river Rhine are raining off potash dumps, large-scale industry waste water and mine waters (Dieperink, 2011).	OGewV: whole water sample AA-EQS 50 µg/l as Cl. ⁱⁱ	Besides contamination scenarios, Cl is used as a tracer in coastal areas and estuaries, e.g., (Prusty et al., 2020).	Usually chlorine is investigated as an element potentially creating interferences in ICP-MS analyses. However, Nelson et al. (2019) used a ICP-QQQ-MS to determine Cl in crude oil.
	Br	The predominant anthropogenic Br into freshwater is from waste water, (e.g., (Zwolsman and van Bokhoven, 2007) or (Soltermann et al., 2016)).	none	Zwolsman and van Bokhoven (2007) as well as Soltermann et al. (2016) describe the Br release to river Rhine.	Ferguson and Grazzini (1999) described the use of ICP-MS to analyse Br as an environmental tracer.
	I	Often elevated iodine concentrations from natural sources are from concern due to health issues (Huang et al., 2020).	none	During the last decade, the medically-derived iodine in surface water received more attention, e.g., (Rose et al., 2013).	The median across Europe in <0.45 µm filtered stream water (n=807) was 0.33 µg/l. ^v Tagami and Uchida (2005) described the sample storage conditions and holding times for the determination of total iodine in natural water for ICP-MS analyses.

ⁱbased on <https://ptable.com> left to rightⁱⁱEuropean Water Framework Directive, German Ordinance on the Protection of Surface Waters (OGewV), ICPR target value (<https://www.iksr.org/en/icpr>)ⁱⁱⁱ<https://iksr.bafg.de>^{iv}maximum allowable concentration (MAC-EQS); annual average value (AA-EQS)^v<http://weppi.gtk.fi/publ/foregsatlas/>

2. Method development

The following tables contain all information regarding the composition of certified reference materials (CRM), calibration check solutions (in the following mentioned as “in-house standards”), spikes and analytical modes considered during method development. Moreover, data regarding background equivalent concentration (BEC), instrument detection limit (IDL), sensitivity and limit of quantifications (LOQ) are given.

Table S2: Element concentrations in the CRM, in-house standards and spikes used during method validation for recovery calculations. All values are in µg/l.

	CRM			In-house									Spikes								
	SPS-SW1	SPS-SW2	TMDA-51.5	In-house 3A	In-house 5A	In-house 7A	In-house 3B	In-house 5B	In-house 7B	In-house 5C	In-house 7C	In-house 9C	Spike 3A	Spike 5A	Spike 7A	Spike 3B	Spike 5B	Spike 7B	Spike 5C	Spike 7C	Spike 9C
Li			19.4	0.1	1	10							0.1	1	10						
Be			10	0.01	0.1	1							0.01	0.1	1						
B	50	250	46.9	0.25	2.5	25							0.25	2.5	25						
C										2500	25000	250000							2500	25000	250000
Na	2000	10000		100	1000	10000							100	1000	10000						
Mg	400	2000		25	250	2500							25	250	2500						
Al	50	250	105	0.15	1.5	15							0.15	1.5	15						
Si	1000	5000		5	50	500							5	50	500						
P	100	500								5	50	500							5	50	500
S	2000	10000								500	5000	50000							500	5000	50000
Cl										1000	10000	100000							1000	10000	100000
K	200	1000		50	500	5000							50	500	5000						
Ca	2000	10000		100	1000	10000							100	1000	10000						
Sc	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Ti			14.1	0.01	0.1	1							0.01	0.1	1						
V	10	50	46.4	0.05	0.5	5							0.05	0.5	5						
Cr	2	10	65.1	0.025	0.25	2.5							0.025	0.25	2.5						
Mn	10	50	78.7	0.05	0.5	5							0.05	0.5	5						
Fe	20	100	108	0.25	2.5	25							0.25	2.5	25						
Co	2	10	68.7	0.0125	0.125	1.25							0.0125	0.125	1.25						

Table S2 continued.

	CRM			In-house									Spikes								
	SPS-SW1	SPS-SW2	TMDA-51.5	In-house 3A	In-house 5A	In-house 7A	In-house 3B	In-house 5B	In-house 7B	In-house 5C	In-house 7C	In-house 9C	Spike 3A	Spike 5A	Spike 7A	Spike 3B	Spike 5B	Spike 7B	Spike 5C	Spike 7C	Spike 9C
Ni	10	50	65.3	0.05	0.5	5							0.05	0.5	5						
Cu	20	100	77.4	0.05	0.5	5							0.05	0.5	5						
Zn	20	100	140	0.05	0.5	5							0.05	0.5	5						
Ga			9.88	0.005	0.05	0.5							0.005	0.05	0.5						
Ge				0.005	0.05	0.5							0.005	0.05	0.5						
As	10	50	16.7	0.05	0.5	5							0.05	0.5	5						
Se	2	10	14.3	0.025	0.25	2.5							0.025	0.25	2.5						
Br										25	250	2500							25	250	2500
Rb	10	50	15.3	0.05	0.5	5							0.05	0.5	5						
Sr	50	250	118	2.5	25	250							2.5	25	250						
Y	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Zr							0.005	0.05	0.5							0.005	0.05	0.5			
Nb				0.005	0.05	0.5							0.005	0.05	0.5						
Mo	10	50	54.9	0.05	0.5	5							0.05	0.5	5						
Ru							0.005	0.05	0.5							0.005	0.05	0.5			
Pd				0.005	0.05	0.5							0.005	0.05	0.5						
Ag			12	0.0075	0.075	0.75							0.0075	0.075	0.75						
Cd	0.5	2.5	25.7	0.01	0.1	1							0.01	0.1	1						
In				0.005	0.05	0.5							0.005	0.05	0.5						
Sn			16.4				0.01	0.1	1							0.01	0.1	1			
Sb			15.2				0.01	0.1	1							0.01	0.1	1			
Te				0.005	0.05	0.5							0.005	0.05	0.5						
I										0.1	1	10							0.1	1	10
Cs	2	10		0.025	0.25	2.5							0.025	0.25	2.5						
Ba	50	250	72.6	0.15	1.5	15							0.15	1.5	15						
La	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Ce	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Pr	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Nd	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						

Table S2 continued.

	CRM			In-house									Spikes								
	SPS-SW1	SPS-SW2	TMDA-51.5	In-house 3A	In-house 5A	In-house 7A	In-house 3B	In-house 5B	In-house 7B	In-house 5C	In-house 7C	In-house 9C	Spike 3A	Spike 5A	Spike 7A	Spike 3B	Spike 5B	Spike 7B	Spike 5C	Spike 7C	Spike 9C
Sm	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Eu	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Gd	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Tb	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Dy	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Ho	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Er	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Tm	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Yb	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Lu	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
Hf							0.005	0.05	0.5							0.005	0.05	0.5			
Ta				0.005	0.05	0.5							0.005	0.05	0.5						
W				0.005	0.05	0.5							0.005	0.05	0.5						
Ir							0.005	0.05	0.5							0.005	0.05	0.5			
Pt							0.005	0.05	0.5							0.005	0.05	0.5			
Au							0.005	0.05	0.5							0.005	0.05	0.5			
Hg							0.01	0.1	1							0.01	0.1	1			
Tl	0.5	2.5	20.3	0.25	2.5	25							0.25	2.5	25						
Pb	5	25	63.5	0.015	0.15	1.5							0.015	0.15	1.5						
Bi			9.67	0.0075	0.075	0.75							0.0075	0.075	0.75						
Th	0.5	2.5		0.005	0.05	0.5							0.005	0.05	0.5						
U	0.5	2.5	28.7	0.015	0.15	1.5							0.015	0.15	1.5						

Table S3: Elements, isotopes and analysis modes considered during method development.

Mass	Element	Cell gas and analysis mode							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
7	Li	x	x	x			x		
9	Be	x	x	x	x		x		
11	B	x	x	x			x	x	x
12	C	x	x	x	x	x	x	x	x
23	Na	x	x	x			x		
24	Mg	x	x	x			x	x	
27	Al	x	x	x			x	x	
28	Si	x	x	x	x		x	x	x
31	P	x	x	x	x		x	x	
32	S	x	x	x	x	x		x	
34	S	x	x	x	x	x	x	x	
35	Cl	x	x	x	x	x	x	x	x
37	Cl	x	x	x	x	x	x	x	x
39	K	x	x	x			x		
43	Ca	x	x	x			x	x	
44	Ca	x	x	x			x	x	
45	Sc	x	x	x	x		x	x	x
47	Ti	x	x	x	x		x	x	
51	V	x	x	x	x		x	x	
52	Cr	x	x	x			x	x	x
55	Mn	x	x	x			x	x	
56	Fe	x	x	x	x		x	x	
59	Co	x	x	x			x	x	
60	Ni	x	x	x			x	x	
63	Cu	x	x	x			x	x	
66	Zn	x	x	x			x	x	
71	Ga	x	x	x			x		
72	Ge	x	x	x			x	x	x
75	As	x	x	x	x		x	x	
78	Se	x	x	x	x		x	x	
79	Br	x	x	x	x	x	x	x	x
85	Rb	x	x	x			x		
88	Sr	x	x	x			x	x	x
89	Y	x	x	x			x	x	x
90	Zr	x	x	x			x	x	x
93	Nb	x	x	x			x	x	x
95	Mo	x	x	x			x	x	x
101	Ru	x	x	x			x	x	x
105	Pd	x	x	x			x	x	
107	Ag	x	x	x			x		
109	Ag	x	x	x			x		
111	Cd	x	x	x			x		x
115	In	x	x	x	x	x	x	x	
118	Sn	x	x	x			x	x	x

Table S3 continued.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
121	Sb	x	x	x			x	x	
125	Te	x	x	x			x	x	
127	I	x	x	x	x	x	x	x	x
133	Cs	x	x	x			x		
137	Ba	x	x	x	x	x	x	x	x
139	La	x	x	x			x	x	x
140	Ce	x	x	x			x	x	x
141	Pr	x	x	x			x	x	x
146	Nd	x	x	x			x	x	x
147	Sm	x	x	x			x	x	x
153	Eu	x	x	x			x	x	x
157	Gd	x	x	x			x	x	x
159	Tb	x	x	x			x	x	x
163	Dy	x	x	x			x	x	x
165	Ho	x	x	x			x	x	x
166	Er	x	x	x			x	x	x
169	Tm	x	x	x			x	x	x
172	Yb	x	x	x			x	x	x
175	Lu	x	x	x			x	x	x
178	Hf	x	x	x			x	x	x
181	Ta	x	x	x			x	x	x
182	W	x	x	x			x	x	x
193	Ir	x	x	x			x	x	x
195	Pt	x	x	x			x	x	
197	Au	x	x	x			x	x	
201	Hg	x	x	x			x	x	
202	Hg	x	x	x			x	x	
205	Tl	x	x	x			x		
208	Pb	x	x	x			x	x	
209	Bi	x	x	x			x	x	
232	Th	x	x	x			x	x	x
238	U	x	x	x			x	x	x

Table S4: Background equivalent concentrations (BEC) determined via external calibration of all analytes and analysis modes considered during method development. The BEC is calculated by the MassHunter Software (MassHunter 4.5, Workingstation, Version C01.05) as the mean of the following equation for each calibration standard: $(I_b/I_{cal}-I_b)*C_{cal}$ (I_b : Counts of the calibration standards with 0 concentration; I_{cal} : Counts of the calibration standards above 0; C_{cal} : measured concentration of the calibration standards). All values are in µg/l.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
7	Li	3.13E-03	1.95E-03	5.98E-03			1.09E-02		
9	Be	1.40E-02	1.34E-05	n.a.	n.a.		7.48E-04		
11	B	6.44E-01	5.16E-01	9.65E-01			1.52E+00	9.36E+00	5.77E+01
12	C	7.48E+04	5.49E+04	5.25E+04	5.78E+04		5.36E+04	5.39E+04	9.31E+04
23	Na	2.97E+00	2.55E+00	2.88E+00			5.46E+00		
24	Mg	6.58E-01	4.71E-01	1.79E-01			4.90E-01	1.54E+00	
27	Al	5.64E-02	6.00E-02	3.14E-02			5.07E-02	9.28E-02	
28	Si	1.26E+01	7.81E+00	8.15E+00	8.51E+00		2.10E+01	4.99E+01	5.44E+01
31	P	1.28E+01	2.04E+00	7.65E+01	3.28E+00		n.a.	9.40E-02	
32	S	n.a.	n.a.	5.37E+04	2.62E+02	3.72E+03		1.37E+00	
34	S	4.88E+03	1.60E+03	1.31E+03	3.01E+01	2.65E+02	n.a.	1.60E+00	
35	Cl	1.95E+02	5.21E+01	1.21E+03	8.71E+02	6.03E+01	n.a.	1.68E+02	1.12E+03
37	Cl	n.a.	4.04E+05	3.21E+03	n.a.	6.59E+01	n.a.	1.80E+02	4.11E+04
39	K	5.06E+01	1.73E+01	1.11E+00			1.46E+00		
43	Ca	4.63E+00	2.67E+00	7.43E+00			8.14E+00	6.18E+00	
44	Ca	7.69E+00	2.88E+00	7.68E+00			5.56E+00	1.35E+00	
45	Sc	4.43E-03	4.90E-04	6.29E-04	8.33E-04		6.92E-03	8.19E-04	1.17E-02
47	Ti	6.92E-03	1.15E-03	1.87E-03	n.a.		1.91E-01	5.12E-03	
51	V	1.10E-02	3.36E-04	1.36E-02	6.77E+00		6.48E-01	1.09E-02	
52	Cr	3.32E-01	3.55E-03	5.52E-03			5.19E-03	7.52E-03	1.13E-02
55	Mn	1.93E-02	1.31E-03	1.72E-03			6.54E-03	8.19E-03	
56	Fe	1.10E+02	2.27E-01	2.72E-02	7.21E+00		3.55E-02	2.08E-02	
59	Co	9.65E-04	2.51E-04	4.98E-04	3.41E-04		1.76E-03	6.11E-04	
60	Ni	2.34E-03	2.71E-03	5.91E-03			6.56E-03	8.96E-03	
63	Cu	1.35E-02	1.25E-02	3.57E-02			5.13E-02	1.50E-01	
66	Zn	1.18E-01	3.24E-01	1.15E-01			2.08E-01	2.39E-02	
71	Ga	9.42E-05	4.63E-05	1.37E-05			9.56E-05		
72	Ge	2.37E-02	6.72E-05	6.23E-05			7.85E-04	1.02E-04	4.12E-03
75	As	4.32E-03	3.19E-04	2.15E-03	n.a.		6.74E-02	8.47E-04	
78	Se	8.30E+00	8.42E-02	4.43E-04	2.22E-02		1.06E-02	3.29E-03	
79	Br	n.a.	4.92E-01	3.14E-01	2.46E-01	8.79E-01	n.a.	3.40E-01	5.49E-01
81	Br	n.a.	5.58E-01	6.08E-01	3.88E-01	n.a.	n.a.	3.67E-01	1.68E+00
85	Rb	4.95E-04	6.51E-04	5.94E-04			9.95E-04		
88	Sr	1.84E-02	1.49E-02	5.71E-03			1.16E-02	1.13E-03	3.81E-03
89	Y	8.00E-05	4.71E-05	2.93E-04			2.03E-02	7.92E-04	3.33E-03
90	Zr	1.30E-04	3.14E-04	4.40E-04			8.42E-02	2.65E-04	
93	Nb	1.10E-04	9.35E-05	1.17E-03			3.39E-02	4.07E-03	3.39E-03
95	Mo	2.30E-04	4.24E-04	1.07E-04			6.96E-03	3.16E-03	2.33E-04
101	Ru	1.87E-03	8.66E-03	3.14E-03			1.94E-03	5.66E-03	

Table S4 continued.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
105	Pd	1.37E-04	2.65E-05	2.81E-04			2.39E-03	4.65E-02	
107	Ag	1.80E-04	1.37E-04	3.98E-05			3.95E-04		
109	Ag	1.60E-04	1.09E-04	6.87E-05			2.90E-04		
111	Cd	1.99E-05	7.56E-05	3.14E-05			9.23E-05		7.00E-03
115	In	2.62E-06	n.a.	8.75E-07	n.a.	n.a.	3.61E-05	5.42E+00	
118	Sn	1.08E-03	8.93E-04	2.03E-03			5.59E-04	8.46E-03	
121	Sb	1.80E-04	2.08E-04	5.35E-04			2.19E-04	4.43E-04	
125	Te	n.a.	n.a.	n.a.			2.24E-04	1.08E-02	
127	I	1.16E-01	1.07E-01	1.52E-02	1.98E-02	n.a.	n.a.	2.24E-02	1.55E-01
133	Cs	3.94E-05	4.38E-05	8.54E-05			1.50E-04		
137	Ba	3.44E-03	3.62E-03	2.83E-03	n.a.	n.a.	3.46E-03	2.26E-03	8.13E-03
139	La	1.77E-04	1.65E-04	2.32E-04			4.15E-02	5.21E-05	1.73E-04
140	Ce	1.01E-04	7.98E-05	4.85E-04			3.97E-02	3.31E-05	n.a.
141	Pr	2.21E-06	7.08E-06	4.44E-05			8.87E-02	8.82E-06	4.43E-04
146	Nd	5.18E-05	3.64E-05	2.34E-04			8.53E-02	3.30E-04	1.51E-03
147	Sm	3.01E-05	4.21E-05	1.85E-05			6.70E-03	3.54E-05	1.29E-02
153	Eu	6.75E-06	n.a.	1.50E-05			3.73E-05	2.15E-05	1.14E-03
157	Gd	1.64E-05	n.a.	4.25E-05			3.50E-04	2.81E-05	6.66E-04
159	Tb	2.37E-05	1.11E-05	4.34E-05			1.01E-03	1.83E-06	2.77E-03
163	Dy	1.06E-05	8.91E-06	2.30E-05			1.24E-02	1.04E-05	5.65E-03
165	Ho	n.a.	2.31E-06	7.47E-06			4.26E-03	3.74E-06	n.a.
166	Er	2.71E-06	n.a.	1.32E-05			1.56E-03	7.09E-06	4.07E-04
169	Tm	2.62E-06	8.12E-06	4.34E-06			6.39E-05	1.22E-05	1.67E-03
172	Yb	3.92E-06	8.53E-06	2.02E-05			1.04E-04	n.a.	1.40E-03
175	Lu	3.45E-06	3.10E-06	8.79E-06			3.00E-04	1.36E-05	2.35E-03
178	Hf	1.43E-04	1.37E-04	2.52E-04			4.13E-01	2.24E-04	
181	Ta	1.98E-02	2.13E-02	1.15E-02			2.00E-03	1.52E-01	2.63E-02
182	W	3.09E-03	4.05E-03	2.71E-03			2.31E-03	6.56E-03	7.04E-03
193	Ir	7.58E-05	1.75E-04	1.57E-04			1.77E-04	8.49E-04	
195	Pt	6.90E-05	2.76E-04	1.47E-04			1.34E-04	1.09E-03	
197	Au	2.21E-04	4.54E-04	3.47E-04			3.43E-04	1.22E-02	
201	Hg	5.52E-03	3.61E-03	2.96E-03			2.48E-03	4.16E+00	
202	Hg	4.12E-03	3.76E-03	1.94E-03			2.36E-03	1.34E-02	
205	Tl	5.55E-01	6.74E-01	2.04E-01			5.18E-01		
208	Pb	8.17E-04	7.63E-04	4.14E-04			7.64E-04	n.a.	
209	Bi	4.29E-04	3.64E-04	7.43E-05			4.08E-04	4.86E-04	
232	Th	4.33E-04	6.11E-04	5.50E-05			n.a.	1.66E-04	1.73E-04
238	U	3.32E-05	5.61E-05	2.92E-05			n.a.	1.10E-03	1.70E-05

n.a.: not available

Table S5: Instrument detection limits (IDL) determined via external calibration of all analytes and analysis modes considered during method development. The IDL is calculated by the MassHunter Software (MassHunter 4.5, Workstation, Version C01.05) as $3 \times \text{SD}_{\text{blank}}/\text{slope}$ of calibration (SD: standard deviation). All values are in $\mu\text{g/l}$.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M^+	He as M^+	H_2 as M^+	H_2 as MH^+	H_2 as MH_2^+	O_2 as M^+	O_2 as MO^+	O_2 as MO_2^+
7	Li	1.06E-03	1.01E-02	7.99E-03			1.54E-02		
9	Be	6.98E-05	n.a.	3.88E-03	n.a.		n.a.		
11	B	1.59E-02	1.60E-01	1.31E-01			6.14E-02	1.98E+00	1.68E+01
12	C	9.16E+03	1.37E+04	5.67E+03	2.36E+04	1.20E+04	n.a.	3.46E+03	1.70E+04
23	Na	1.05E-01	5.20E-01	3.74E-01			1.61E-01		
24	Mg	5.71E-02	3.22E-01	5.66E-02			3.39E-02	3.40E-01	
27	Al	4.52E-03	8.08E-02	1.73E-02			7.59E-03	2.99E-02	
28	Si	4.69E-01	2.47E-01	6.07E-01	7.70E-01		3.25E-01	9.94E+00	1.10E+01
31	P	7.32E-01	9.22E-01	1.32E+01	3.32E+00		n.a.	2.98E-02	
32	S	n.a.	n.a.	8.44E+02	1.11E+01	2.02E+02		3.00E-01	
34	S	2.88E+02	5.15E+01	1.98E+01	1.65E+02		n.a.	6.51E-01	
35	Cl	4.99E+00	8.24E+01	2.78E+03	8.00E+02	3.09E+01	n.a.	8.44E+01	4.75E+03
37	Cl	n.a.	1.80E+04	3.34E+03	n.a.	6.21E+01	n.a.	1.15E+02	5.49E+04
39	K	9.85E-01	1.34E+00	7.45E-02			6.92E-02		
43	Ca	8.60E-01	6.69E+00	2.53E+00			1.17E+00	6.40E+00	
44	Ca	3.18E-01	1.03E+00	7.53E-01			3.41E-01	6.60E-01	
45	Sc	3.77E-04	1.53E-03	6.18E-04	4.33E-03		7.05E-04	7.22E-04	3.28E-02
47	Ti	8.46E-03	5.96E-03	7.83E-03	n.a.		1.09E-01	2.83E-03	
51	V	9.44E-04	1.29E-03	9.72E-03	6.86E+00		1.14E-01	1.54E-03	
52	Cr	1.27E-02	2.40E-03	5.74E-03			1.24E-03	4.43E-03	4.41E-02
55	Mn	1.66E-03	1.86E-03	1.02E-03			1.19E-03	1.08E-02	
56	Fe	2.52E+00	3.63E-02	6.37E-03	6.46E+00		1.04E-02	1.41E-02	
59	Co	4.04E-04	3.88E-04	1.53E-03			2.23E-04	1.48E-03	
60	Ni	1.51E-03	2.70E-03	1.50E-02			2.10E-03	2.68E-02	
63	Cu	3.03E-03	3.14E-03	1.69E-02			1.77E-02	1.33E-01	
66	Zn	9.45E-03	4.21E-01	2.61E-02			1.79E-02	8.35E-02	
71	Ga	1.47E-04	2.41E-04	7.12E-05			1.63E-04		
72	Ge	4.38E-03	3.49E-04	3.24E-04			3.88E-04	5.28E-04	2.14E-02
75	As	1.99E-03	n.a.	8.38E-03	n.a.		8.09E-02	1.04E-03	
78	Se	9.03E-02	3.46E-02	1.67E-03	7.66E-02		4.02E-03	3.87E-03	
79	Br	n.a.	3.59E-01	1.75E-01	2.14E-01	2.92E+00	n.a.	4.30E-01	2.85E+00
81	Br	n.a.	2.67E-01	1.78E-01	2.40E-01	n.a.	n.a.	5.52E-01	5.04E+00
85	Rb	1.54E-04	1.06E-03	2.68E-04			2.49E-04		
88	Sr	4.48E-03	8.07E-03	8.02E-04			8.02E-04	2.79E-03	1.05E-02
89	Y	7.29E-05	2.45E-04	1.63E-04			3.52E-02	2.92E-04	3.36E-03
90	Zr	1.30E-04	3.14E-04	4.40E-04			8.42E-02	2.65E-04	
93	Nb	5.72E-05	1.49E-04	2.29E-03			7.97E-02	7.57E-03	3.62E-03
95	Mo	4.73E-04	1.21E-03	5.54E-04			2.19E-02	1.10E-02	6.78E-04
101	Ru	1.87E-03	8.66E-03	3.14E-03			1.94E-03	5.66E-03	
105	Pd	5.48E-05	1.13E-04	5.29E-04			6.48E-04	4.28E-02	
107	Ag	1.86E-04	2.01E-04	1.55E-04			1.88E-04		

Table S5 continued.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
109	Ag	2.47E-04	1.46E-04	2.03E-04			2.55E-04		
111	Cd	1.04E-04	3.93E-04	1.63E-04			4.79E-04		3.64E-02
115	In	2.23E-05	6.15E-05	2.37E-05	n.a.	n.a.	3.94E-05	1.03E+01	
118	Sn	1.08E-03	8.93E-04	2.03E-03			5.59E-04	8.46E-03	
121	Sb	1.80E-04	2.08E-04	5.35E-04			2.19E-04	4.43E-04	
125	Te	n.a.	n.a.	n.a.			1.16E-03	3.47E-02	
127	I	8.21E-03	2.67E-02	1.48E-03	1.03E-01	n.a.	n.a.	1.37E-02	8.05E-01
133	Cs	5.33E-05	2.28E-04	1.85E-04			1.08E-04		
137	Ba	1.97E-03	4.59E-03	1.71E-03	n.a.	n.a.	1.98E-03	7.95E-03	4.23E-02
139	La	1.11E-04	2.36E-04	1.78E-04			1.08E-01	3.36E-05	4.52E-04
140	Ce	9.70E-05	9.83E-05	6.58E-04			2.06E-01	2.99E-05	n.a.
141	Pr	7.67E-06	3.68E-05	8.00E-05			1.87E-01	3.29E-05	1.15E-03
146	Nd	1.68E-04	9.47E-05	3.92E-04			3.22E-01	4.43E-04	7.86E-03
147	Sm	9.35E-05	2.19E-04	9.63E-05			1.90E-02	6.41E-05	3.86E-02
153	Eu	1.75E-05	n.a.	6.12E-05			4.94E-05	5.60E-05	4.02E-03
157	Gd	5.67E-05	n.a.	1.77E-04			1.09E-03	1.46E-04	3.46E-03
159	Tb	6.41E-05	3.47E-05	7.29E-05			5.25E-03	9.49E-06	5.01E-03
163	Dy	5.49E-05	4.63E-05	8.15E-05			5.19E-02	5.39E-05	1.20E-02
165	Ho	n.a.	1.20E-05	2.32E-05			1.61E-02	1.03E-05	n.a.
166	Er	1.41E-05	n.a.	6.86E-05			4.05E-03	2.36E-05	2.11E-03
169	Tm	1.36E-05	2.91E-05	1.50E-05			8.34E-05	3.39E-05	5.17E-03
172	Yb	2.04E-05	4.43E-05	7.03E-05			1.61E-04	n.a.	7.29E-03
175	Lu	1.35E-05	1.61E-05	3.81E-05			1.56E-03	1.87E-05	4.51E-03
178	Hf	1.43E-04	1.37E-04	2.52E-04			4.13E-01	2.24E-04	
181	Ta	1.81E-02	3.92E-02	1.22E-02			4.85E-03	7.90E-01	2.81E-02
182	W	8.83E-04	2.09E-03	9.49E-04			5.99E-03	1.71E-02	1.65E-03
193	Ir	7.58E-05	1.75E-04	1.57E-04			1.77E-04	8.49E-04	
195	Pt	6.90E-05	2.76E-04	1.47E-04			1.34E-04	1.09E-03	
197	Au	2.21E-04	4.54E-04	3.47E-04			3.43E-04	1.22E-02	
201	Hg	1.86E-03	8.54E-03	1.04E-03			1.08E-03	5.28E+00	
202	Hg	8.35E-04	1.13E-03	6.81E-04			8.91E-04	4.12E-02	
205	Tl	2.20E-01	1.25E+00	5.96E-01			7.95E-01		
208	Pb	3.92E-04	4.21E-04	3.88E-04			4.03E-04	n.a.	
209	Bi	1.47E-04	2.07E-04	6.16E-05			1.82E-04	1.27E-03	
232	Th	2.91E-04	2.13E-04	7.56E-05			n.a.	1.45E-04	1.53E-04
238	U	2.54E-05	1.47E-04	6.67E-05			n.a.	5.73E-03	2.65E-05

n.a.: not available

Table S6: Sensitivity as counts per seconds (cps) per concentration in µg/l. The sensitivity was calculated as the mean between the cps/(µg/l) values of all calibration standards. Values <100 are highlighted in italic font. Please note that some table entries are strongly influenced by non-resolved interferences and do not represent the true sensitivity of the method towards the analyte (e.g., especially in no gas mode).

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
7	Li	145000	374	1240			1390		
9	Be	23000	271	417	8		2610		
11	B	94800	714	5620			28500	1740	786
12	C	21600	191	16	2	7	23	188	4
23	Na	180000	3350	16400			180000		
24	Mg	81000	1010	6020			53200	1620	
27	Al	198000	597	13700			87700	2540	
28	Si	553000	1720	10600	5030		157000	183000	3440
31	P	127000	123	1530	47		18800	22100	
32	S	27700000	45700	2050000	3870	3940		8910	
34	S	123000	244	10600	30	19	1670	436	
35	Cl	1770	9	1	4	40	6	103	0
37	Cl	0	3160	6	0	19	176	37	4
39	K	1760000	4870	13800			151000		
43	Ca	2860	25	275			2870	22	
44	Ca	51800	496	4690			45100	238	
45	Sc	1240000	4750	61500	1070		693000	113000	3800
47	Ti	14800	350	1190	13		1950	9150	
51	V	211000	11900	17500	1520		22500	167000	
52	Cr	1460000	16300	11400			103000	10500	153
55	Mn	210000	8400	71200			182000	6830	
56	Fe	41300000	20100	53800	165		140000	10300	
59	Co	155000	28400	14500			121000	9370	
60	Ni	39500	8860	1410			34600	894	
63	Cu	114000	29500	2420			131000	168	
66	Zn	330000	45700	46600			522000	84	
71	Ga	94300	4610	41800			81100		
72	Ge	321000	2910	12600			36100	2410	323
75	As	20900	1490	1210	18		550	17300	
78	Se	4830000	2330	2000	106		7910	917	
79	Br	n.a.	538	2170	699	18	2670	940	1
81	Br	n.a.	595	3750	633	4	3000	727	24
85	Rb	175000	7430	77900			142000		
88	Sr	251000	11700	130000			215000	5910	867
89	Y	285000	24400	166000			491	252000	3360
90	Zr	61700	8250	11400			37	674000	130000
93	Nb	184000	35100	7890			1470	2060	219000
95	Mo	37600	10600	3640			775	492	30000
101	Ru	537	328	141			3170	4540	3490
105	Pd	45900	14600	6270			124000	1210	
107	Ag	134000	46100	14600			108000		

Table S6 continued.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
109	Ag	122000	45100	14700			100000		
111	Cd	24100	6460	15400			21800		570
115	In	257000	32000	196000	1	0	242000	435	
118	Sn	80100	13500	49500			82600	8510	197
121	Sb	80700	12600	39500			53400	20400	
125	Te	3590	256	2260			2780	227	
127	I	206000	19900	149000	6	0	323000	26100	169
133	Cs	241000	23200	157000			213000		
137	Ba	36700	5290	25900	1	0	30000	1520	252
139	La	314000	66000	89000			208	243000	2630
140	Ce	269000	77600	113000			21	223000	2370
141	Pr	296000	69800	193000			699	259000	1370
146	Nd	52900	13000	35000			371	54500	882
147	Sm	41900	10800	27000			1060	41900	642
153	Eu	168000	48600	102000			134000	22800	1930
157	Gd	49600	18300	31600			3500	40500	1020
159	Tb	298000	108000	183000			1120	276000	2880
163	Dy	74400	27900	46300			193	74200	245
165	Ho	279000	103000	171000			801	286000	1320
166	Er	93800	36200	57900			443	96200	570
169	Tm	284000	117000	176000			40100	253000	2100
172	Yb	63800	26700	40600			61500	7860	273
175	Lu	280000	74900	171000			2560	282000	2820
178	Hf	40400	15300	15400			349	207000	81800
181	Ta	8230	4290	5900			1150	212	4380
182	W	190000	111000	739000			533	724	63700
193	Ir	135000	87500	60400			128000	31500	2490
195	Pt	51300	35100	6150			53000	2070	
197	Au	46200	28500	3380			42500	323	
201	Hg	28100	17300	40600			19200	984	
202	Hg	38900	23300	87700			43500	450	
205	Tl	4970	4360	474			5810		
208	Pb	218000	109000	142000			190000	1000	
209	Bi	170000	77400	118000			174000	3310	
232	Th	164000	85200	89200			34	31600	77800
238	U	189000	106000	112000			67	318	143000

Table S7: Limit of quantifications (LOQ) calculated as mean of blank measurements + 10 σ in $\mu\text{g/l}$.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
7	Li	6.58E-02	7.11E-02	6.15E-02			3.94E-02		
9	Be	5.42E-04	4.67E-03	4.16E-03	7.33E-02		7.23E-04		
11	B	6.60E+00	4.28E+00	6.94E+00			1.07E+01	1.33E+01	9.99E+02
12	C	2.16E+04	4.20E+04	3.07E+03	6.62E+03	6.89E+03	1.91E+05	1.33E+05	1.51E+05
23	Na	4.33E+01	2.42E+01	7.65E+01			6.85E+01		
24	Mg	1.58E-02	4.94E-02	8.50E-01			6.23E-01	7.96E-01	
27	Al	5.80E-03	1.49E-02	2.51E-03			3.18E-03	2.53E-01	
28	Si	5.82E+02	1.64E+02	6.62E+01	6.98E+01		6.09E+02	7.81E+02	8.57E+02
31	P	1.27E+00	1.97E+00	n.a.	9.86E+00		6.21E+02	8.66E-01	
32	S	3.98E+04	1.44E+05	n.a.	5.94E-02	2.09E+02		1.34E+01	
34	S	5.49E+03	4.15E+01	n.a.	1.29E+01	1.43E+02	2.88E+03	1.39E+01	
35	Cl	4.07E+03	3.05E+03	6.07E+03	6.53E+03	6.14E+03	1.62E+04	6.29E+03	7.20E+03
37	Cl	1.87E+05	4.70E+04	7.81E+03	6.86E+03	6.17E+03	2.44E+05	5.12E+03	4.36E+03
39	K	3.89E+01	1.49E+01	5.44E+00			3.83E+00		
43	Ca	3.01E-01	5.09E+00	6.09E-01			5.94E-01	4.18E+01	
44	Ca	2.88E+00	8.15E-01	n.a.			9.12E-01	4.45E+01	
45	Sc	1.40E-02	1.50E-02	9.46E-03	2.76E-02		2.41E-02	2.62E-02	4.41E-02
47	Ti	3.55E-02	3.64E-02	1.94E-02	1.08E+00		4.15E-01	1.05E-02	
51	V	2.83E-01	4.69E-03	2.22E-01	8.93E+01		1.94E+01	3.54E-03	
52	Cr	3.08E-01	3.72E-03	5.61E-03			2.24E-03	1.21E-02	1.17E-01
55	Mn	1.53E-01	5.06E-03	8.31E-03			4.79E-03	6.02E-03	
56	Fe	1.32E+02	7.17E-02	6.32E-02	5.11E+00		2.51E-02	1.78E-01	
59	Co	2.26E-03	8.90E-04	9.98E-04			2.75E-03	6.53E-03	
60	Ni	7.95E-03	7.63E-03	2.86E-02			4.96E-03	5.30E-02	
63	Cu	1.51E-02	1.54E-03	3.38E-03			5.62E-03	3.66E-01	
66	Zn	1.02E-02	n.a.	n.a.			3.17E-02	1.12E+00	
71	Ga	8.06E-04	5.90E-04	4.89E-04			6.87E-04		
72	Ge	3.13E-02	2.31E-03	6.99E-04			2.03E-03	3.13E-03	5.05E-02
75	As	1.19E-01	5.83E-03	1.07E-03	7.23E-02		2.73E-01	4.21E-03	
78	Se	6.70E+00	1.51E-01	4.42E-03	2.95E-02		2.21E-02	8.32E-03	
79	Br	n.a.	1.45E+01	7.93E+00	8.44E+00	8.09E+00	1.51E+01	1.19E+01	2.32E+01
81	Br	n.a.	5.79E+00	7.96E+00	8.00E+00	1.07E+01	1.50E+01	1.15E+01	1.41E+01
85	Rb	1.28E-02	1.02E-02	1.25E-02			1.10E-02		
88	Sr	4.18E-03	2.22E-03	2.65E-02			2.27E-02	5.16E-02	6.12E-02
89	Y	1.15E-03	4.80E-04	1.88E-04			6.06E-02	2.82E-04	1.23E-03
90	Zr	5.65E-01	8.19E-01	2.20E-01			1.23E+00	1.27E+00	1.19E+00
93	Nb	7.83E-03	1.35E-02	9.37E-03			1.36E-01	1.26E-02	1.01E-02
95	Mo	1.18E-02	1.12E-02	1.77E-02			4.83E-02	5.04E-02	3.07E-02
101	Ru	2.13E-03	4.58E-03	1.81E-03			6.26E-02	9.99E+02	1.67E+03
105	Pd	6.27E-03	1.00E-02	9.75E-03			1.28E-02	1.67E-02	
107	Ag	1.37E-03	3.81E-03	2.82E-03			6.87E-03		
109	Ag	1.32E-03	3.90E-03	2.80E-03			6.89E-03		
111	Cd	1.10E-03	1.30E-03	2.66E-04			2.52E-04		4.47E-02
115	In	4.30E-03	5.36E-03	2.51E-03	3.95E+03	n.a.	3.97E-03	1.25E+01	
118	Sn	1.35E-02	1.59E-02	1.42E-02		1.00E+00	1.13E-02	3.86E-02	2.53E-01

Table S7 continued.

Mass	Element	Cell gas and analysis mode in Q2							
		No gas as M ⁺	He as M ⁺	H ₂ as M ⁺	H ₂ as MH ⁺	H ₂ as MH ₂ ⁺	O ₂ as M ⁺	O ₂ as MO ⁺	O ₂ as MO ₂ ⁺
121	Sb	6.24E-03	8.30E-03	7.72E-04		n.a.	2.64E-03	3.36E-03	
125	Te	3.28E-03	4.28E-03	8.46E-04			2.13E-03	2.46E-02	
127	I	4.77E-01	3.79E-01	3.34E-01	5.51E-01	2.27E+00	6.15E-01	6.87E-01	1.85E+00
133	Cs	6.49E-04	7.27E-04	1.31E-03			1.37E-03		
137	Ba	5.65E-03	5.43E-03	1.84E-03	1.52E+00	n.a.	4.59E-03	5.12E-02	8.89E-02
139	La	1.73E-04	3.35E-04	4.29E-05			1.22E-01	1.68E-03	3.62E-03
140	Ce	1.05E-04	1.71E-04	8.59E-04			2.04E-01	7.10E-04	3.23E-03
141	Pr	2.00E-04	8.69E-05	4.53E-05			4.06E-01	2.31E-04	6.28E-03
146	Nd	1.26E-03	6.30E-04	1.64E-04			3.32E-01	3.85E-04	4.65E-02
147	Sm	1.80E-03	3.53E-04	1.88E-04			1.09E-01	7.74E-04	5.23E-02
153	Eu	2.09E-04	2.69E-04	1.53E-04			5.64E-04	7.91E-04	8.82E-03
157	Gd	3.24E-04	3.17E-04	1.96E-04			2.94E-03	6.32E-04	2.28E-02
159	Tb	2.23E-04	2.73E-04	3.01E-05			9.18E-03	4.15E-04	5.59E-03
163	Dy	2.02E-04	1.82E-04	1.88E-04			4.26E-02	5.72E-04	1.88E-02
165	Ho	1.57E-04	1.19E-04	7.06E-05			6.38E-02	4.03E-04	4.96E-03
166	Er	2.74E-04	2.99E-04	4.15E-04			1.74E-02	8.18E-04	4.88E-03
169	Tm	1.52E-04	6.62E-05	7.97E-05			1.14E-04	1.94E-04	1.07E-02
172	Yb	2.04E-04	1.63E-04	2.53E-04			2.57E-04	1.33E-03	1.87E-02
175	Lu	2.40E-04	2.50E-04	4.19E-04			1.28E-03	8.88E-04	6.85E-03
178	Hf	1.70E-01	2.86E-01	1.66E-01			4.84E-01	3.84E-01	3.98E-01
181	Ta	1.09E-01	1.24E-01	2.10E-01			3.10E-03	1.34E-01	2.37E-01
182	W	5.52E-01	8.20E-01	4.18E-01			9.83E-03	1.07E+00	1.05E+00
193	Ir	6.34E-03	9.72E-03	6.87E-03			1.27E-02	1.29E-02	1.59E-02
195	Pt	4.08E-03	3.37E-03	4.84E-03			5.68E-02	4.60E-02	
197	Au	7.73E-03	6.04E-03	1.50E-03			9.01E-02	1.31E-01	
201	Hg	4.70E-02	5.54E-02	2.42E-02			7.62E-02	2.17E+00	
202	Hg	5.05E-02	5.24E-02	2.42E-02			7.68E-02	1.05E+00	
205	Tl	5.66E+00	6.12E+00	1.07E+01			3.87E+00		
208	Pb	6.94E-04	2.07E-04	2.73E-04			1.14E-03	2.87E-02	
209	Bi	1.19E-02	1.70E-02	4.45E-03			1.51E-02	2.36E-02	
232	Th	6.81E-04	9.87E-04	2.38E-03			1.74E+00	5.21E-03	4.69E-03
238	U	9.71E-04	1.31E-03	3.24E-03			1.90E+00	2.52E-02	2.84E-03

n.a.: not available

3. Spectroscopic Interferences

The following tables show the method development results of the interference elimination tests for the different analysis modes. Potential spectroscopic interferences were based on the Agilent MassHunter Software (MassHunter 4.5, Workingstation, Version C01.05) and on existing literature (May and Wiedmeyer, 1998; Sugiyama and Shikamori, 2015; Machado et al., 2017; Flores et al., 2020).

The chosen concentrations for Si of 0.1 µg/l and 1.0 µg/l were below LOQ in the measurements. Therefore, these measurements could not be evaluated for interference elimination. The analyses of “worst-case” matrices were not the only criteria within the method development. The further quality controls using reference materials, calibration check solutions, and spiked samples also lead to the conclusion that for the underlying matrix (river water samples), a simultaneous quantification of all 68 elements of the final method is achievable in at least one analysis mode.

Table S8A: Simulation of spectroscopic interferences (doubly charged, polyatomic) of selected analytes. In total, 40 different standard compositions were measured. Each table contains information about 5 standards. STD X.1 (X:1-8) and STD X.2 contain only the analytes, whereas STD X.3 and X.4 contain analytes and possibly interfering elements. STD X.5 contains only the possibly interfering elements. The accepted range of 80 to 120 % is highlighted as bold.

	Element Isotope	Analytes						
		Rb 85	Y 89	Zr 90	Cs 133	Ba 137	Nd 146	Sm 147
Nominal analyte concentrations in the interference check solutions (µg/l)	STD 1.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 1.2	1	1	1	1	1	1	1
	STD 1.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 1.4	1	1	1	1	1	1	1
	STD 1.5	-	-	-	-	-	-	-
Examples of potentially occurring polyatomic and doubly charged interferences		$^{84}\text{Sr}^{16}\text{O}^+$, $^{69}\text{Ga}^{16}\text{O}^+$, $^{170}\text{Er}^{++}$, $^{178}\text{Hf}^{++}$, $^{49}\text{Ti}^{40}\text{Ar}^+$, $^{180}\text{Hf}^{++}$, $^{117}\text{Sn}^{16}\text{O}^+$, $^{101}\text{Ru}^{16}\text{O}_2^+$, $^{120}\text{Sn}^{16}\text{O}^{16}\text{H}^+$, $^{98}\text{Ru}^{16}\text{O}_3^+$, $^{98}\text{Ru}^{16}\text{O}_3^+$						
		Recovery in %						
No gas as M ⁺	STD 1.1	113	96	29	100	112	110	109
	STD 1.2	111	97	53	99	111	110	110
	STD 1.3	119	101	250	101	115	110	106
	STD 1.4	110	98	109	101	109	110	109
	STD 1.5	-	-	-	-	-	-	-
He as M ⁺	STD 1.1	106	103	44	106	114	101	99
	STD 1.2	108	100	61	105	107	105	105
	STD 1.3	208	106	262	107	116	103	107
	STD 1.4	119	102	104	108	110	107	107
	STD 1.5	-	-	-	-	-	-	-

Table S8A continued.

H ₂ as M ⁺	STD 1.1	106	102	32	106	114	107	108
	STD 1.2	105	98	60	106	107	106	108
	STD 1.3	108	102	291	106	116	107	105
	STD 1.4	106	101	110	107	110	109	110
	STD 1.5	-	-	-	-	-	-	-
O ₂ as M ⁺	STD 1.1	103	75	41	107	98	0	109
	STD 1.2	101	108	56	104	98	31	90
	STD 1.3	108	96	555	105	103	111	136
	STD 1.4	100	89	100	103	98	30	94
	STD 1.5	-	-	-	-	-	-	-
O ₂ as MO ⁺	STD 1.1	x ¹	105	18	x ¹	135	102	101
	STD 1.2	x ¹	110	42	x ¹	110	110	109
	STD 1.3	x ¹	120	382	x ¹	112	114	114
	STD 1.4	x ¹	112	108	x ¹	108	112	111
	STD 1.5	-	-	-	-	-	-	-
O ₂ as MO ₂ ⁺	STD 1.1	x ¹	111	16	x ¹	107	125	121
	STD 1.2	x ¹	106	40	x ¹	109	110	121
	STD 1.3	x ¹	107	361	x ¹	185	143	128
	STD 1.4	x ¹	107	102	x ¹	113	109	122
	STD 1.5	-	-	-	-	-	-	-

x¹: Analytical mode not considered for this element

Table S8B: see Table S8A.

		Analytes										
	Element	Al	Ga	Ge	As	Se	Sr	Y	Mo	Sb	Te	Bi
	Isotope	27	71	72	75	78	88	89	95	121	125	209
Nominal analyte concentrations in the interference check solutions (µg/l)	STD 2.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 2.2	1	1	1	1	1	1	1	1	1	1	1
	STD 2.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 2.4	1	1	1	1	1	1	1	1	1	1	1
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-
Examples of potentially occurring polyatomic and doubly charged interferences		$^{12}\text{C}^{15}\text{N}^+$, $^{13}\text{C}^{14}\text{N}^+$, $^{12}\text{C}^{14}\text{N}^1\text{H}^+$	$^{36}\text{S}^{17}\text{O}^{18}\text{O}^+$, $^{38}\text{Ar}^{33}\text{S}^+$, $^{35}\text{Cl}^{18}\text{O}_2^+$, $^{37}\text{Cl}^{17}\text{O}^{18}\text{O}^+$, $^{37}\text{Cl}^{17}\text{O}_2^+$, $^{36}\text{Ar}^{35}\text{Cl}^+$	$^{36}\text{S}^{18}\text{O}_2^+$, $^{37}\text{Cl}^{17}\text{O}^{18}\text{O}^+$, $^{35}\text{Cl}^{37}\text{Cl}^+$, $^{36}\text{Ar}_2^+$, $^{40}\text{Ar}^{32}\text{S}^+$, $^{40}\text{Ar}^{16}\text{O}_2^+$, $^{56}\text{Fe}^{16}\text{O}^+$	$^{40}\text{Ar}^{35}\text{Cl}^+$, $^{38}\text{Ar}^{37}\text{Cl}^+$, $^{39}\text{Ar}^{36}\text{S}^+$, $^{12}\text{C}^{31}\text{P}^{16}\text{O}_2^+$, $^{36}\text{Ar}^{39}\text{K}^+$, $^{59}\text{Co}^{16}\text{O}^+$, $^{150}\text{Nd}^{++}$, $^{150}\text{Sm}^{++}$	$^{35}\text{Cl}^{37}\text{Cl}^{16}\text{O}^+$, $^{41}\text{K}^{37}\text{Cl}^+$, $^{39}\text{K}^{39}\text{K}^+$	$^{176}\text{Lu}^{++}$, $^{176}\text{Hf}^{++}$	$^{178}\text{Hf}^{++}$	$^{40}\text{Ar}^{39}\text{K}^{16}\text{O}^+$, $^{79}\text{Br}^{16}\text{O}^+$	$^{105}\text{Pd}^{16}\text{O}^+$	-	$^{193}\text{Ir}^{16}\text{O}^+$
		Recovery in %										
No gas as M ⁺	STD 2.1	102	106	104	120	1192	91	95	92	101	84	105
	STD 2.2	119	104	100	114	192	107	95	95	100	100	105
	STD 2.3	252	191	246	228	1505	96	100	109	118	125	106
	STD 2.4	112	113	115	120	249	104	98	98	107	103	106
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-
He as M ⁺	STD 2.1	196	92	94	104	119	93	101	103	108	91	97
	STD 2.2	101	96	91	107	80	104	99	101	109	100	98
	STD 2.3	212	649	619	617	4255	102	107	112	116	108	106
	STD 2.4	101	144	136	148	499	94	98	98	104	105	105
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-

Table S8B continued.

H ₂ as M ⁺	STD 2.1	130	106	94	106	103	97	98	101	99	105	53
	STD 2.2	107	101	95	100	107	101	98	100	97	109	51
	STD 2.3	198	142	175	474	174	100	97	114	111	114	53
	STD 2.4	103	101	100	127	109	100	97	101	100	110	52
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-
H ₂ as MH ⁺	STD 2.1	x1	x1	x1	137	43	x1	x1	x1	x1	x1	x1
	STD 2.2	x1	x1	x1	84	106	x1	x1	x1	x1	x1	x1
	STD 2.3	x1	x1	x1	91	51	x1	x1	x1	x1	x1	x1
	STD 2.4	x1	x1	x1	50	120	x1	x1	x1	x1	x1	x1
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-
O ₂ as M ⁺	STD 2.1	90	99	93	152	87	83	109	86	94	98	92
	STD 2.2	104	100	93	91	92	94	101	98	93	101	93
	STD 2.3	264	131	189	6664	287	91	141	151	110	107	99
	STD 2.4	110	102	102	730	115	93	89	103	97	101	93
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-
O ₂ as MO ⁺	STD 2.1	133	x1	88	105	86	97	109	81	109	83	108
	STD 2.2	118	x1	82	96	88	107	99	98	94	90	102
	STD 2.3	204	x1	103	95	95	108	101	128	106	132	129
	STD 2.4	106	x1	83	100	89	96	104	95	101	90	110
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-
O ₂ as MO ₂ ⁺	STD 2.1	x ¹	x ¹	95	x ¹	x ¹	130	103	103	x ¹	x ¹	x ¹
	STD 2.2	x ¹	x ¹	77	x ¹	x ¹	131	93	101	x ¹	x ¹	x ¹
	STD 2.3	x ¹	x ¹	76	x ¹	x ¹	125	107	112	x ¹	x ¹	x ¹
	STD 2.4	x ¹	x ¹	84	x ¹	x ¹	125	104	98	x ¹	x ¹	x ¹
	STD 2.5	-	-	-	-	-	-	-	-	-	-	-

x¹: Analytical mode not considered for this element

Table S8C: see Table S8A.

		Analytes							
		Y 89	Pd 105	Cd 111	W 182	Au 197	Gd 157	Tm 169	Lu 175
Nominal analyte concentrations in the interference check solutions (µg/l)	STD 3.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 3.2	1	1	1	1	1	1	1	1
	STD 3.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 3.4	1	1	1	1	1	1	1	1
	STD 3.5	-	-	-	-	-	-	-	-
Examples of potentially occurring polyatomic and doubly charged interferences		$^{178}\text{Hf}^{++}$	$^{40}\text{Ar}^{65}\text{Cu}^{+}$	$^{95}\text{Mo}^{16}\text{O}^{+}$, $^{39}\text{K}_2^{16}\text{O}_2^{1}\text{H}^{+}$, $^{94}\text{Zr}^{16}\text{O}^{1}\text{H}^{+}$	$^{166}\text{Er}^{16}\text{O}^{+}$	$^{181}\text{Ta}^{16}\text{O}^{+}$	$^{138}\text{Ba}^{19}\text{F}^{+}$	$^{153}\text{Eu}^{16}\text{O}^{+}$	$^{159}\text{Tb}^{16}\text{O}^{+}$
		Recovery in %							
No gas as M ⁺	STD 3.1	98	96	111	125	57	100	101	92
	STD 3.2	96	100	108	121	43	96	97	91
	STD 3.3	111	109	120	212	120	99	102	149
	STD 3.4	98	103	108	131	115	96	98	96
	STD 3.5	-	-	-	-	-	-	-	-
He as M ⁺	STD 3.1	101	96	100	143	52	108	109	107
	STD 3.2	97	97	103	131	40	105	107	104
	STD 3.3	112	103	105	182	99	104	108	151
	STD 3.4	102	102	103	139	107	102	103	107
	STD 3.5	-	-	-	-	-	-	-	-
H ₂ as M ⁺	STD 3.1	97	103	94	152	68	99	106	105
	STD 3.2	94	100	93	142	45	96	101	101
	STD 3.3	110	111	98	240	182	97	103	136
	STD 3.4	98	102	95	148	120	98	103	105
	STD 3.5	-	-	-	-	-	-	-	-

Table S8C continued.

O ₂ as M ⁺	STD 3.1	125	99	95	1	55	0	84	16
	STD 3.2	100	97	96	2	31	1	84	18
	STD 3.3	137	99	98	10932	107	2	105	7618
	STD 3.4	105	98	100	1141	95	1	90	800
	STD 3.5	-	-	-	-	-	-	-	-
O ₂ as MO ⁺	STD 3.1	105	60	14	209	50	89	103	99
	STD 3.2	104	73	11	174	25	89	99	96
	STD 3.3	115	42	1156	373	2735	94	98	95
	STD 3.4	107	82	139	193	363	91	100	97
	STD 3.5	-	-	-	-	-	-	-	-
O ₂ as MO ₂ ⁺	STD 3.1	104	x ¹	x ¹	211	x ¹	101	108	92
	STD 3.2	104	x ¹	x ¹	177	x ¹	91	105	98
	STD 3.3	117	x ¹	x ¹	214	x ¹	127	106	91
	STD 3.4	101	x ¹	x ¹	184	x ¹	92	112	105
	STD 3.5	-	-	-	-	-	-	-	-

x¹: Analytical mode not considered for this element

Table S8D: see Table S8A.

		Analytes						
		Si	Cd	Tb*	Dy*	Ho*	Er*	Yb
	Isotope	28	111	159	163	165	166	172
Nominal analyte concentrations in the interference check solutions (µg/l)	STD 4.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 4.2	1	1	1	1	1	1	1
	STD 4.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 4.4	1	1	1	1	1	1	1
	STD 4.5	-	-	-	-	-	-	-
Examples of potentially occurring polyatomic and doubly charged interferences		$^{12}\text{C}^{16}\text{O}^+$	$^{39}\text{K}_2^{16}\text{O}_2^1\text{H}^+$, $^{94}\text{Zr}^{16}\text{O}^1\text{H}^+$, $^{95}\text{Mo}^{16}\text{O}^+$	$^{143}\text{Nd}^{16}\text{O}^+$	$^{147}\text{Sm}^{16}\text{O}^+$	$^{149}\text{Sm}^{16}\text{O}^+$	$^{150}\text{Nd}^{16}\text{O}^+$, $^{150}\text{Sm}^{16}\text{O}^+$	$^{156}\text{Gd}^{16}\text{O}^+$
		Recovery in %						
No gas as M^+	STD 4.1	n.a.	118	105	103	103	108	106
	STD 4.2	n.a.	116	107	105	105	110	107
	STD 4.3	n.a.	235	123	120	112	140	155
	STD 4.4	n.a.	129	109	106	106	113	111
	STD 4.5	-	-	-	-	-	-	-
He as M^+	STD 4.1	n.a.	106	103	103	105	106	100
	STD 4.2	n.a.	106	101	102	105	104	99
	STD 4.3	n.a.	141	109	108	114	118	119
	STD 4.4	n.a.	112	103	101	109	108	104
	STD 4.5	-	-	-	-	-	-	-
H_2 as M^+	STD 4.1	n.a.	104	104	104	105	105	111
	STD 4.2	n.a.	97	103	103	104	105	106
	STD 4.3	n.a.	115	116	117	110	124	138
	STD 4.4	n.a.	100	106	104	107	108	111
	STD 4.5	-	-	-	-	-	-	-

Table S8D continued.

O ₂ as M ⁺	STD 4.1	n.a.	98	11	35	72	15	93
	STD 4.2	n.a.	100	16	26	72	16	92
	STD 4.3	n.a.	102	8049	6648	3277	8140	138
	STD 4.4	n.a.	100	832	737	347	793	95
	STD 4.5	-	-	-	-	-	-	-
O ₂ as MO ⁺	STD 4.1	n.a.	0	96	109	103	108	116
	STD 4.2	n.a.	4	89	91	89	93	94
	STD 4.3	n.a.	11293	176	181	175	184	192
	STD 4.4	n.a.	868	85	111	108	113	117
	STD 4.5	-	-	-	-	-	-	-
O ₂ as MO ₂ ⁺	STD 4.1	n.a.	x ¹	102	138	96	115	133
	STD 4.2	n.a.	x ¹	96	99	96	100	86
	STD 4.3	n.a.	x ¹	219	552	235	212	488
	STD 4.4	n.a.	x ¹	125	168	119	121	154
	STD 4.5	-	-	-	-	-	-	-

x¹: Analytical mode not considered for this element

n.a.: not applicable

*In subsequent measurements (n=3), the mode O₂ as MO⁺ showed superior results with recoveries ranging from 95 to 108 % (Tb), 100 to 115 % (Dy), 94 to 107 % (Ho) and 90 to 104 % (Er).

Table S8E: see Table S8A.

		Analytes											
	Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se
	Isotope	45	47	51	52	55	56	59	60	63	66	75	78
Nominal analyte concentrations in the interference check solutions (µg/l)	STD 5.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 5.2	1	1	1	1	1	1	1	1	1	1	1	1
	STD 5.3	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	STD 5.4	1	1	1	1	1	1	1	1	1	1	1	1
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-
Examples of potentially occurring polyatomic and doubly charged interferences		$^{28}\text{Si}^{16}\text{O}^+\text{H}$, $^{12}\text{C}^{35}\text{Cl}^+$, $^{38}\text{Ar}^{13}\text{C}^+$, $^{40}\text{Ar}^{12}\text{C}^+$, $^{23}\text{Na}^{32}\text{S}^+$, $^{36}\text{Ar}^{23}\text{Na}^+$, $^{23}\text{Na}^{37}\text{Cl}^+$, $^{40}\text{Ar}^{23}\text{Na}^+$, $^{34}\text{S}^{16}\text{O}_2^+$, $^{40}\text{Ar}^{35}\text{Cl}^+$, $^{35}\text{Cl}^{37}\text{Cl}^{16}\text{O}^+$ $^{29}\text{Si}^{16}\text{O}^+$, $^{30}\text{Si}^{16}\text{O}^+\text{H}^+$, $^{34}\text{S}^{16}\text{O}^+\text{H}^+$, $^{34}\text{S}^{18}\text{O}^+$, $^{36}\text{S}^{16}\text{O}^+$, $^{37}\text{Cl}^{17}\text{O}^+\text{H}$, $^{24}\text{Mg}^{35}\text{Cl}^+$, $^{44}\text{Ca}^{16}\text{O}^+$, $^{36}\text{Ar}^{12}\text{C}^{14}\text{N}^+\text{H}$, $^{33}\text{S}^{16}\text{O}_2^+\text{H}^+$, $^{38}\text{Ar}^{37}\text{Cl}^+$, $^{39}\text{Ar}^{36}\text{S}^+$, $^{35}\text{Cl}^{37}\text{Cl}^{16}\text{O}^+$ $^{13}\text{C}^{16}\text{O}_2^+$, $^{31}\text{P}^{16}\text{O}^+$, $^{33}\text{S}^{18}\text{O}^+$, $^{35}\text{Cl}^{16}\text{O}^+$, $^{37}\text{Cl}^{17}\text{O}^+$, $^{43}\text{Ca}^{16}\text{O}^+$, $^{43}\text{Ca}^{16}\text{O}^+\text{H}$, $^{14}\text{N}^{12}\text{C}^{37}\text{Cl}^+$, $^{33}\text{S}^{16}\text{O}^{17}\text{O}^+$, $^{23}\text{Na}^{12}\text{C}^{40}\text{Ar}$, $^{32}\text{S}^{14}\text{N}^+\text{H}^+$, $^{32}\text{S}^{15}\text{N}^+$, $^{35}\text{Cl}^{16}\text{O}^+$, $^{37}\text{Cl}^{15}\text{N}^+$, $^{39}\text{K}^{16}\text{O}^+$, $^{32}\text{S}^{34}\text{S}^+$, $^{33}\text{S}_2^+$, $^{36}\text{Ar}^{39}\text{K}^+$, $^{43}\text{Ca}^{16}\text{O}_2^+$, $^{41}\text{K}^{37}\text{Cl}^+$, $^{39}\text{K}^{39}\text{K}^+$											
		Recovery in %											
No gas as M ⁺	STD 5.1	27	91	112	193	146	36178	108	109	102	39	114	1505
	STD 5.2	30	90	102	118	109	4828	104	107	108	106	112	218
	STD 5.3	84	4707	168	134	147	8871	107	140	402	619	127	1383
	STD 5.4	37	569	107	105	109	444	102	107	136	150	103	239
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-
He as M ⁺	STD 5.1	87	100	95	101	108	134	105	103	104	357	102	107
	STD 5.2	91	101	99	96	105	118	105	103	110	100	102	81
	STD 5.3	91	247	103	97	105	142	99	105	100	717	96	112
	STD 5.4	87	92	96	96	98	109	97	99	99	170	99	91
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-

Table S8E continued.

H ₂ as M ⁺	STD 5.1	72	102	112	107	107	103	107	131	90	35	121	116
	STD 5.2	74	96	98	104	103	102	104	102	105	104	112	115
	STD 5.3	82	2044	158	104	122	181	100	111	119	564	102	110
	STD 5.4	74	299	104	101	102	108	104	96	97	141	100	104
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-
H ₂ as MH ⁺	STD 5.1	11	944	0	105	x ¹	632	x ¹	x ¹	x ¹	x ¹	46	125
	STD 5.2	9	94	364	105	x ¹	624	x ¹	x ¹	x ¹	x ¹	86	106
	STD 5.3	78	10643	9789	109	x ¹	36905	x ¹	x ¹	x ¹	x ¹	95	154
	STD 5.4	20	1035	782	106	x ¹	3471	x ¹	x ¹	x ¹	x ¹	117	86
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-
O ₂ as M ⁺	STD 5.1	0	0	399	93	107	105	103	101	57	0	131	99
	STD 5.2	0	0	138	97	102	99	101	103	97	100	91	95
	STD 5.3	72	61703	3037	105	114	299	103	113	61	572	135	100
	STD 5.4	8	7089	526	96	103	120	97	98	91	131	93	94
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-
O ₂ as MO ⁺	STD 5.1	52	88	87	84	95	106	99	96	172	76	104	92
	STD 5.2	72	88	92	107	97	95	100	100	101	42	100	87
	STD 5.3	100	112	92	99	90	361	112	246	163	486	98	86
	STD 5.4	85	95	95	96	96	125	95	103	99	69	99	85
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-
O ₂ as MO ₂ ⁺	STD 5.1	50	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹
	STD 5.2	80	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹
	STD 5.3	110	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹
	STD 5.4	94	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹	x ¹
	STD 5.5	-	-	-	-	-	-	-	-	-	-	-	-

x¹: Analytical mode not considered for this element

Table S8F: see Table S8A.

		Analytes									
	Element Isotope	Zr 90	Ru 101	Ir 193	Pt 195	Au 197		Sn 118	Sb 121		Na 23
Nominal analyte concentrations in the interference check solutions (µg/l)	STD 6.1	0.1	0.1	0.1	0.1	0.1	STD 7.1	0.1	0.1	STD 8.1	25
	STD 6.2	1	1	1	1	1	STD 7.2	1	1	STD 8.2	250
	STD 6.3	0.1	0.1	0.1	0.1	0.1	STD 7.3	0.1	0.1	STD 8.3	25
	STD 6.4	1	1	1	1	1	STD 7.4	1	1	STD 8.4	250
	STD 6.5	-	-	-	-	-	STD 7.5	-	-	STD 8.5	-
Examples of potentially occurring polyatomic and doubly charged interferences		¹⁸⁰ Hf ⁺⁺ , ⁵⁵ Mn ³⁵ Cl ⁺	²⁰² Hg ⁺⁺ , ⁶¹ Ni ⁴⁰ Ar ⁺ , ⁶⁴ Ni ³⁷ Cl ⁺ , ⁶⁶ Zn ³⁵ Cl ⁺ , ⁸⁵ Rb ¹⁶ O ⁺	¹⁵³ Eu ⁴⁰ Ar ⁺ , ¹⁵⁸ Gd ³⁵ Cl ⁺ , ¹⁷⁵ Lu ¹⁸ O ⁺ , ¹⁷⁷ Hf ¹⁶ O ⁺	¹⁷⁹ Hf ¹⁶ O ⁺	¹⁶² Dy ³⁵ Cl ⁺ , ¹⁸¹ Ta ¹⁶ O ⁺		¹⁰² Pd ¹⁶ O ⁺ , ¹⁰² Ru ¹⁶ O ⁺	¹⁰⁵ Pd ¹⁶ O ⁺		⁴⁶ Ca ⁺⁺ , ⁴⁶ Ti ⁺⁺
		Recovery in %						Recovery in %			Recovery in %
No gas as M ⁺	STD 6.1	67	90	101	102	79	STD 7.1	103	99	STD 8.1	170
	STD 6.2	64	97	99	100	101	STD 7.2	98	93	STD 8.2	125
	STD 6.3	219	91	120	166	288	STD 7.3	106	104	STD 8.3	200
	STD 6.4	98	97	102	107	118	STD 7.4	102	98	STD 8.4	133
	STD 6.5	-	-	-	-	-	STD 7.5	-	-	STD 8.5	-
He as M ⁺	STD 6.1	46	87	101	99	68	STD 7.1	109	95	STD 8.1	135
	STD 6.2	33	97	98	97	90	STD 7.2	105	94	STD 8.2	104
	STD 6.3	630	91	103	121	142	STD 7.3	116	110	STD 8.3	163
	STD 6.4	111	97	99	99	97	STD 7.4	108	97	STD 8.4	109
	STD 6.5	-	-	-	-	-	STD 7.5	-	-	STD 8.5	-
H ₂ as M ⁺	STD 6.1	46	96	111	111	83	STD 7.1	93	91	STD 8.1	139
	STD 6.2	39	98	106	108	105	STD 7.2	88	95	STD 8.2	117
	STD 6.3	480	98	122	314	1009	STD 7.3	95	103	STD 8.3	167
	STD 6.4	100	98	106	129	197	STD 7.4	92	99	STD 8.4	118
	STD 6.5	-	-	-	-	-	STD 7.5	-	-	STD 8.5	-

Table S8F continued.

O ₂ as M ⁺	STD 6.1	131	88	107	110	71	STD 7.1	101	94	STD 8.1	133
	STD 6.2	27	98	106	108	97	STD 7.2	98	94	STD 8.2	103
	STD 6.3	892	89	114	137	49	STD 7.3	106	105	STD 8.3	162
	STD 6.4	122	98	105	109	92	STD 7.4	101	98	STD 8.4	109
	STD 6.5	-	-	-	-	-	STD 7.5	-	-	STD 8.5	-
O ₂ as MO ⁺	STD 6.1	37	87	105	103	649	STD 7.1	119	99	STD 8.1	x ¹
	STD 6.2	23	95	108	101	128	STD 7.2	105	99	STD 8.2	x ¹
	STD 6.3	636	91	153	769	128050	STD 7.3	119	95	STD 8.3	x ¹
	STD 6.4	99	94	106	180	14235	STD 7.4	110	98	STD 8.4	x ¹
	STD 6.5	-	-	-	-	-	STD 7.5	-	-	STD 8.5	-

x¹: Analytical mode not considered for this element

Table S9: The composition of each standard regarding the interfering elements is presented in the following. STD X.1 (X:1-8) and STD X.2 contain only the analytes, whereas STD X.3 and X.4 contain analytes and possibly interfering elements. STD X.5 contains only the possibly interfering elements.

		C	Si	Ca	Er	Ru	Al	Sr	Lu	Hf	Ti	Ga	Sn
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 1.1	-	-	-	-	-	-	-	-	-	-	-	-
	STD 1.2	-	-	-	-	-	-	-	-	-	-	-	-
	STD 1.3	10000	10	2000	10	10	10	10	10	10	10	10	10
	STD 1.4	10000	10	2000	10	10	10	10	10	10	10	10	10
	STD 1.5	10000	10	2000	10	10	10	10	10	10	10	10	10

		C	P	S	Cl	K	Fe	Si	Co	Er	Nd	Sm	Pd	Mg	Dy	Gd	Ce	Pt	Ir	Ni	Cu	Hf	Zr	Nb	Br	Pb	Lu
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 2.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	STD 2.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	STD 2.3	10000	5000	5000	1000	100	100	1000	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	STD 2.4	10000	5000	5000	1000	100	100	1000	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	STD 2.5	10000	5000	5000	1000	100	100	1000	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10

		Cl	K	Ni	Cu	Er	Hf	Zr	Nb	Br	Pb	Mo	Ho	Ta	Ba	B	F	Eu	Tb	Mg
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 3.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	STD 3.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	STD 3.3	5000	100	100	100	10	10	10	10	10	10	10	10	10	10	10	10	10	10	1000
	STD 3.4	5000	100	100	100	10	10	10	10	10	10	10	10	10	10	10	10	10	10	1000
	STD 3.5	5000	100	100	100	10	10	10	10	10	10	10	10	10	10	10	10	10	10	1000

		C	S	K	Nd	Sm	Gd	Hf	Mg	Zr	Mo
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 4.1	-	-	-	-	-	-	-	-	-	-
	STD 4.2	-	-	-	-	-	-	-	-	-	-
	STD 4.3	10000	5000	100	10	10	10	10	2000	10	100
	STD 4.4	10000	5000	100	10	10	10	10	2000	10	100
	STD 4.5	10000	5000	100	10	10	10	10	2000	10	100

Table S9 continued.

		C	Na	Mg	Si	P	S	Cl	Ca	K	Ba			
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 5.1	-	-	-	-	-	-	-	-	-	-			
	STD 5.2	-	-	-	-	-	-	-	-	-	-			
	STD 5.3	5000	10000	1000	100	5000	5000	5000	2000	2000	10			
	STD 5.4	5000	10000	1000	100	5000	5000	5000	2000	2000	10			
	STD 5.5	5000	10000	1000	100	5000	5000	5000	2000	2000	10			
		Hf	Mn	Y	Eu	Gd	Lu	Mo	Hg	Zn	Rb	Ni	Dy	Ta
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 6.1	-	-	-	-	-	-	-	-	-	-	-	-	-
	STD 6.2	-	-	-	-	-	-	-	-	-	-	-	-	-
	STD 6.3	10	10	10	10	10	10	10	10	10	10	10	10	10
	STD 6.4	10	10	10	10	10	10	10	10	10	10	10	10	10
	STD 6.5	10	10	10	10	10	10	10	10	10	10	10	10	10
		Co	Ni	Ru	Pd	Sr	Ag	Y	Ba	Pr	Dy			
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 7.1	-	-	-	-	-	-	-	-	-	-			
	STD 7.2	-	-	-	-	-	-	-	-	-	-			
	STD 7.3	10	10	10	10	10	10	10	10	10	10			
	STD 7.4	10	10	10	10	10	10	10	10	10	10			
	STD 7.5	10	10	10	10	10	10	10	10	10	10			
		Ca	Ti											
Nominal concentrations of interfering elements in the interference check solutions (µg/l)	STD 8.1	-	-											
	STD 8.2	-	-											
	STD 8.3	10000	10											
	STD 8.4	10000	10											
	STD 8.5	10000	10											

4. Rinsing procedure

As one example, Figure S2 shows the rinsing procedure results for Boron regarding the importance of different rinsing solutions and of the rinsing times. Overall, the rising time is very important but also a sensitive parameter with respect to economic considerations (prolonging the measuring time).

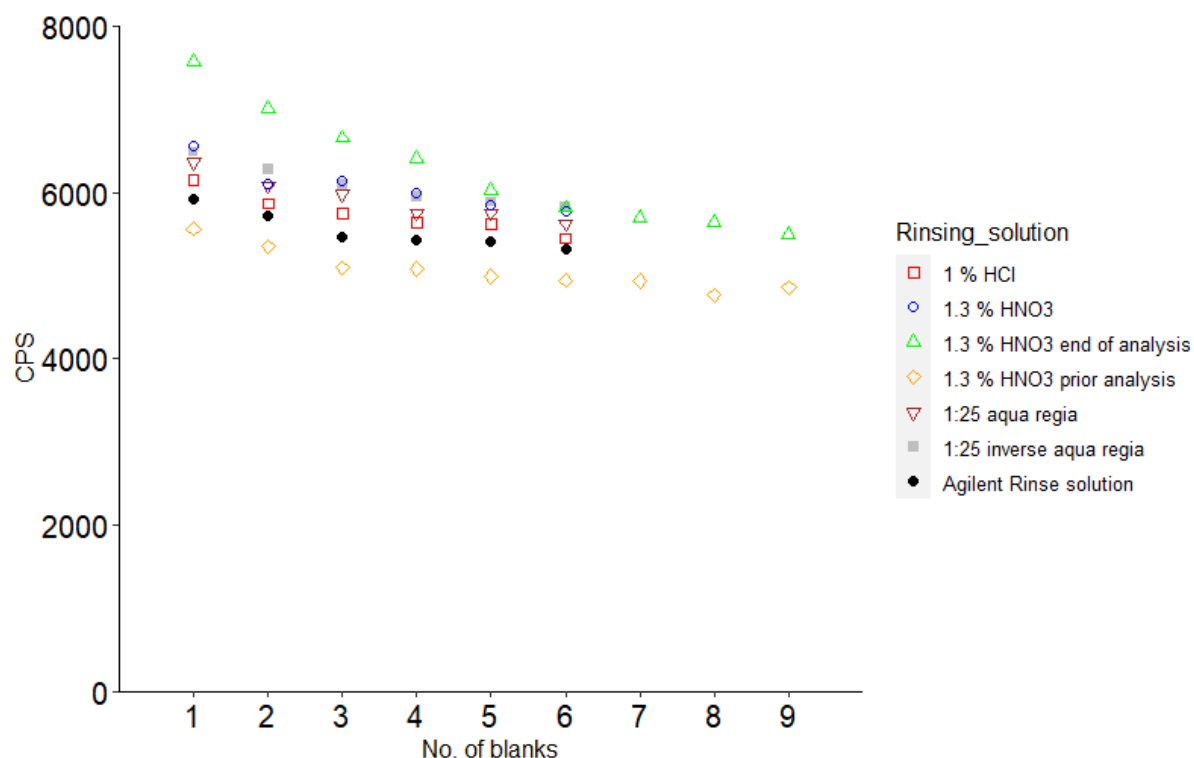


Figure S1: Counts per seconds (CPS) detected on mass to charge ratio (m/z) 11 in on-mass mode with O₂ in a blank series (1.3% HNO₃) after measuring three solutions of 5 µg/l of boron in a row. The blank series consist of six blanks. Nine blanks were measured before and after the whole measurement run. The sample loop was rinsed with different rinsing solutions: 1% HCl, 1.3% HNO₃, aqua regia (1HNO₃:3HCl) and inverse aqua regia (3HNO₃:1HCl) as well as a so-called “Agilent rinse solution” according to Fryer and Woods (2008). The “Agilent Rinse solution” contains EDTA, Triton X-100, NH₃ and H₂O₂ and is diluted with ultrapure water.

5. Method validation

Table S10: Calibration ranges of all elements considered in method validation. As described in section 2.5 of the manuscript, three calibration series were applied: i) HNO₃ stabilised elements, ii) HCl stabilised elements and iii) non-metals.

Cali- bration series	Concentration of the calibration solutions in µg/l												
	Mass	Element	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	Stock
i	7	Li	0.01	0.02	0.1	0.2	1	2	10	20	100	200	2000
i	9	Be	0.001	0.002	0.01	0.02	0.1	0.2	1	2	10	20	200
i	11	B	0.025	0.05	0.25	0.5	2.5	5	25	50	250	500	5000
i	23	Na	10	20	100	200	1000	2000	10000	20000	100000	200000	400000
i	24	Mg	2.5	5	25	50	250	500	2500	5000	25000	50000	100000
i	27	Al	0.015	0.03	0.15	0.3	1.5	3	15	30	150	300	3000
i	28	Si	0.5	1	5	10	50	100	500	1000	5000	10000	100000
i	39	K	5	10	50	100	500	1000	5000	10000	50000	100000	200000
i	43	Ca	10	20	100	200	1000	2000	10000	20000	100000	200000	400000
i	45	Sc	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	47	Ti	0.001	0.002	0.01	0.02	0.1	0.2	1	2	10	20	200
i	51	V	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	52	Cr	0.0025	0.005	0.025	0.05	0.25	0.5	2.5	5	25	50	500
i	55	Mn	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	56	Fe	0.025	0.05	0.25	0.5	2.5	5	25	50	250	500	5000
i	59	Co	0.00125	0.0025	0.0125	0.025	0.125	0.25	1.25	2.5	12.5	25	250
i	60	Ni	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	63	Cu	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	66	Zn	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	71	Ga	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	72	Ge	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	75	As	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	78	Se	0.0025	0.005	0.025	0.05	0.25	0.5	2.5	5	25	50	500
i	85	Rb	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	88	Sr	0.25	0.5	2.5	5	25	50	250	500	2500	5000	50000
i	89	Y	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	93	Nb	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	95	Mo	0.005	0.01	0.05	0.1	0.5	1	5	10	50	100	1000
i	105	Pd	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	107	Ag	0.00075	0.0015	0.0075	0.015	0.075	0.15	0.75	1.5	7.5	15	150
i	111	Cd	0.001	0.002	0.01	0.02	0.1	0.2	1	2	10	20	200
i	115	In	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	125	Te	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	133	Cs	0.0025	0.005	0.025	0.05	0.25	0.5	2.5	5	25	50	500
i	137	Ba	0.015	0.03	0.15	0.3	1.5	3	15	30	150	300	3000
i	139	La	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	140	Ce	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	141	Pr	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	146	Nd	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	147	Sm	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	153	Eu	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	157	Gd	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100

Table S10 continued.

Cali- bration series	Mass	Element	Concentration of the calibration solutions in µg/l										Stock
			No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8	No. 9	No. 10	
i	159	Tb	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	163	Dy	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	165	Ho	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	166	Er	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	169	Tm	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	172	Yb	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	175	Lu	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	181	Ta	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	182	W	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	205	Tl	0.025	0.05	0.25	0.5	2.5	5	25	50	250	500	5000
i	208	Pb	0.0015	0.003	0.015	0.03	0.15	0.3	1.5	3	15	30	300
i	209	Bi	0.00075	0.0015	0.0075	0.015	0.075	0.15	0.75	1.5	7.5	15	150
i	232	Th	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
i	238	U	0.0015	0.003	0.015	0.03	0.15	0.3	1.5	3	15	30	300
ii	90	Zr	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
ii	101	Ru	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
ii	118	Sn	0.001	0.002	0.01	0.02	0.1	0.2	1	2	10	20	200
ii	121	Sb	0.001	0.002	0.01	0.02	0.1	0.2	1	2	10	20	200
ii	178	Hf	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
ii	193	Ir	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
ii	195	Pt	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
ii	197	Au	0.0005	0.001	0.005	0.01	0.05	0.1	0.5	1	5	10	100
ii	202	Hg	0.001	0.002	0.01	0.02	0.1	0.2	1	2	10	20	200
iii	12	C	5	10	50	100	500	1000	5000	10000	50000	100000	200000
iii	31	P	0.05	0.1	0.5	1	5	10	50	100	500	1000	2000
iii	32	S	5	10	50	100	500	1000	5000	10000	50000	100000	200000
iii	35	Cl	10	20	100	200	1000	2000	10000	20000	100000	200000	400000
iii	79	Br	0.25	0.5	2.5	5	25	50	250	500	2500	5000	10000
iii	127	I	0.001	0.002	0.01	0.02	0.1	0.2	1	2	10	20	40

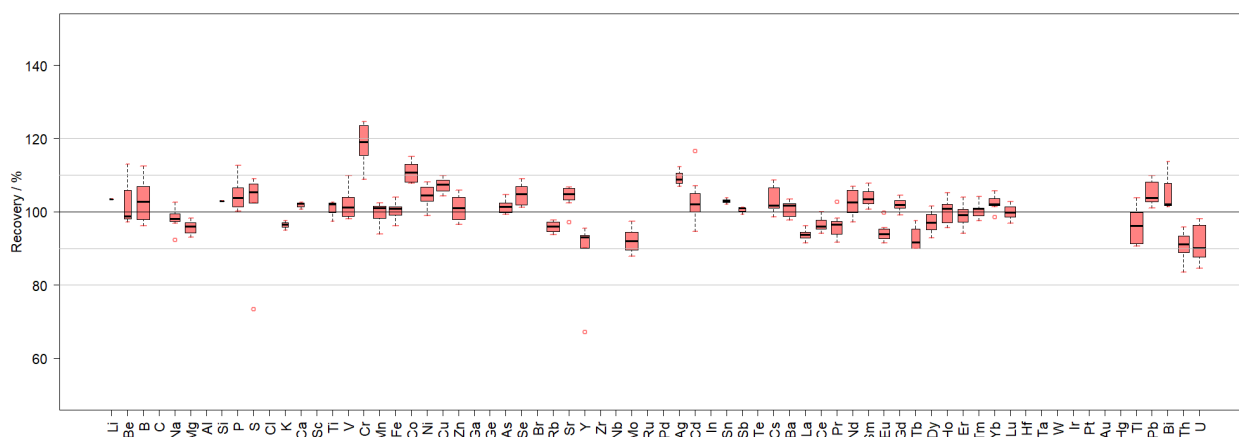


Figure S2: Method cross validation on Agilent 8800 ICP-QQQ-MS. Recoveries of all elements in the reference materials SPS-SW1, SPS-SW2 and TMDA-51.5 of one measurement on the Agilent 8800 ICP-QQQ-MS by applying the best-practice advice introduced in the manuscript.

6. Further discussion about section 3 “Results and discussion” of the manuscript

6.1. Alkali metals

Lithium is generally not affected by spectroscopic interferences in ICP-MS due to its low mass. Most of the theoretically occurring interferences potentially affecting the quantification of Na (e.g., ${}^7\text{Li}^{16}\text{O}^+$ or ${}^{46}\text{Ti}^{++}$ on ${}^{23}\text{Na}^+$, May and Wiedmeyer (1998)) can be considered to be not relevant in river water due to the typically high Na concentrations in the 10 to 100 mg/l range. However, Ca appears in high concentrations in the 50 to 100 mg/l range in river water. Therefore, it might have a significant contribution on ${}^{23}\text{Na}$ (${}^{46}\text{Ca}^{++}$). K is also found in the mg/l concentration range in the river water samples and could be mainly affected by Ar-based interferences on ${}^{39}\text{K}$ (${}^{38}\text{Ar}^1\text{H}^+$) (May and Wiedmeyer, 1998; Wollenweber et al., 1999). Lomax-Vogt et al. (2021) recently published a database for spectroscopic interferences in which ${}^{23}\text{Na}^{16}\text{O}^+$ is listed as potential interference on ${}^{39}\text{K}$. However, according to the reaction data of Sugiyama and Nakano (2014) a formation of NaO^+ species should not be likely to be relevant. In total, for all three elements (Na, K, Ca), very acceptable results regarding the recoveries in the CRM and calibration check solutions were achieved with He as collision gas (cf. Figure 2 of the manuscript). Since Li sensitivity is better in no gas mode, our decision to add the element by applying the He mode was based on the fact that tuning of another mode as well as shifting to this mode during each measurement is time-consuming and can be avoided due to the relatively high Li concentration in river water (here: 2.3 to 21 $\mu\text{g/l}$), in order to save analysis time, argon, and thereby costs. Wollenweber et al. (1999) reported ICP-Q-MS analyses for Li, Na,

and K by cold plasma (620 W instead of 1350 W in their study) reducing Ar-based signals such as $^{38}\text{Ar}^1\text{H}^+$ on ^{39}K . A higher sensitivity and lower background levels could be achieved by cold plasma. However, it was also stated that a cold plasma is only advisable for low mass analytes with low ionisation potentials (Wollenweber et al., 1999). Therefore, a cold plasma approach is not advisable for multi-elemental approaches considering low and high mass analytes.

From the potential interferences on ^{85}Rb (e.g., $^{84}\text{Sr}^1\text{H}^+$, $^{69}\text{Ga}^{16}\text{O}^+$, $^{170}\text{Er}^{++}$, $^{170}\text{Yb}^{++}$) (May and Wiedmeyer, 1998) mainly $^{84}\text{Sr}^1\text{H}^+$ should be considered in river water analyses. Sr concentrations (typically in the range of 100 to 1000 $\mu\text{g/l}$) are often 100 times higher than Rb (here: 1.4 to 22 $\mu\text{g/l}$). While measuring the interference check solutions, better results were achieved by on-mass measurements with H_2 or O_2 than with He (refer to Table S8A-S8F). Making use of the potential of solving Sr-based interferences by mass-shifting the SrH^+ -ion, the quantification of Rb in the O_2 or H_2 on-mass modes is recommended. Zhu et al. (2018) recommended a measurement with CH_3F for mass-shifting Sr-based interferences by fluorine. Single-quadrupole (Burney and Neal, 2019) or measurements with no gas in ICP-QQQ-MS (Deng et al., 2021) were reported but are not recommended due to the above-mentioned reasons.

For Cs, good recoveries as well as LOQs in the ppt-range were achieved in on-mass measurements with all three cell gases. Due to the very low Cs concentrations in the assessed river water samples (0.1 to 10 $\mu\text{g/l}$ range) and European median surface water concentrations of 6 ng/l, spectroscopic interferences such as $^{117}\text{Sn}^{16}\text{O}^+$ and $^{101}\text{Ru}^{16}\text{O}_2^+$ on ^{133}Cs need to be considered ((May and Wiedmeyer, 1998), Table S8A-S8F). Again, good results were achieved with He as well as with H_2 and O_2 as cell gases. Deng et al. (2021) reported measurements in no gas ICP-QQQ-MS which can be also applied based on the data obtained in this study. However, as already mentioned for Li, the number of analytical modes should be kept as low as possible for routine multi-elemental analyses. While the radionuclides ^{134}Cs , ^{135}Cs and ^{137}Cs are standard analytes in the context of radiological environmental monitoring programs (Ohno and Muramatsu, 2014; Zhu et al., 2020), total concentrations of Cs are less frequently determined so far, and should be more frequently addressed in monitoring approaches.

6.2. Alkaline earth metals

In river water, spectroscopic interferences are generally not an issue on ^9Be . However, they are to be expected on the commonly used isotopes ^{24}Mg , ^{44}Ca , ^{88}Sr and ^{137}Ba . ^{24}Mg analysis can be impacted by $^{12}\text{C}_2^+$ and $^{48}\text{Ca}^{++}$ (May and Wiedmeyer, 1998). Regarding Ca analyses, the most abundant Ca isotope ^{40}Ca cannot be analysed using standard plasma conditions due to the isobaric overlap from $^{40}\text{Ar}^+$. The most important potential interferences on its second most abundant isotope ^{44}Ca include $^{12}\text{C}^{16}\text{O}_2^+$, $^{14}\text{N}_2^{16}\text{O}^+$ and $^{28}\text{Si}^{16}\text{O}^+$ as well as doubly charged $^{88}\text{Sr}^{++}$ ions (May and Wiedmeyer, 1998). Next to Li, Na and K, Wollenweber et al. (1999) reported also an enhancement for Mg and Ca by cold plasma in ICP-Q-MS which is not feasible for multi-elemental analyses due to the above mentioned reason. Spectroscopic interferences on ^{88}Sr ($^{72}\text{Ge}^{16}\text{O}^+$, $^{176}\text{Yb}^{++}$, $^{176}\text{Lu}^{++}$, $^{176}\text{Hf}^{++}$) and ^{137}Ba ($^{120}\text{Sn}^{16}\text{O}^+\text{H}^+$, $^{121}\text{Sb}^{16}\text{O}^+$) were selectively checked during method development (May and Wiedmeyer (1998); Table S8A-S8F). Besides radionuclides of Cs, the Sr isotope ^{90}Sr is a standard analyte in radiological environmental samples and it is addressed in several publications for ICP-QQQ-MS analyses using separation and pre-concentration techniques as well as on-mass approaches with O_2 to overcome spectroscopic interferences (Ohno et al., 2018; Wang et al., 2021b). According to the reaction data of Sugiyama and Nakano (2014) on-mass as well as mass-shift approaches with O_2 are possible for Sr. However, doubly charged interferences can only be overcome by mass-shifting.

6.3. Transition and post-transition metals

Based on the results of this study and of others, the transition and post-transition metals can be divided into elements which are preferably measured in mass-shift mode with O_2 (Sc, Ti, V, Cr, Y, Zr, Nb, Hf, Ta) and elements best analysed on-mass using He, H_2 or O_2 as cell gas (Al, Mo, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ru, Pd, Ag, Cd, In, Sn, W, Ir, Pt, Au, Hg, Tl, Pb, Bi). It is known, that group 3 to 6 elements of the periodic table are preferably reacting with O_2 in the CRC (Sugiyama and Nakano, 2014). Accordingly, for all these elements, analysis as MO^+ was selected for the final method. However, good results for most of these elements were also obtained when analysing in on-mass mode with He as collision gas (see Table 2 of the manuscript). Mo and W which are group 6 elements led to better results by measurement in He mode, however, a measurement as MO^+ and MO_2^+ species for Mo and W, respectively, is also an option and already described in the literature such as for W as MO_2^+ (Deng et al., 2021).

The detection of the elements Sc, Ti, V, Cr, Y, Zr, Nb, Hf, and Ta as MO^+ is advisable due to the avoidance of polyatomic interferences and their expected low concentrations in the dissolved fraction of river water ($<0.45 \mu\text{m}$). Examples are S-, C- and Cl-based interferences on ^{51}V (e.g., $^{34}\text{S}^{16}\text{O}^{1}\text{H}^+$, $^{35}\text{Cl}^{16}\text{O}^+$, $^{38}\text{Ar}^{13}\text{C}^+$) or ^{52}Cr (e.g., $^{36}\text{S}^{16}\text{O}^+$, $^{40}\text{Ar}^{12}\text{C}^+$, $^{35}\text{Cl}^{16}\text{O}^{1}\text{H}^+$) (May and Wiedmeyer, 1998). $^{12}\text{C}^{35}\text{Cl}^+$, $^{30}\text{Si}^{16}\text{O}^{1}\text{H}^+$, $^{31}\text{P}^{16}\text{O}^+$, $^{32}\text{S}^{14}\text{N}^{1}\text{H}^+$, and $^{32}\text{S}^{15}\text{N}^+$ are well known ^{47}Ti interferences (May and Wiedmeyer, 1998). Measurement as MO^+ in ICP-QQQ-MS was also described for Sc (Deng et al., 2021) and V (D'Illio et al., 2011). The full list on checked interferences is given in Tables S8A-S8F.

As mentioned, often similarly good results were obtained using several cell gases for Mn, Fe, Cu, Zn, Co, and Ni (cf. Table 2 of the manuscript). In the case of Fe, on-mass measurements using He or H_2 were the only modes without observable impact by relevant polyatomic interferences at $1 \mu\text{g/l}$ ($^{37}\text{Cl}^{18}\text{O}^{1}\text{H}^+$, $^{40}\text{Ca}^{16}\text{O}^+$, $^{40}\text{Ar}^{16}\text{O}^+$, refer to Tables S8A-S8F) (May and Wiedmeyer, 1998). In river water samples, Fe is to be expected in higher $\mu\text{g/l}$ concentrations and Cl-, Ca-, or Ar-based interferences may have a significant impact. Moreover, for Cu, as one example, the lowest LOQ was achieved in He mode during method development. The minimal LOQ achieved during method validation was at 4.8 ng/l . Jackson et al. (2018) recommended on-mass measurements with O_2 for Mn, Ni, and Cu as well as with H_2 for Fe and Zn to overcome spectroscopic interferences and reach high sensitivity. O_2 and H_2 were the only two gases which were studied (Jackson et al., 2018). This emphasises that the mentioned elements are measurable in several on-mass modes.

Being part of the group 8 to 10 elements, the analysis of the PGE (Ru, Pd, Pt, Ir) was challenging in single quadrupole ICP-MS measurements due to several interferences and expected low river water concentrations in ng/l ranges. The best opportunity was to include correction equations or matrix removal measures (Djingova et al., 2003). The most relevant spectroscopic interferences in river water analysis such as $^{202}\text{Hg}^{++}$, $^{61}\text{Ni}^{40}\text{Ar}^+$, $^{64}\text{Ni}^{37}\text{Cl}^+$, $^{66}\text{Zn}^{35}\text{Cl}^+$, $^{85}\text{Rb}^{16}\text{O}^+$ on ^{101}Ru , $^{177}\text{Hf}^{16}\text{O}^+$, $^{175}\text{Lu}^{18}\text{O}^+$, $^{158}\text{Gd}^{35}\text{Cl}^+$, $^{153}\text{Eu}^{40}\text{Ar}^+$ on ^{193}Ir or $^{179}\text{Hf}^{16}\text{O}^+$, $^{100}\text{Mo}^{95}\text{Mo}^+$, $^{156}\text{Gd}^{40}\text{Ar}^+$ on ^{195}Pt (Sugiyama and Shikamori, 2015) were checked during method development. In contrast to the other above-mentioned elements, Pd was present in concentrations between 100 and 500 ng/l above LOQ in the river water samples. The main Pd interference is $^{40}\text{Ar}^{65}\text{Cu}^+$ (May and Wiedmeyer, 1998). Ru, Pd, Pt and Ir can all be measured on-mass. Sugiyama and Shikamori (2015) suggested using an on-mass method for Ru and Pd and mass-shift

for Ir and Pt when applying NH₃/He as cell gas. However, NH₃ was not assessed in this study, in order to avoid long measuring times for the monitoring approaches and to remain with a maximum of three cell gases (O₂, H₂, and He).

Analysis of Ag was challenging regarding the HCl content. Trace Cl⁻ concentrations cause significant AgCl precipitation, but at elevated Cl⁻ concentrations soluble AgCl complexes are formed (Fritz, 1985). Hence, challenges in multi-element analysis can be less ascribed to challenges in ICP measurements (Ag can be analysed in all on-mass modes), but to stability problems in contact with Cl⁻ during sample preparation, calibration, and sample introduction.

Based on the method development results, we advise to analyse group 13 post-transition elements Al, Ga, In, and Tl by applying He or H₂ as cell gases. For ²⁷Al (mostly interfered by polyatomic interferences containing C, e.g.: ¹²C¹⁵N⁺, ¹³C¹⁴N⁺, ¹²C¹⁴N¹H⁺) and ⁷¹Ga (³⁶S¹⁷O¹⁸O⁺, ³⁸Ar³³S⁺, ³⁵Cl¹⁸O₂⁺, ³⁷Cl¹⁷O¹⁸O⁺, ³⁷Cl¹⁷O₂⁺, ³⁶Ar³⁵Cl⁺) (May and Wiedmeyer, 1998), best results were achieved in H₂ mode which was also considered by Deng et al. (2021) as analytical mode for analysis.

For Sn, best results were achieved by applying He or O₂ as cell gas, reaching acceptable recoveries between 80 and 120% of the CRMs, calibration check solutions and spiked river water samples (cf. Figure 2 of the manuscript). Possible spectroscopic interferences such as ¹⁰²Pd¹⁶O⁺ or ¹⁰²Ru¹⁶O⁺ (Machado et al., 2017) were assessed (cf. Tables S8A-S8F). Machado et al. (2017) measured Sn also in an on-mass approach using O₂ as the only cell gas for mass-shift (Rh, Pt) and on-mass analyses (Sn, Cd, Pd). The use of only one cell gas is also an option to reduce time in monitoring and should be considered as an option for multi-element approaches. However, the set of analytes in this study was measured in all routine cell gases to reflect on the different strength of the applied cell gases in regard of the assessed criteria.

The measurement of the heavier elements, ²⁰⁸Pb (¹⁹²Pt¹⁶O⁺) and ²⁰⁹Bi (¹⁹³Ir¹⁶O⁺) (May and Wiedmeyer, 1998), is very unlikely to be biased by spectroscopic interferences in river water due to the expected low concentrations in the low ng/l range for Pt and Ir. Since both, Pt and Ir, were found below LOQ in 91% (Pt) and 99% (Ir) of the analysed river water samples, significant disturbances are not to be expected, at least in major German rivers. Pb and Bi can be measured in all on mass modes using He, O₂ or H₂ in the CRC. For Bi, better spike recoveries were achieved using He. For Pb, lowest LOQ and best CRM recoveries were obtained by using He as collision gas. Jackson et

al. (2018) measured Pb in ocean water by ICP-QQQ-MS with O₂ in the CRC after a pre-concentration step. A comparison between the no gas mode and the cell gases He, H₂ and O₂ led to the conclusion that the highest signal intensity was achieved using O₂ (Jackson et al., 2018) for the matrix ocean water. Burney and Neal (2019) reported further spectroscopic interferences on ²⁰⁹Bi (¹⁶⁹Tm⁴⁰Ar⁺, ¹⁷⁴Yb³⁵Cl⁺, ¹⁷⁷Hf¹⁶O₂⁺) by measuring interfering solutions in HR-ICP-MS to subtract the contribution from the mass of interest 209 which is not a necessary step in ICP-QQQ-MS anymore. Moreover, Deng et al. (2021) reported ICP-QQQ-MS measurements of ²⁰⁸Pb and ²⁰⁹Bi in no gas and He mode in sediment digests, respectively. In this case, it has to be kept in mind that the overall conclusion is the possibility of measurements in all on-mass approaches. However, details have to be examined separately regarding which mode is more suitable for a certain sample matrix. In this study, best overall results in all criteria were achieved in He mode.

6.4. Lanthanides and Actinides

In their quantification by ICP-MS, spectroscopic interferences such as low mass REE-oxide ions overlapping high mass REEs (e.g., ¹⁵³Eu¹⁶O⁺ on ¹⁶⁹Tm⁺, ¹⁵⁹Tb¹⁶O⁺ on ¹⁷⁵Lu⁺ or ¹⁵⁶Gd¹⁶O⁺ on ¹⁷²Yb⁺) have to be considered (May and Wiedmeyer, 1998). The different approaches to solve these interferences have recently been reviewed by Wysocka (2021). Successful approaches include the analyses by ICP-QQQ-MS as MO⁺ (Ardini et al., 2010; Zhu, 2020) or with N₂O as cell gas (Ardini et al., 2010; Klein et al., 2021). However, Eu and Yb only react with O₂ to a small extent, which leads to a significantly reduced sensitivity (Ardini et al., 2010; Sugiyama and Nakano, 2014; Sugiyama, 2020). Thus, if N₂O is not available or the use of another mode is too time and cost intensive, we recommend the measurement in He mode for both elements.

The actinides Th and U naturally occur as isotopes with very long (²³⁸U, ²³⁵U, ²³²Th), intermediate (²³⁴U, ²³⁰Th) or short (²²⁷Th, ²²⁸Th, ²³¹Th, ²³⁴Th, ²³¹Th) half-lives. However, the isotopes ²³⁸U (99.274%) and ²³²Th (~100%) are by far the most abundant. The potential of ICP-Q-MS for the quantification of Th and U was already addressed in several studies (Holmes and Pilvio, 2000; Holmes, 2001; Santos et al., 2010; Tuovinen et al., 2015). For U, the sensitivity can further be improved, with O₂ as reaction gas and analyses as MO₂⁺ (e.g., for the purpose of determining isotope ratios (Wang et al., 2021c)). For both elements, good results were achieved both, in on-mass measurements with He or H₂ as cell gas and in the no gas mode. In He mode, the

LOQs were in the low ng/l range between 0.090 to 6.0 ng/l for Th and 0.5 to 49 ng/l for U. This allowed the concentrations of both elements to be determined in the used river water samples with quantification frequencies of 46% (Th) and 100% (U).

6.5. Metalloids

For Si, method development showed best results by measuring both in on-mass using H₂ and in mass-shift using O₂. However, better recoveries in CRM, calibration check solutions, and spiked samples were achieved in quantification as MO⁺ during method validation. Main polyatomic interferences in river water on ²⁸Si are ¹⁴N₂⁺ and ¹²C¹⁶O⁺ (Aureli et al., 2020). Gourgiotis et al. (2017) performed Si isotope ratio analyses on enriched experimental samples (²⁹Si/²⁸Si and ³⁰Si/²⁸Si) using O₂ in the CRC and analysis of Si as MO₂⁺ since the described polyatomic interferences ¹⁴N₂⁺ and ¹²C¹⁶O⁺ can also form ¹⁴N₂O⁺ and ¹²C¹⁶O₂⁺ (Gourgiotis et al., 2017). In this study, measurement in MO⁺ lead to overall good recoveries in the range of 80 to 120% in CRM and calibration check solutions. The low recovery of the spikes can be ascribed to the chosen low concentrations for spiking as already explained in section 3.1. Arsenic quantification is known to be achieved by measurement as MO⁺ in ICP-QQQ-MS (D'Illio et al., 2011) which is also supported by the data obtained in this study, leading to an interference elimination of the possible polyatomic ions ⁴⁰Ar³⁵Cl⁺, ⁵⁹Co¹⁶O⁺, ³⁸Ar³⁷Cl⁺, ³⁶Ar³⁹K⁺, ¹²C³¹P¹⁶O₂⁺ and the doubly charged ions Nd⁺⁺ and Sm⁺⁺ (May and Wiedmeyer, 1998). ⁷⁸Se only occurs in trace concentrations in river waters. During its quantification by ICP-MS, Cl⁻ and K-based interferences (³⁵Cl³⁷Cl¹⁶O⁺, ⁴¹K³⁷Cl⁺, ³⁹K³⁹K⁺) are of highest concern (May and Wiedmeyer, 1998). However, as for the other elements of this group discussed before, good results were obtained measuring the interference check solutions by analysis as MO⁺. This analysis mode was also chosen by others (e.g., (Bishop et al., 2015; Jackson et al., 2015)).

Antimony analysis is preferably performed in on-mass modes unlike As, although that both belong to group 15 of the periodic table. ¹²¹Sb can be mainly affected by ¹⁰⁵Pd¹⁶O⁺ (May and Wiedmeyer, 1998). The Sb standard used was stabilised in HCl, which entails the described challenges when creating the multi-element stock solutions. He mode leads to good Sb recoveries in all quality standards (cf. Figure 2 of the manuscript). ICP-QQQ-MS measurements in He mode were also conducted by Deng et al. (2021).

Analyses of Ge and Te appear possible in all on-mass modes based on the addressed criteria. However, measurements for method validation were conducted in He mode as collision gas according to existing literature reporting ICP-QQQ-MS measurements with He for Ge (Lehmann et al., 2019) and ICP-Q-MS analysis for Te (Reynolds et al., 2009).

Boron has no relevant spectroscopic interferences except for a possible peak tailing of ^{12}C on ^{11}B (Lomax-Vogt et al., 2021). Even though this issue is not of relevance anymore thanks to the increased mass resolution of triple quadrupole devices, C calibration standards prepared from tartaric and oxalic acid might leach B from the instruments tubing as observed during method development. Therefore, care must be taken with regard to the evaluation of boron blank values and the calculation of LOQs. Moreover, its analysis is often problematic due to memory effects of boron (Kmieciak et al., 2016). Thus, relatively high LOQs between 1.35 and 17.9 $\mu\text{g/l}$ were obtained throughout method validation. With a quantification frequency of 99%, analyses were possible above LOQ in the German river water samples with concentrations between 11.2 and 121 $\mu\text{g/l}$ as seen in Figure 3 of the manuscript. During method development, best results in CRM, spike recovery and LOQ were obtained measuring on-mass with O_2 . Boron quantification with O_2 in an on-mass approach has already been described in the literature by Diez Fernández et al. (2015).

6.6. Non-metals

6.7.1. Polyatomic non-metals

Although Amaral et al. (2015) showed that a C measurement is in principal possible in different analytical modes including MO^+ , the best results in terms of LOQs and recovery are achieved as MO^+ . The question has to be asked which of the different dissolved carbon species are addressed by ICP-MS and to which convention in fractionation (e.g., total organic carbon (TOC), particulate organic carbon (POC), dissolved organic carbon (DOC) (Niemirycz et al., 2006)) the results can be best compared to. However, the analyses herein are mainly used to observe trends regarding the carbon content in the dissolved fraction ($<0.45 \mu\text{m}$) of river waters after acidification with HNO_3 . Therefore, the ICP based results could be compared to the DOC over time since inorganic carbon should not be present anymore after acidification. This has to be further evaluated. The available carbon ICP standards are made from tartaric or oxalic acid. Both standards increased the concentrations of the

elements B, Al, Si, Ti, V, Cr, Mn, Fe, Zn, Rb, Y, Zr, Ba, Au, Hg and Pb during method development above C calibration standard concentrations of 50000 µg/l. A distinct leaching behaviour was observable in subsequently measured blanks, leading to the conclusions that chelating effects occurred which was caused by the carbon species from the instrument's sample introduction system. Thus, when including C into the analytical run, special care must be taken with regard to the rinsing procedure, the evaluation of blank values and the calculation of LOQs. In particular, when measuring B, this problem can easily be enhanced by peak tailing from ^{12}C to ^{11}B , which B can suffer from in single quadrupole devices (Sah and Brown, 1997; Kmiecik et al., 2016).

7. References

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