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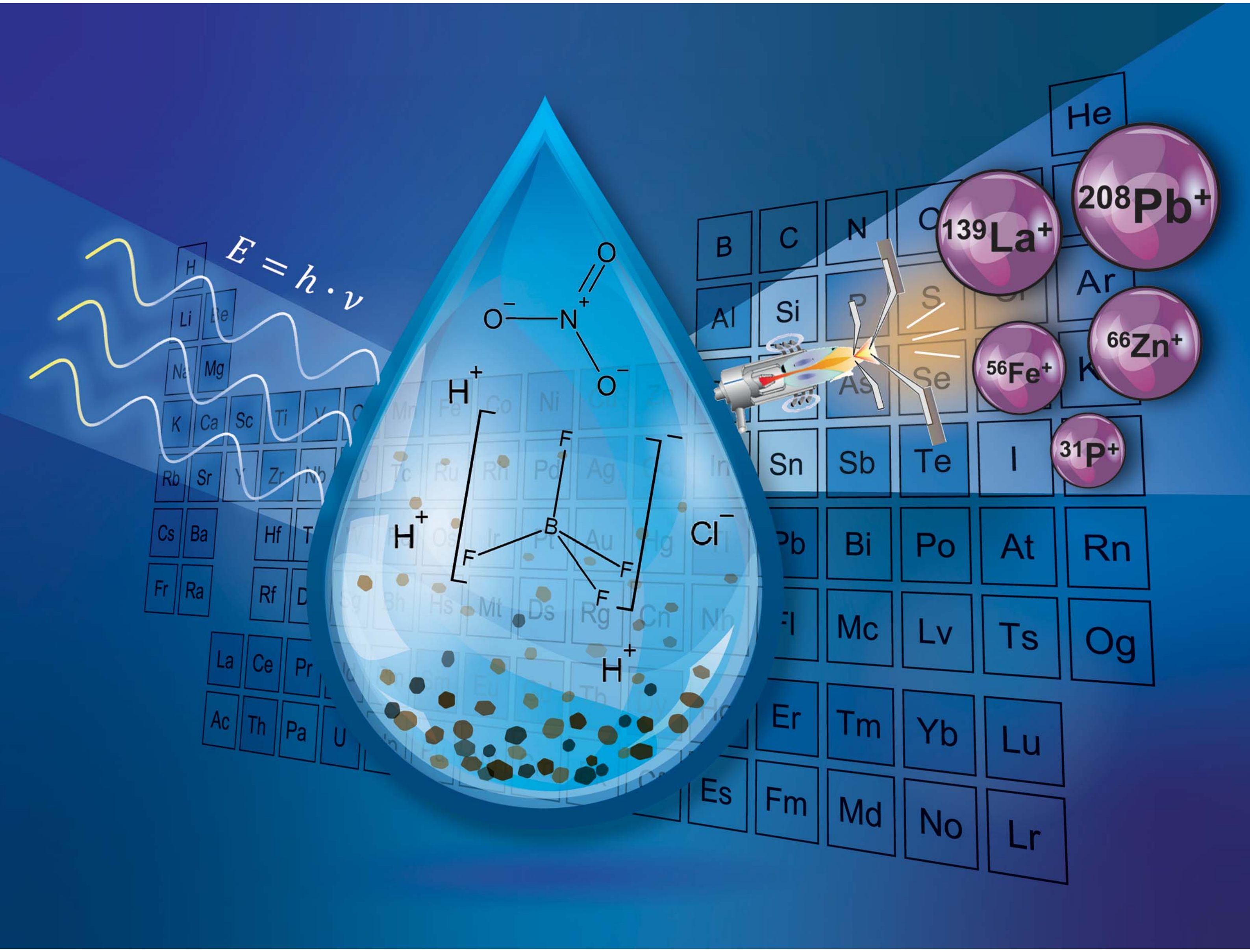

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Substituting HF by HBF_4 – an optimized digestion method for multi-elemental sediment analysis *via* ICP-MS/MS†

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Determination of elemental mass fractions in sediments plays a major role in evaluating the environmental status of aquatic ecosystems. Herewith, the optimization of a new total digestion protocol and the subsequent analysis of 48 elements in different sediment reference materials (NIST SRM 2702, GBW 07313, GBW 07311 and JMC-2) based on ICP-MS/MS detection is presented. The developed method applies microwave acid digestion and utilizes HBF_4 as fluoride source for silicate decomposition. Similar to established protocols based on HF, HBF_4 ensures the dissolution of the silicate matrix, as well as other refractory oxides. As HBF_4 is not acutely toxic; no special precautions have to be made and digests can be directly measured *via* ICP-MS without specific sample inlet systems, evaporation steps or the addition of *e.g.* H_3BO_3, in order to mask excess HF. Different acid mixtures with and without HBF_4 were evaluated in terms of digestion efficiency based on the trace metal recovery. The optimized protocol (5 mL HNO_3, 2 mL HCL, 1 mL HBF_4) allows a complete dissolution of the analyzed reference materials, as well as quantitative recoveries for a wide variety of certified analytes. Low recoveries for *e.g.* Sr, Ba and rare earth elements due to fluoride precipitation of HF-based digestions protocols, can be avoided by the usage of HBF_4 instead. Based on the usage of high purity HBF_4 all relevant trace, as well as matrix elements can be analyzed with sufficiently low LOQs (0.002 $\mu g\ L^{-1}$ for U up to 6.7 $\mu g\ L^{-1}$ for Al). In total, 34 elements were within a recovery range of 80%–120% for all three analyzed reference materials GBW 07313, GBW 07311 and JMC-2. 14 elements were outside a recovery range of 80%–120% for at least one of the analyzed reference materials.

Introduction

Levels of toxic heavy metals in the aquatic environment play a key role for the chemical and ecological quality status of habitats, which is reflected by the implementation of limit values of metals in a multitude of matrices covered by different directives (*e.g.* Water Framework Directive 2000/60/EC,[1] Marine Strategy Framework Directive 2008/56/EG[2] or the OSPAR[3]). Therefore, the permanent and extensive monitoring of metals is essential. In addition to the legacy metal pollutants (Ni, Cu, Zn, Cd, Hg, Pb), there is growing concern about different emerging metal contaminants, *i.e.* metal species such as Gd-based[4] contrast agents or metal containing pharmaceuticals, as well as the so called technology-critical elements (TCE), which may become emerging pollutants in the near future due to their broad application, as well as missing technology for their recycling to support a circular economy.[5–7] Due to the accumulation of metal contaminants over time, especially sediments may serve as time records/memories of aquatic systems' pollution by metals, posing a meaningful indicator to establish changes in rivers, estuaries and coastal areas and reflect the time-integrated pollution status.[8,9]

Today, flame or electrothermal atomic absorption spectroscopy (FAAS, ETAAS), as well as plasma-based techniques like inductively coupled plasma-optical emission spectroscopy (ICP-OES) and especially inductively coupled plasma-mass spectrometry (ICP-MS) are most frequently used for multi-elemental analysis in environmental samples.[10,11] For the analysis of sediment samples, the great majority of these methods require the dissolution of the analytes and herewith decomposition or leaching of the sample matrix.[12] As of yet, various leaching protocols have been described in the literature *e.g.* based on NH_3–HCl, acidified H_2O_2 or acetic acid, as proposed by the United Nations Environment Program for the extraction of heavy metal fraction from sediments originating from

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anthropogenic sources.[13,14] However, leaching procedures will only determine the leachable, weak bound fraction of heavy metals, as the sample matrix (silicate) will not be decomposed. Therefore, the selected chemicals allow the mobilization of a specific element fraction. Consequently, elemental mass fractions determined by leaching procedures are not comparable to elemental mass fractions of total digestion protocols, as they serve different purposes.

Fusion approaches based on alkaline, acid and peroxide fusion using *e.g.* $KNaCO_3$, KI, LiF, $LiBO_2/Li_2B_4O_7$, Li_2CO_3, Na_2CO_3, $NaHCO_3$, $NaNO_3$, $NaHSO_4$, Na_2O_2, NaOH, $NH_4F \cdot HF$ are frequently applied for dissolution of silicate-based matrices in geological applications.[15–18] However, fusion techniques involve large quantities of the flux relative to the sample size. Therefore, impurities in the fusion salts pose a tremendous contamination source and may lead to elevated detection limits, as well as biased results. Moreover, high salt matrices pose a problem for atomic spectroscopy and mass spectrometric detection techniques (*e.g.* instability and high background readings, as well as interferences).

Acid digestions of silicate-based matrices involve the use of strong mineral acids like HNO_3, HCl or $HClO_4$ often in combination with HF. Today, closed-vessel/microwave-assisted digestion is considered superior to open-vessel/hot-plate based techniques for reasons like efficient, homogeneous and fast heat transfer, prevention of loss of volatile elements and compounds (chlorides and fluorides), as well as minimization of airborne contamination.[19,20] Analyses of sediment reference materials *via* microwave-assisted digestion have shown that HF-based digestion protocols lead to significantly higher metal mass fractions (up to ∼20% for Cd and Cr) since it allows the mobilization of the element fraction bound to the silicate-matrix and other refractory oxides, that cannot be decomposed and dissolved by HNO_3 and/or HCl.[21] Therefore, digestions using *aqua regia* (*e.g.* DIN 38414 (1983) or ISO 11466, (1995)) can only provide pseudo total mass fractions.[22] As the term pseudo total mass fractions implies a leaching with *aqua regia* may be sufficient to determine the total amount of selected elements. Indeed achievable recoveries highly depend on the analyte, as well as the matrix composition. Even though HF is considered highly hazardous and corrosive for all glass/quartz parts of analytical instruments, its usage is necessary to break down SiO_2 compounds for different analytical applications.[23] Besides difficulties in handling highly toxic HF, its use may also lead to considerable underestimation of a variety of other metals (*e.g.* Al, Ba, Ca, Mg and Se) due to formation of fluoride-based precipitates.[24] Furthermore, the formation of insoluble fluorides may lead to the co-precipitation of other elements, as reported for the rare earth elements (REE).[25] When using ICP-MS detection the entire sample introduction has to be changed to a PFA/Pt/Al/sapphire-based one (nebulizer, spray chamber, connectors, injector, torch) to avoid any damage due to the HF residues of the samples. Sample evaporation to remove the HF, as well as a reconstitution of the sample using HNO_3 or *aqua regia* afterwards is a frequently applied approach, however this procedure is time consuming and loss of analytes has been observed. Often boric acid (H_3BO_3) is used to mask HF residues after total digestion, however this will again increase the matrix load of the digest, as well as the chance of sample contamination due to possible impurities of the used chemicals.

Alternative approaches to overcome difficulties in using/handling HF involve the use of *in situ* generation of HF by combination of fluoride-containing chemicals like NH_4F or $NH_4F \cdot HF$ with mineral acids.[26] Formation of fluoride precipitation for these alternative digestion protocols is significantly lower than for conventional HF digests.[27] Nevertheless, ammonium fluoride salts still require safe handling, as they are highly toxic. HF-free digestion protocols can also involve the use of H_3PO_4. Under high temperatures H_3PO_4 undergoes condensation reactions leading to the formation of condensed species (*e.g.* $H_4P_2O_7$) capable of forming soluble SiP_2O_7.[28] Although, chemicals of acute toxicity can be avoided with this approach, the use of H_3PO_4 leads to the formation of various polyatomic interferences in ICP-MS, thus hindering the detection of selected elements (*e.g.* ^{63}Cu ($^{31}P^{16}O_2$), ^{64}Zn ($^{31}P^{16}O_2{}^{1}H$; $^{31}P^{16}O^{17}O$) or ^{87}Sr ($^{40}Ar^{31}P^{16}O$)).

The increasing number of metal contaminants of interest and the last decades' advances in mass spectrometry enabling time-efficient quantification of >50 metals in one run by ICP-MS/MS techniques demand for versatile and accurate sample preparation protocols. Thus, this work aims at the development and validation of an efficient protocol for complete microwave-assisted acid digestion of sediments using high-purity HBF_4 as fluoride source, for subsequent analysis of >45 metals based on ICP-MS/MS. HBF_4 is capable of *in situ* generation of HF, without being acutely toxic. An additional advantage of using HBF_4 is that excess fluoride ions are directly complexed by H_3BO_3 and HBF_3OH thus preventing precipitation of metal fluorides.[25,29] This allows the direct analysis of the samples without any further measures, which helps to speed up sample preparation, as well as to avoid errors *e.g.* due to contamination or analyte loss. Despite the clear advantages of HBF_4 over HF, as well as published applications of HBF_4 based digestion protocols *e.g.* for the determination of rare earth elements[25] and trace elements in peat[30,31] or trace elements in bituminous sand mineral,[32] its use is not widely recognized so far.

Experimental

Reagents and standards

All preparatory laboratory work was performed in a class 10 000/1000 clean room. Type I reagent grade water (>18.2 MΩ cm) was obtained from an ultrapure water system consisting of an Elix 3 module (Merck Millipore, Darmstadt, Germany), a Milli-Q element module (Merck Millipore, Darmstadt, Germany) and a Q-POD element (Merck Millipore, Darmstadt, Germany). Analytical grade HNO_3 (65% w/w, Fisher Scientific GmbH) and analytical grade HCl (30% w/w, Carl Roth GmbH + Co. KG, Karlsruhe, Germany) were further purified either by double sub-boiling in perfluoralkoxy-polymer (PFA)-subboling stills (DST-4000 & DST-1000, Savillex, Minnesota, USA) or by double sub-boiling using a cascade of two quartz stills (AHF Analysentechnik, Tübingen, Germany) operated under clean room conditions. HBF_4 (38% w/w, Chem-Lab, Zedelgem, Belgium) and HF (Carl Roth GmbH, Karlsruhe, Germany) were used in ultra-pure quality for sample digestion without any further purification. For the initial development of the digestion method, HBF_4 (48% w/w) with unknown elemental purity was used (Sigma Aldrich, Missouri, USA), as at this point of the work high purity HBF_4 supplied by Chem-Lab was not yet available.

External calibration standard solutions for quantification (all traceable to NIST standards) were prepared from custom-made multi-element standards of different composition (Inorganic Ventures, Christiansburg, USA).

The reference marine sediments NIST SRM 2702 (National Institute of Standards and Technology, Gaithersburg, USA), GBW 07313 (National Research Centre for Certified Reference Materials, Beijing, China) and JMS-2 (Geological Survey of Japan, Tokyo, Japan) as well as the reference stream sediment GBW 07311 (National Research Centre for Certified Reference Materials) were used for method development and validation.

Sediment digestion

50 mg aliquots of the sediment samples were digested either with a MARS Xpress or a MARS 6 (CEM Corp., Kamp Lintfort, Germany) microwave system. Digestion took place at 180 °C for 300 min using 35 mL pre-cleaned TFM digestion vessels. In total, six different acid mixtures were applied for sediment digestion: 2 mL HNO_3/6 mL HCl; 5 mL HNO_3/1 mL HF; 5 mL HNO_3/2 mL HCl/1 mL HF; 5.5 mL HNO_3/2 mL HCl/0.5 mL HBF_4; 5 mL HNO_3/2 mL HCl/1 mL HBF_4 and 4 mL HNO_3/2 mL HCl/2 mL HBF_4. The corresponding acid volumes of each acid composition (total volume of 8 mL) were chosen based on the manufacturer recommendations. It should be noted that higher acid volumes will lead to higher pressures during digestion, which may consequently lead to a pressure release during digestion, including a possible loss of analyte. On the other hand, we wanted to make sure to use an acid volume as high as possible in order to prevent a shortage of acid. After digestion, the clear sample solutions were quantitatively transferred to 50 mL pre-cleaned DigiTUBEs (SCP Science, Quebec, Canada) and diluted to a final volume of 50 mL with type I reagent grade water. After each digestion, all vessels were cleaned by running three blank digests using a HNO_3/HCl mixture. Digestions containing HF were evaporated to dryness using an evaporation unit (XpressVap, CEM Corp., Kamp Lintfort, Germany). HF-containing fumes were neutralized using a cascade of gas washing bottles containing Milli-Q water and KOH solution, respectively. After evaporation, the samples were re-dissolved in 2 mL concentrated HCl and 4 mL type I reagent grade water using a MARS Xpress. A detailed description of the used microwave parameters is shown in Table 1.

Table 1 Microwave programs used for dissolution of the sediments, as well as evaporation of HF containing digests und re-dissolution

Microwave program for sediment dissolution (temperature controlled)			
Power [W]	Temperature [°C]	Ramp. [min]	Hold [min]
1600	180	60	240
Microwave program for evaporation of HF containing digests (power controlled)			
Power [W]	Hold [min]		Hold [min]
800	90		90
Microwave program for re-dissolution of HF containing digests (temperature controlled)			
Power [W]	Temperature [°C]	Ramp. [min]	Hold [min]
1600	80	20	60

Instrumentation and measurement procedures

Determination of elemental concentrations in the sediment digests was performed using an ICP-MS/MS (Agilent 8800, Agilent Technologies, Tokyo, Japan) coupled to an ESI SC-4 DX FAST autosampler (Elemental Scientific, Omaha, Nebraska, USA) equipped with a discrete sampling system with a loop volume of 1.5 mL. A list of measured isotopes and their detection modes, as well as a detailed description of all ICP-MS/MS operating parameters and used cell gas modes can be found in the ESI Table A1 and Table A2,† respectively. In total four different cell gas modes were used: no gas, He, H_2 and O_2, of which O_2 was applied as reaction gas in MS/MS mode. Selection of the analyzed isotope, as well as cell gas mode was based on the achieved sensitivity and occurrence of spectral interferences (isobaric, as well as polyatomic interferences). In depth, extensive reviews about the working principles of ICP-MS/MS and potential isobaric interferences can be found in the literature.[33,34] Based on the presented set-up the analysis of one sample took approx. 240 seconds. The instrument was optimized on a daily basis using a tune solution containing Li, Co, Y, Ce, and Tl (10 $\mu g\ L^{-1}$). Quantification was performed based on external calibration, covering a concentration range from 0.1 $\mu g\ L^{-1}$ to 100 $\mu g\ L^{-1}$ for all analytes. Solutions were prepared on a daily basis from custom made multi-element standards (Inorganic Ventures, Christiansburg, USA). Wash blanks of 2% (w/w) HNO_3 were measured after each sample triplicate to monitor potential carry-over effects.

Data processing and calculations

Multi-element data were processed using MassHunter versions 4.2 to 4.4 (Agilent Technologies, Tokyo, Japan) and a custom-written Excel© spreadsheet. Limits of detection (LOD) (3 × SD) and limits of quantification (LOQ) (10 × SD) of the method were calculated in accordance with MacDougall *et al.* from procedural blanks ($n = 3$).[35] Combined uncertainties with a coverage factor of 2 (U, $k = 2$) were calculated taking into account reproducibility of multiple digests and measurement precision of the samples.

The significant number of digits of mass fractions are given according to GUM and EURACHEM guidelines, whereby the uncertainty determines the significant number of digits to be presented with the value.[36,37]

Zeta sores (ζ) that are usually applied in interlaboratory studies were adapted, in order to provide an easy to grasp overview over the performance of the digestion protocol for each analyte. The zeta sores were calculated according to following equation, with x_{lab} measured mass fraction, X_{ref} certified mass fraction, U_{lab} expanded uncertainty of the measured mass fraction and U_{ref} expanded uncertainty of certified mass fraction. Similar to z scores zeta scores outside ±2 are commonly regarded as questionable. Indeed, if expanded uncertainties are used instead of standard uncertainties zeta scores will only be about one half, leading to the fact that values outside ±1 should be regarded questionable.[38]

$$\zeta = \frac{x_{\mathrm{lab}} - X_{\mathrm{ref}}}{\sqrt{{U_{\mathrm{lab}}}^2 + {U_{\mathrm{ref}}}^2}}$$

Results and discussion

Based on initial experiments, the efficiency of the digest was evaluated in terms of sample weight, temperature and duration of the digestion. For this purpose, samples of 50 mg and 100 mg of NIST SRM 2702 were digested for three hours at a temperature of 180 °C. The resulting data indicates that with the time setting and the amount of acid used, a sample weight of 50 ± 5 mg results in better overall recovery. Therefore, all further experiments were conducted with a sample weight of 50 mg. Experiments showed that temperatures higher than 180 °C may be achieved with the used microwave set-up, but at the cost of evaporation of the digest, due to a possible pressure release during digestion. Since the digestion temperature was limited to 180 °C, it was decided to extend the duration of the digestion to 300 minutes, in order to ensure a quantitative digestion of the matrix.

Recoveries of NIST SRM 2702 for digestion protocols based on HF

In order to develop a quantitative digestion protocol for a large variety of analytes, the marine sediment reference material NIST SRM 2702 was used for method development. This reference material is certified for a large variety of analytes and can be purchased from the National Institute of Standards & Technology (NIST). Fig. 1 shows recoveries for certified elements using *aqua regia*, a mixture of HNO_3 and HF, as well as a mixture of HNO_3, HCl and HF for digestion.

The aim of this first step of method development was the application and comparison of achievable recoveries of different commonly used acid compositions. This includes strongly oxidizing *aqua regia*, which may be used to determine "pseudo total" mass fractions for some analytes, *e.g.* according to ISO 11466:1995 (soil quality – extraction of trace elements soluble in *aqua regia*). Other commonly used acid mixtures for the digestion of geological samples comprise of HNO_3 and HF in varying mixing ratios. HNO_3 is a strong oxidizing agent combined with the capability of HF to dissolve silicate and other refractory oxides. The last acid composition applies HCl in combination with HNO_3 and HF. Hereby, the complexing ability of Cl^- may help to improve recoveries for some elements. Furthermore, HCl is capable of digesting many metal oxides.

Achieved recoveries for the *aqua regia* digest (2 mL HNO_3 and 6 mL HCl) ranged from 14.3% ± 1.4% for Al to 96% ± 8% for Nd, for digests using a mixture of HNO_3 and HF (5 mL/1 mL) from 25% ± 5% for Cs to 107% ± 19% for Cd and for digests using a mixture of HNO_3, HCl and HF (5 mL/2 mL/1 mL) from 8.8% ± 1.6% for Mg to 99% ± 11% for W.

For some analytes, a leaching with *aqua regia* is already sufficient for their quantitative extraction. This is true for selected heavy metals *e.g.* Pb (recovery: 96% ± 6%) or the REE *e.g.* Nd (recovery: 96% ± 8%). Therefore, treatment with *aqua regia* is a commonly used method for the determination of selected heavy metals in sediments, *e.g.* when looking for the maximum bioavailable fraction. Nevertheless, leaching efficiency highly depends on the matrix composition of the digested sediments, as *aqua regia* does not dissolve silicates and other refractory oxides. Results might therefore be prone to error. As a result, a pure leaching is not sufficient for a multi-element analysis, when aiming for the fingerprinting of the total elemental composition of the analyzed sediment sample.

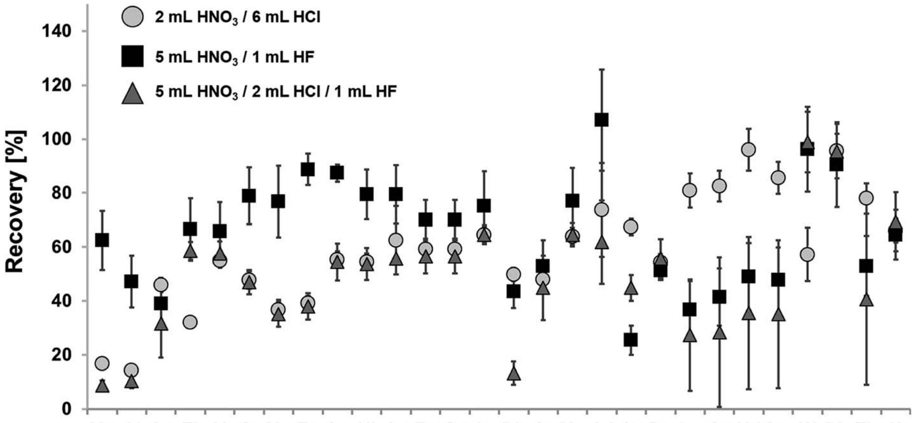

Fig. 1 Recoveries for the digestion of 50 mg of NIST SRM 2702 using different acid mixtures (2 mL HNO_3/6 mL HCl (circle); 5 mL HNO_3/1 mL HF (square); 5 mL HNO_3/2 mL HCl/1 mL HF (triangle)) digested at 180 °C for 300 min. Error bars correspond to expanded uncertainties U ($k = 2$), $n = 3$; if not visible they are in the range of spot size.

Significantly higher recoveries for transition metals (Co, Ni, Cu) can be achieved by using an acid mixture consisting of HNO_3 and HF. Besides, the dissolution of the silicate matrix, HF will also lead to the dissolution of refractory oxides like Cr_2O_3 and Fe_2O_3, thus achieving significantly higher recoveries for these metals in comparison to a pure leaching with *aqua regia*. On the other hand, the formation of insoluble fluoride precipitates, mainly consisting of Mg, Al, Ca and Na fluorides, during HF digestions has been described in the literature.[25] Therefore, co-precipitation of certain elements like Rb, Sr, Cs, Ba, REE or Th may occur. This hinders the accurate determination of these elements, as displayed in Fig. 1. One way to suppress this effect may be the addition of Mg. Takei *et al.* attributed a reduced fluoride formation to the ratio of Mg and Ca to Al.[39] However, this procedure has the disadvantage that Mg cannot be an analyte and it additionally introduces a risk of contamination due to impurities of the used Mg salt.

Similar observations can be made for an acid mixture containing HNO_3, HCl and HF. Again, recoveries especially for the REE are not quantitative. Furthermore, overall recoveries for almost all elements are significantly lower than for the acid composition containing only HNO_3 and HF. During this work, digests containing HF were evaporated and re-dissolved prior to analysis *via* ICP-MS, which is necessary in order to remove unreacted HF from the sample solution. Indeed, this step may also lead to the loss of volatile analytes such as Hg.

Taking into account the results of the applied acid mixtures, it was decided to proceed the method development with an acid mixture of 5 mL HNO_3 and 2 mL HCl for the following replacement of HF with HBF_4. Even though, the acid mixture of HNO_3 and HF (5 mL/1 mL) achieved higher recoveries for some analytes than the acid mixture of HNO_3, HCl and HF (5 mL/2 mL/1 mL). The addition of HCl is assumed unavoidable for a digestion protocol aiming at the accurate determination of a wide variety of analytes, due to the complexing abilities of Cl^- as most chloride complexes are very stable in aqueous solution.[40]

Digestion protocol based on HBF_4

Fig. 2 shows recoveries for certified elements in NIST SRM 2702 using a mixture of HNO_3, HCl and varying amounts of HBF_4 for digestion. Achieved recoveries for the digest using 0.5 mL of HBF_4 ranged from 58% ± 7% for Sc to 158% ± 20% for As, for digests using 1 mL of HBF_4 from 56% ± 11% for Sc to 237% ± 49% for As and for digests using 2 mL HBF_4 from 45% ± 1% for Mg to 426% ± 40% for As.

All used acid mixtures containing HBF_4 achieved significantly higher recoveries and precision than the afore described acid mixtures. Recoveries were >80% (within uncertainty) for all analyzed elements with the exception of Mg, Al, Sc, Ti, V, Zn, Ga and U. The formation of insoluble fluoride precipitates is significantly lower than for HF-containing digestion protocols, leading to recoveries for Mg of up to 78% ± 4%. Furthermore, co-precipitation of *e.g.* REE can be avoided, leading to quantitative REE recoveries. Nevertheless, co-precipitation may become significant for high amounts of HBF_4, as shown for the acid mixture containing 2 mL HBF_4, leading to low recoveries for Mg and Al (45% ± 1%, 54% ± 3%). The use of HBF_4 also enables the digestion refractory oxides like Cr_2O_3 and Fe_2O_3, resulting in quantitative recoveries for both elements for all acid mixtures (>91% ± 7% Cr, 89% ± 4% Fe). As shown in Table 2, low purity HBF_4 may contain significant amounts of *e.g.* Mn, As, Sr and Mo, which may significantly bias the recoveries of these elements. This is evident in case of As for which recoveries ranged between 158% ± 20% to 426% ± 40%. Therefore, blank contributions of all potential analytes should be monitored on a regular basis.

In conclusion, the mixture of 5 mL HNO_3, 2 mL HCl and 1 mL HBF_4 has been shown to give the most consistent results for the broadest number of elements. Hence, this acid mixture was used for all following considerations.

Achievable LOQ for HBF_4 containing digests

As can be seen in Fig. 2, recoveries for some analytes significantly increase above 100% with increasing HBF_4 amounts *e.g.*

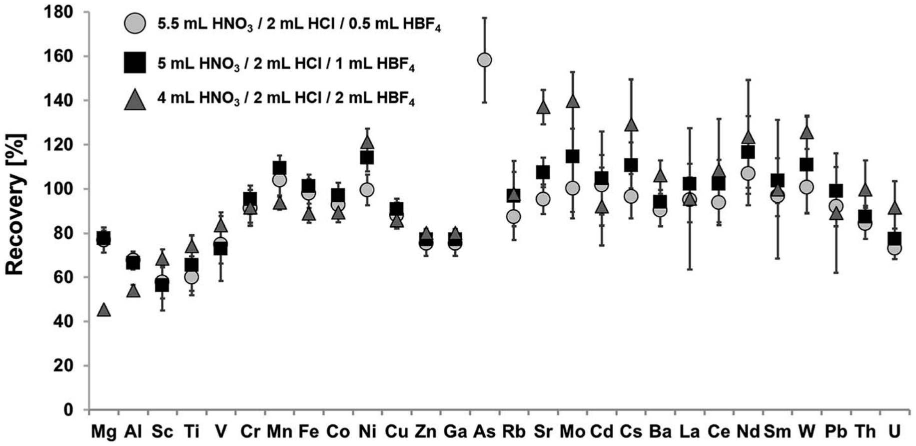

Fig. 2 Recoveries for 50 mg of NIST SRM 2702 sediment for different HBF_4 containing acid mixtures (5.5 mL HNO_3/2 mL HCl/0.5 mL HBF_4 (circle); 5 mL HNO_3/2 mL HCl/1 mL HBF_4 (square); 4 mL HNO_3/2 mL HCl/2 mL HBF_4 (triangle)) digested at 180 °C for 300 min. Values of As for the acid mixtures 5 mL HNO_3/2 mL HCl/1 mL HBF_4 (square) and 4 mL HNO_3/2 mL HCl/2 mL HBF_4 (triangle) are not shown (recoveries: 237% ± 49% and 426% ± 40%). Error bars correspond to expanded uncertainties U ($k = 2$), $n = 3$; if not visible they are in the range of spot size.

Table 2 LOQs of selected analytes for ultrapure HBF_4 and for HBF_4 with unknown purity, based on digestion blanks of 5 mL HNO_3, 2 mL HCl and 1 mL HBF_4 ($n = 3$). Based on the certified elemental mass fractions, the LOQ of each element and a sediment sample weight of 50 mg SRM 2702 the corresponding blank contribution in % was calculated

Element	LOQ [$\mu g\ L^{-1}$] unknown purity HBF_4	Blank contribution [%]	LOQ [$\mu g\ L^{-1}$] ultra pure HBF_4	Blank contribution [%]	Element	LOQ [$\mu g\ L^{-1}$] unknown purity HBF_4	Blank contribution [%]	LOQ [$\mu g\ L^{-1}$] ultra pure HBF_4	Blank contribution [%]
Mg	85	0.9	1.9	0.019	Rb	0.15	0.12	0.02	0.016
Al	32	0.04	6.7	0.008	Sr	22	18	0.02	0.016
Sc	0.4	1.6	0.05	0.17	Mo	3	31	0.02	0.15
Ti	250	2.8	0.2	0.0024	Cd	0.02	2.1	0.011	1.3
V	0.5	0.13	0.03	0.007	Cs	0.9	12	0.02	0.3
Cr	11	3	0.3	0.10	Ba	2.1	0.5	0.014	0.003
Mn	156	9	0.07	0.004	La	0.04	0.06	0.004	0.006
Fe	94	0.13	0.2	0.0003	Ce	0.09	0.08	0.005	0.004
Co	0.14	0.5	0.017	0.06	Nd	0.09	0.16	0.006	0.011
Ni	12	15	0.04	0.06	Sm	0.01	0.14	0.005	0.05
Cu	2.4	2.0	0.11	0.10	W	0.6	10	0.03	0.4
Zn	2.7	0.6	>0.48	>0.10	Pb	0.3	0.19	1.2	0.9
Ga	0.7	2.9	>0.005	>0.021	Th	0.2	1.2	0.08	0.4
As	84	185	0.7	1.5	U	0.5	5	0.002	0.018

As with 426% ± 42%, Sr with 137% ± 8% and Mo with 140% ± 13% for the digestion mixture using 2 mL of HBF_4. This increase can be assigned to impurities of the used HBF_4. In fact, to the authors knowledge, there is currently only one supplier of high purity HBF_4. Unfortunately, high purity HBF_4 was not available for the initial experiments conducted in the previous two chapters. However, this allowed for the comparison of achievable LOQs for two different HBF_4 suppliers, as shown in Table 2. Furthermore, Table 2 shows the corresponding blank contribution in % based on the analysis of 50 mg SRM 2702. This will facilitate an easy comparison of possible blank contributions influencing the elemental recovery for each element.

As enumerated in Table 2, main impurities of the used HBF_4 are Mg, Al, Ti, Mn, Fe, As and Sr. Since Mg, Al, Ti and Fe are main matrix components (% range), possible contaminations are only of minor concern. *E.g.* the blank contribution of Ti for HBF_4 with low purity is 2.8%, which is in the range of the measurement uncertainty, but still significantly lower than the combined uncertainty. Nevertheless, significantly higher recoveries (>100%) were observed for elements like Ni, As and Sr or Mo which are clearly associated with high blank levels of these elements. The blank contribution (Ni: 15%, As: 185%, Sr: 18%, Mo: 31%) of these elements significantly influence the achieved recoveries, thus leading to wrong results. High purity HBF_4 blank levels of these elements are significantly lower, thus minimizing possible contamination. The highest blank contribution of 1.5% for use of the high purity HBF_4 was found for As. With the exception of Cd, Cs, W, Pb and Th blank contributions of all other analyzed elements are lower than 0.2%. Even if the use of low purity HBF_4 is sufficient for correct quantification of many elements, a universal multi-elemental digestion protocol clearly benefits from high purity HBF_4. If high purity HBF_4 is not available, careful blank monitoring of all analytes is advisable.

Reference materials digested with optimized digestion protocol

The developed digestion protocol using 5 mL HNO_3, 2 mL HCl and 1 mL high purity HBF_4 was applied for the analysis of different other sediment reference materials (GBW 07313, GBW 07311 and JMS-2). Results for all analyzed elements can be found in Table 3. All three reference materials were quantitatively digested by the optimized digestion protocol, resulting in clear particle-free digests.

In order to give a first overview over the overall performance of the developed digestion protocol Table 4 presents zeta scores for all certified elements of the three analyzed reference materials. Within this context a value outside of ±1 is usually regarded as questionable, as in this case zeta scores were calculated based on combined uncertainties.[38] It should be emphasized that proficiency testing tools like the zeta score are usually used within a different context *e.g.* for long term inter-laboratory studies, as zeta scores may easily demonstrate the performance of a laboratory/method. However, a low zeta score does not necessarily indicate good quality of analytical results,

Table 3 Measured and certified mass fractions of the analyzed reference materials GBW 07313 ($n = 35$), GBW 07311 ($n = 17$) and JMS-2 ($n = 18$). Errors correspond to expanded uncertainties U ($k = 2$)

	GBW 07313 ($n = 35$)			GBW 07311 ($n = 17$)			JMS-2 ($n = 18$)		
Element	Measured [mg kg^{-1}]	Certified range [mg kg^{-1}]	Recovery [%]	Measured [mg kg^{-1}]	Certified range [mg kg^{-1}]	Recovery [%]	Measured [mg kg^{-1}]	Certified range [mg kg^{-1}]	Recovery [%]
Be	1.8 ± 0.6			25 ± 8	26 ± 3	95	1.6 ± 0.3	1.8 ± 0.1	90
Mg	19 000 ± 5000	20 400 ± 300	93	3300 ± 800	3700 ± 400	89	16 000 ± 3000	19 540 ± 120	80
Al	69 000 ± 13 000	72 800 ± 500	95	40 000 ± 26 000	54 900 ± 500	72	53 000 ± 26 000	75 000 ± 500	70
P	1500 ± 500	2000 ± 100	75	219 ± 26	255 ± 27	86	5800 ± 500	5500 ± 90	105
K	24 000 ± 5000	24 500 ± 400	98	28 000 ± 5000	27 200 ± 600	101	18 800 ± 2700	22 410 ± 170	84
Ca				3400 ± 700	3360 ± 210	100	32 000 ± 4000	33 500 ± 400	97
Sc	27 ± 5	25.6 ± 2.9	105	4 ± 4	7.4 ± 0.4	50	18 ± 13		
Ti	4000 ± 900	4000 ± 100	100	2000 ± 700	2100 ± 100	97	8100 ± 700	8391 ± 120	97
V	110 ± 18	112 ± 5	98	49 ± 6	47 ± 3	104	187 ± 14	183 ± 3	102
Cr	61 ± 10	58.4 ± 1.3	104	44 ± 8	40 ± 3	109	77 ± 8	78 ± 1	98
Mn	3300 ± 700	3300 ± 100	100	2700 ± 400	2490 ± 80	110	16 000 ± 1600	17 500 ± 160	91
Fe	45 000 ± 8000	46 000 ± 500	98	32 000 ± 5000	30 700 ± 500	106	68 000 ± 700	76 700 ± 600	89
Co	78 ± 14	76.7 ± 1.2	102	9.3 ± 1.1	8.5 ± 0.8	110	224 ± 13	226 ± 2	99
Ni	150 ± 28	150 ± 4	100	16.9 ± 2.1	14.3 ± 1.0	118	301 ± 21	311 ± 3	97
Cu	390 ± 70	424 ± 8	92	80 ± 10	79 ± 3	102	368 ± 22	447 ± 2	82
Zn	150 ± 25	160 ± 3	94	333 ± 40	373 ± 14	89	123 ± 7	166 ± 2	74
Ga	28 ± 5	23.7 ± 1.7	118	20.5 ± 2.2	18.5 ± 0.9	111	25 ± 4		
As	10.0 ± 1.4	5.8 ± 0.8	172	217 ± 29	188 ± 13	116	39 ± 4	35 ± 1	112
Rb	100 ± 17	97.3 ± 2.6	103	490 ± 110	408 ± 11	124	65 ± 22	65 ± 1	99
Sr	260 ± 60	267 ± 15	97	35 ± 4	29 ± 4	119	491 ± 30	454 ± 4	108
Zr	150 ± 23	177 ± 10	85	70 ± 17	153 ± 13	46	210 ± 18	220 ± 3	95
Mo	7.3 ± 1.1	7.2 ± 0.5	101	7.2 ± 0.8	5.9 ± 0.6	121	23 ± 2		
Ag	0.11 ± 0.03			3.2 ± 0.3	3.2 ± 0.4	99	0.26 ± 0.03		
Cd	0.38 ± 0.09			2.2 ± 0.5	2.3 ± 0.2	94	0.44 ± 0.07		
Sb	2.5 ± 0.5	1.9 ± 0.4	135	23 ± 3	14.9 ± 1.2	154	5.6 ± 0.5	4.5 ± 0.2	124
Te	0.32 ± 0.10			0.7 ± 0.5	0.40 ± 0.10	181	1.5 ± 0.7	1.38 ± 9	109
Cs	9.1 ± 1.4	9.4 ± 0.7	97	21 ± 3	17 ± 1	120	3.5 ± 0.3	3.0 ± 0.2	116
Ba	4500 ± 1000	4400 ± 200	102	260 ± 340	260 ± 17	102	1881 ± 124	1856 ± 16	101
La	71 ± 10	67.8 ± 2.9	105	23 ± 10	30 ± 2	79	107 ± 52		
Ce	96 ± 15	92 ± 8	104	50 ± 16	58 ± 4	86	133 ± 48		
Pr	22 ± 3	20.1 ± 1.9	109	6.3 ± 2.2	7.4 ± 0.5	85	31 ± 9		
Nd	93 ± 13	92 ± 4	101	24 ± 8	27 ± 2	89	135 ± 38		
Sm	22 ± 3	21.5 ± 1.3	102	7.2 ± 2.5	6.2 ± 0.3	116	38 ± 10		
Eu	5.8 ± 0.9	5.3 ± 0.3	109	0.7 ± 0.3	0.60 ± 0.06	124	10.1 ± 2.4		
Gd	23 ± 3	22.0 ± 1.2	105	7.2 ± 2.8	5.9 ± 0.4	121	45 ± 12		
Tb	3.6 ± 0.5	3.4 ± 0.3	106	1.2 ± 0.5	1.13 ± 0.09	108	7.2 ± 1.6		
Dy	21 ± 3	19.9 ± 1.8	106	7 ± 3	7.2 ± 0.6	101	43 ± 9		
Ho	4.1 ± 0.6	4.3 ± 0.2	95	1.4 ± 0.6	1.4 ± 0.2	98	8.6 ± 1.6		
Er	12.0 ± 1.6	11.0 ± 0.7	109	4.1 ± 1.8	4.6 ± 0.5	90	25 ± 4		
Tm	1.60 ± 0.22	1.54 ± 0.14	104	0.6 ± 0.3	0.74 ± 0.09	86	3.3 ± 0.5		
Yb	10.00 ± 1.4	9.8 ± 1.1	102	4.3 ± 1.9	5.1 ± 0.6	85	21 ± 4		
Lu	1.60 ± 0.22	1.46 ± 0.19	110	0.6 ± 0.3	0.78 ± 0.06	82	3.3 ± 0.5		
W	5.7 ± 0.8	5.5 ± 0.6	104	133 ± 16	126 ± 9	106	6.2 ± 0.5		
Tl	0.97 ± 0.20			2.9 ± 0.4	2.9 ± 0.4	99	2.67 ± 0.18		
Pb	29 ± 8	29.3 ± 1.1	99	690 ± 150	636 ± 22	111	84 ± 12	88 ± 2	96
Bi	0.92 ± 0.19			63 ± 9	50 ± 4	126	1.45 ± 0.09		
Th	14 ± 4	13.9 ± 1.1	101	22 ± 10	23.3 ± 1.2	95	11 ± 10		
U	1.7 ± 0.3	2.0 ± 0.5	86	10.2 ± 1.4	9.1 ± 0.9	112	2.92 ± 0.21		

by stating an unrealistically high uncertainty zeta scores may be artificially decreased. Therefore, zeta scores presented here are meant to give a first comprehensive overview in order to easily identify the performance for each analyte of the developed digestion protocol. For elemental mass fractions certified in all three analyzed reference materials only zeta scores for Sb were outside ±1 for all three materials. For the elements As and Cs, two of three reference materials were outside the range of ±1. Considering the analysis of 48 elements in total, the presented zeta scores already underpin the multi-elemental capabilities of the developed digestion protocol.

This is also reflected in almost quantitative recoveries for the main components Mg, Al, P, K, Ca, and Fe (<70%), even though relative combined uncertainties of the results are significantly

Table 4 Zeta-scores for all certified elements of the analyzed reference materials GBW 07313 ($n = 35$), GBW 07311 ($n = 17$) and JMS-2 ($n = 18$)

Zeta-score ζ			
Element	GBW 07313 ($n = 35$)	GBW 07311 ($n = 17$)	JMS-2 ($n = 18$)
Be		−0.15	−0.49
Mg	−0.30	−0.45	−1.18
Al	−0.29	−0.57	−0.85
P	−0.96	−0.97	0.59
K	−0.11	0.16	−1.33
Ca		0.05	−0.37
Sc	0.24	−0.84	
Ti	0.00	−0.14	−0.41
V	−0.11	0.27	0.25
Cr	0.26	0.45	−0.15
Mn	0.00	0.56	−0.93
Fe	−0.12	0.34	−9.44
Co	0.09	0.60	−0.19
Ni	0.00	1.15	−0.46
Cu	−0.52	0.14	−3.52
Zn	−0.40	−0.95	−5.92
Ga	0.76	0.84	
As	2.60	0.93	1.09
Rb	0.16	0.74	−0.02
Sr	−0.12	0.96	1.20
Zr	−1.08	−3.92	−0.58
Mo	0.08	1.24	
Ag		−0.06	
Cd		−0.27	
Sb	1.07	2.87	2.14
Te		0.70	0.18
Cs	−0.19	1.35	1.23
Ba	0.10	0.00	0.20
La	0.31	−0.67	
Ce	0.24	−0.45	
Pr	0.52	−0.50	
Nd	0.09	−0.36	
Sm	0.16	0.39	
Eu	0.55	0.55	
Gd	0.28	0.45	
Tb	0.34	0.19	
Dy	0.32	0.02	
Ho	−0.34	−0.05	
Er	0.57	−0.26	
Tm	0.23	−0.36	
Yb	0.11	−0.40	
Lu	0.48	−0.50	
W	0.20	0.40	
Tl		−0.04	
Pb	−0.04	0.36	−0.30
Bi		1.35	
Th	0.03	−0.12	
U	−0.48	0.67	−0.49

higher than for trace components. Measured mass fractions of "classical" heavy metals such as Co, Ni, Cu, Zn, Cd or Pb all overlapped within the stated uncertainties with the certified values (except Cu and Zn for JMS-2). The use of HBF_4 as fluorine source also achieves the digestion of refractory oxides like Cr_2O_3 and ZrO_2, which are challenging to dissolve. Measured mass fractions of Cr and Zr overlapped within the stated uncertainties with the certified values (except Zr for GBW 07311).

The quantitative recovery of elements like Rb, Sr, Ba, Cs, which are known to suffer from non-quantitative recoveries due to fluoride co-precipitation, indicates no formation of insoluble fluorides during the presented digestion protocol, which can be explained by the equilibrium between HBF_4, free HF and free H_3BO_3 during digestion. Moreover, this also results in quantitative recovery of all REE.

Conclusion

With the continuously improving multi-element capabilities of modern ICP-MS(/MS) instruments the quasi-simultaneous analysis of most elements of the periodic table became possible. Besides the analysis of classical heavy metals such as Cu, Zn, Cd and Pb the same sample can now be analyzed for a large set of elements without significantly increasing analysis time, which opens challenging new research questions in various scientific fields, *e.g.* the analysis of TCE in environmental matrices or multi-element trace and fingerprint analysis. However, this requires validated sample preparation protocols specifically designed for such kind of multi-element analysis.

Sample preparation, including sample dissolution can still be regarded as the bottleneck during elemental analysis. Up to now, the majority of digestion protocols is based on the use of HF, in order to dissolve the silicate matrix and refractory oxides. Nevertheless, loss of specific analytes due to fluoride co-precipitation have been reported, making it difficult to establish multi-elemental extraction procedures for specific analytes. Furthermore, the acute toxicity of HF requires careful sample handling or its use is restricted in many labs which requires additional sample preparation steps like evaporation and re-dissolution. The presented digestion protocol uses the less dangerous and non-acute toxicity source of fluoride HBF_4, thus risks of handling HF-containing solutions is greatly decreased. During digestion, HF is generated *in situ* and excess fluoride ions are directly complexed by *in situ* generated H_3BO_3. Therefore, digests can be directly measured *e.g. via* ICP-MS without the need of further sample preparation steps or HF resistant sample introduction systems. Based on the same reaction the formation of fluoride precipitates is also minimized, as free HF during digestion either reacts with the sample or is being neutralized by H_3BO_3 to form HBF_4 again. Thus, sample digestion based on HBF_4 is suitable for the quantification of a large variety of elements with a minimum of sample preparation steps.

In comparison to other multi-elemental digestion protocols based on the use of *e.g.* a combination of HNO_3, HCl and HF, LOQs of the presented HBF_4 based digestion protocol are comparable (*e.g.* Ni: 0.016 $\mu g\ L^{-1}$ *vs.* 0.04 $\mu g\ L^{-1}$ for this study) or even lower (*e.g.* Fe: 1.70 $\mu g\ L^{-1}$ *vs.* 0.2 $\mu g\ L^{-1}$ for this study).[41] Similar studies dedicated to the multi-elemental analysis of sediment reference materials achieved comparable mass fractions for a large variety of analytes. *E.g.* Fiket *et al.* analyzed 46 elements in sediment and soil reference materials including the reference material GBW 07311 analyzed in this study. For 31 analyzed elements of the reference material GBW 07311 recoveries ranged from 90% (Tl) to 104% (Ag), based on the use of 4 mL HNO_3, 1 mL HCl and 1 mL HF.[42] Roje *et al.* analyzed the mass fractions of 26 elements of the reference material GBW 07311 based on different acid composition (HNO_3, *aqua regia* and a mixture of HNO_3, HCl and HF) and reported recoveries ranging from 9% (Sn) to >100% (Ag, Be, Bi, Li, Mn, Pb, Ti).[41]

As a future application, the new digestion protocol may also be used for the dissolution of geological samples for isotope ratio analysis *e.g.* Sr, Nd or Pb in isotope geochemistry. As a proof of principle, the presented digestion protocol has already been applied within this context.[43] Furthermore, large-scale environmental studies analyzing *e.g.* sediment samples will benefit from easier sample preparation and improvements in analysis and sample preparation time. Therefore, the presented study proposes use of HBF_4 as alternative to HF for the digestion of sediments during environmental analysis. Specifically, a mixture of 5 mL HNO_3, 2 mL HCl and 1 mL HBF_4, which allows the routine microwave-assisted digestion of a 50 mg sediment sample, which is sufficient for multi-element analysis as demonstrated for a variety of reference materials.

Future studies should also further evaluate the suitability of the substitution of HF by HBF_4 for the digestion of other geological matrices like different types of rock samples, soil samples or dusts.

Conflicts of interest

The authors have no competing interests to declare.

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