Efficiency of acid digestion procedures for geochemical analysis of tungsten mining wastes

Zhengdong Han¹, Mansour Edraki¹*, Ai Duc Nguyen² and Marietjie Mostert²

¹Centre for Mining Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, St Lucia, QLD 4072, Australia
²School of Earth & Environmental Sciences, The University of Queensland, St Lucia, QLD 4072, Australia

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Abstract: There is an increasing global demand for tungsten, which is a critical element used in various industries. Tungsten has wide applications across the mining, metalworking, petroleum, construction, jewellery and aerospace industries with few replacement opportunities. Scheelite and wolframite are the two main minerals for tungsten production, containing 0.08–1.5% tungsten trioxide (WO₃) (Mulenshi et al. 2019). The increasing demand for tungsten commodities in recent years (Dvořáček et al. 2017) has triggered increased production of tungsten and generation of large amounts of processing waste around the world, which pose threats to soil, water and air, and potential risks to human health (Liu et al. 2015). To avoid the potential risks from tungsten tailings and understand its geochemistry and mode of occurrence in mine tailings, analytical techniques such as inductively coupled plasma optical emission spectroscopy (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are commonly used to characterize tungsten tailing materials. However, it is challenging to achieve complete dissolution of tungsten minerals through regular acid digestion methods, because scheelite and wolframite react with strong acids such as nitric acid (HNO₃), hydrofluoric acid (HF), and hydrochloric acid (HCl) to generate water-insoluble tungstic acid (H₂WO₄) (Shen et al. 2019). When 2% nitric acid is employed as the matrix to prepare ICP analysis samples, unlike other totally digested minerals, a visible yellowish tungstic acid precipitate is repeatedly generated, which significantly impacts the elemental results. In the literature, several methods have been suggested to achieve total digestion of tungsten minerals, such as sulphuric–phosphoric acid (H₂SO₄–H₃PO₄) mixed-acid digestion (Chen et al. 2020), sulphuric–hydrogen peroxide (H₂SO₄–H₂O₂) solution digestion (Zhang et al. 2020), caustic soda (NaOH) digestion (Queneau et al. 1982), and ammonium carbonate (NH₄)₂CO₃ solution digestion (Xiangming et al. 2018). However, it is technically difficult to obtain a high-purity grade of these reagents, as they cannot be redistilled in the laboratory and usually contain non-negligible impurities, which could introduce significant interference and result in overestimation of element concentrations, especially for trace element analysis. For example, it has been reported that analytically pure H₂SO₄ contains 0.0001 to 0.0005 mg kg⁻¹ heavy metals like cadmium, copper, manganese, nickel, lead and zinc (Cd, Cu, Mn, Ni, Pb and Zn) and 0.0001 mg kg⁻¹ arsenic (As) (Tabekh et al. 2012). Therefore, these methods cannot be considered as appropriate analytical digestion methods for tungsten tailing trace element analysis.

In this research, we implemented highly purified reagents to test and digest certified reference materials (CRMs) and tungsten tailing samples in an ultra-clean lab of the Radiogenic Isotope Facility at The University of Queensland. The newly developed tungsten tailings digestion procedures applied more concentrated HCl in the matrix to increase the concentration of sodium chloride (NaCl) at low pH, which will effectively improve tungstic acid solubility (Wesolowski et al. 1984). The tungsten tailing samples were completely digested, as demonstrated by a much better recovery of tungsten in comparison to other common rock sample digestion methods.

Experiment

Reagents and vessels

All HNO₃, HF and HCl used in this research were produced by Thermo Fisher Scientific, for ultra-trace element analysis. Alkali fusion flux, lithium metaborate (LiBO₂), lithium tetraborate (Li₂B₄O₇) and lithium bromide (LiBr) were purchased from Sigma Aldrich, all purities ≥99.9%. The deionized water used was Milli-Q™ reference ultrapure water, generated by a Fisher scientific MilliporeSigma™ Milli-Q™ Reference Ultrapure Water Purification System and had a resistivity of 18.2 MΩ cm.
All HNO₃, HF and HCl were double (sub-boiling) distilled, and the concentrations used in experiments were 70% (15.8 mol l⁻¹), 50% (29.0 mol l⁻¹) and 36% (11.6 mol l⁻¹), respectively. Research-grade argon (99.999%) and helium (99.999%) were supplied by Coregas (Darra, QLD, Australia).

The vessels used in this research were all acid cleaned. Falcon tubes (50 ml) were first soaked in 10% nitric acid for a week, then cooked with Milli-Q water at 220°C on a hotplate for one day; 10 ml ICP tubes were first cooked with 20% nitric acid at 220°C for one day on a hotplate, rinsed with Milli-Q water, and then cooked with Milli-Q water at 220°C for one more day. Polytetrafluoroethylene (PTFE) beakers were sequentially cooked with 5% Decon solution, 30% aqua regia, 35% nitric acid, and lastly with Milli-Q water on a hotplate at 300°C. Each step of the cleaning procedure ran overnight and involved rinsing with deionized water before the next. All vessels were dried in a fume hood and packed for analysis.

**Instruments (ICP-OES and ICP-MS)**

The elemental compositions of tungsten tailing samples, a tungsten tailing acid mine drainage (AMD) sediment sample, and CRMs were determined by ICP-OES (Perkin Elmer, Optima 8300), generally following US EPA Method 6010C with modifications for tungsten waste samples. The plasma was working at 1450 W, and the nebulizer gas flow rate was 0.70 ml min⁻¹. The concentration of tungsten was determined by a 207.912 nm emission line after correction for 187Re as internal standard. The other elements were determined through US EPA Method 3050B with modifications for tungsten waste samples. In this research, hotplate digestion was accomplished by acid attack under low pressure in screw-capped PTFE vessels. However, hotplate digestion is not considered to be a total digestion method for most rock and tailing samples, although it is a strong acid digestion that can extract most elements. Aluminium, antimony, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, vanadium, magnesium, manganese, molybdenum, nickel, sodium and zinc (Al, Sb, Ba, Be, Cd, Ca, Cr, Co, Cu, Fe, Pb, V, Mg, Mn, Mo, Ni, Na and Zn) are the recommended elements to be determined through US EPA Method 3050B. But it is also reported that if a precipitate is present in the solution after hotplate digestion, there will be an underestimation of rubidium, strontium, caesium, barium, rare-earth elements (REEs), lead, thorium and uranium (Rh, Sr, Cs, Ba, REEs, Pb, Th and U) (Okina et al. 2018). Tungsten, which is less often sought as an analyte, was also found to be underestimated using hotplate digestion.

**Bomb digestion**

Bomb digestion is a frequently used closed-vessel digestion method. The procedure is as follows: place 0.1 g sample in the PTFE vessel, add oxidizing reagents, and cap the PTFE vessel. The PTFE vessels are then coated with bomb jackets and closed by tightening the screw cap (Colina et al. 1996). In bomb digestion, temperature and pressure can have synergic effects to effectively decompose refractories, while an open-vessel acid digestion system results only in partial decomposition (Hu 2014). This pressurized wet digestion system is considered to be the most advanced sample decomposition method for trace element determination (Flores et al. 2007). Sediments, soils and rock samples can be completely dissolved in this pressurized PTFE vessel acid digestion system (Zhang et al. 2007). This method can also reduce the consumption of reagents and avoid contamination (Alsleleh et al. 2018). In this research, for better analysis of trace elements, after bomb digestion, the vessels were opened, and silica was removed as a volatile in the form of silicon tetrafluoride (SiF₄) on a hotplate.

**Coldblock™ digestion**

ColdBlock™ digestion is a novel sample digestion method that implements intense short-wavelength infrared (IR) radiation lamps to digest samples that transmit IR energy directly to the surface of the sample particles to digest. The cooling block on the top of the digestion vessels is another major part of ColdBlock™, which can create a condensation effect to reduce the loss of volatile elements and acid by evaporation. ColdBlock™ digestion provides much faster, safer and more flexible sample digestion compared to other
existing digestion methods (Wang et al. 2014). However, a drawback of this method is that the vessels are made of quartz and quartz-rich samples cannot be fully digested because highly concentrated hydrofluoric acid cannot be introduced during digestion to break down and remove silica. Particularly in this research, tungsten minerals and other minerals not fully liberated from quartz would show an obvious underestimation of element concentrations. The CB15S ColdBlock™ digester (maximum power input 30 A, 230 V, 50 Hz, with timer) used in this research is manufactured by DKSH, Australia.

Alkali fusion

Alkali fusion is a good option for samples rich in refractory minerals, which cannot be decomposed by acids. Lithium metaborate ($\text{LiBO}_2$) is a non-oxidative alkali flux and a kind of plain flux usually used in most fusion experiments for ICP-OES analysis. It can be used as a flux to decompose all rock-forming minerals and most accessory minerals in rock samples (Hu and Qi 2014). For tailings and rock samples that could be readily decomposed by fusion flux, $\text{LiBO}_2$ could be used as a single flux to decompose samples. Nevertheless, in this research, beads created by tungsten tailings fused with a single $\text{LiBO}_2$ flux cannot fully dissolve in a 5% HNO$_3$ solution, and undissolved brown to black particles were usually found in the bottom of the beakers. Under this circumstance, a strong flux (a mixture of $\text{LiBO}_2$, $\text{Li}_2\text{B}_4\text{O}_7$, and $\text{LiBr}$, ratio = 2:2:1) was applied to fuse tungsten waste samples and CRMs and, as a result, all glass beads were fully dissolved in 5% nitric acid solution (Mostert et al. 2017). However, due to the strong flux introducing a mixture of impurities, it was only used to determine major element concentrations and was not suitable for trace element analysis. Alkali fusion is also not a feasible sample preparation method for ICP-MS because fusion solutions are rich in salt content, which will contaminate the instrument in the process of measurement (Okina et al. 2018). In addition, a high concentration of Li and B in the solution will severely contaminate the ICP-MS.

Calibration and quality control

The calibration standards used in this research are NIST-traceable standards from High-Purity Standards. Elements including the

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**Table 1. Procedures of sample digestions and fusion used in this research**

| Step | Hotplate | Bomb | ColdBlock™ | Fusion |
|------|----------|------|------------|--------|
| 1    | 0.1 g aliquot of the sample powder in PTFE beaker with screwcap. | 0.1 g aliquot of the sample powder in bomb PTFE beaker with cap. | 0.1 g aliquot of the sample powder in a quartz tube with PTFE watch glass. | 0.1 g aliquot of the sample with the platinum beaker. |
|      | 2 ml 70% nitric acid heat at 140°C overnight, dry out at 90°C. | 3 ml 70% nitric acid heat at 90°C overnight, dry out at 90°C. | 5 ml 70% nitric acid + 2 ml 36% hydrochloric acid, heat by 50% power (maximum power 7 kW) for a total of 16 min. | Sample first ignited at 1000°C in the furnace for 6 hours. |
| 2    | 1 ml 70% nitric acid + 3 ml 50% hydrofluoric acid heat at 140°C overnight, dry out at 90°C. | 1 ml 70% nitric acid + 3 ml 50% hydrofluoric acid heat at 140°C overnight, dry out at 90°C. | Wait 10 minutes to cool down and take the PTFE watch glass off. | Mixed with 2.5 g strong flux (lithium metaborate, lithium tetraborate, lithium bromide, ratio = 2:2:1). |
| 3    | 2 ml 1:1 hydrochloric acid heat at 140°C overnight. | 1 ml 70% nitric acid + 3 mL 50% hydrofluoric acid, heat at 185°C in the oven for two days. Dry out at 90°C after bomb digestion. | Take the quartz tube out of the holder and decant the aliquot solution to a 50 ml acid-cleaned Falcon tube. | Fuse in the furnace at 1200°C for 10 min. |
| 4    | Cool down capped PTFE beakers and add 1 ml 70% nitric acid heat at 140°C overnight, dry out at 90°C. | 3 ml 36% hydrochloric acid heat at 140°C overnight, dry out at 90°C. | Rinse quartz tube three times with Milli-Q water and quantitatively transfer contents to Falcon tube. Add 70% nitric acid to make the final 5% nitric acid matrix. | Dissolve glass bead in 100 ml 5% nitric acid solution. |
| 5    | 2 ml 6 mol L$^{-1}$ nitric acid heat at 140°C overnight. | 1 ml 70% nitric acid + 3 ml 36% hydrochloric acid (aqua regia) heat at 140°C overnight, dry out at 90°C. | Centrifuge Falcon tube and transfer 10 ml supernatant to ICP tube. | Transfer 50 ml aliquot supernatant to Falcon tube. |
| 6    | Cool down and quantitatively transfer the aliquot from PTFE beakers to 10 ml ICP tubes. Centrifuge the ICP tubes at 4000 rpm for 5 min. | 3 ml 36% hydrochloric acid heat at 140°C, frequently check the precipitates in the bottom of the beakers, until the solution is clear, with no visible precipitation. | Transfer 10 ml supernatant to Falcon tube. | Transfer 10 ml solution from Falcon tube to ICP tube. |
| 7    | Transfer 5 ml superannuants to new acid cleaned 10 ml ICP tubes and make up to 10 ml with the nitric acid matrix. The final matrix is 5% nitric acid. | Dilute the aliquot solution with Milli-Q water to 20% hydrochloric acid matrix and make a further dilution of 20% hydrochloric acid to the 10 ml for analysis. | | |
REEs were calibrated through multi-element calibration standards; only Bi, Mo and W were calibrated by single calibration standards, all at 10, 5, 1, 0.5, 0.25, and 0.1 mg l$^{-1}$ for each element. Scandium (Sc) (1 mg l$^{-1}$), yttrium (Y) (1 mg l$^{-1}$) and lutetium (Lu) (3 mg l$^{-1}$) were used as internal standards for instrumental drift correction. The REEs were calibrated through NIST-traceable standard from High-Purity Standards, at 10, 5, 1, 0.5, 0.25 and 0.1 mg l$^{-1}$ of each element, and 2 mg l$^{-1}$ silver (Ag) was used as an internal standard for instrumental drifts correction. The ICP-MS was calibrated using standards of 100, 50, 25, 10, 1 µg l$^{-1}$ for instrumental drifts correction during analysis. The ICP-OES and ICP-MS calibration responses were linear, and the correlation coefficients of all elements in the ICP-OES analysis were above 0.999, while those in the ICP-MS analysis were above 0.9999. Calibration verification generally follows EPA method 6010C with modifications for tungsten waste samples. An independent mid-concentration calibration standard (3.000 and 0.030 mg l$^{-1}$ for ICP-OES and ICP-MS, respectively) was used as a blank spike sample in each experiment, which was diluted from NIST-traceable calibration standards using the same matrix as the samples. These spike samples were also analysed in the middle of the experiments to calculate blank spike recoveries of each element. All calculated element recoveries were within the error range of ±10% of the certified values. More than seven instrumental blanks in each experiment, which were made from the same acid matrix as the test samples, were analysed to determine the detection limits of each element in each experiment. Procedural blanks were analysed to calculate the digestion and fusion blanks of each element in each experiment. One in every 10 samples was analysed in duplicate or larger numbers of replicates to assess the reproducibility. A monitor solution with the same matrix was frequently analysed to correct for any additional drift of the instrument.

Results

Major elements

Aluminium, Ca, Fe, K, Mg, Mn and Na in the tailing samples and CRMs, which are usually present at contents greater than 1%, were defined as the major elements in this research. The experimental data for two CRMs, two tungsten tailing samples, and one tungsten AMD sediment sample were used to compare the three different digestion methods and fusion. Because there is no certified tungsten tailing and AMD sediment reference material, one pyroxenite rock (SARM5) and one marine sediment (MESS3) CRM were chosen as reference materials to simulate tungsten tailing and AMD sediment CRMs. The results are listed in Tables 2 and 3.

The tungsten tailing samples, the tungsten AMD sediment sample, and the CRMs were totally decomposed by fusion and bomb digestion, and no visible precipitate was observed in digestion and fusion vessels or in tubes after dilution, whereas the hotplate digestion and ColdBlock$^\text{TM}$ digestion did not offer complete digestion. Therefore, precipitates were not detected in the test samples, which were analysed to determine the detection limits of each element. Procedural blanks were analysed to calculate the digestion and fusion blanks of each element in each experiment. One in every 10 samples was analysed in duplicate or larger numbers of replicates to assess the reproducibility. A monitor solution with the same matrix was frequently analysed to correct for any additional drift of the instrument.

| Table 2. Comparison of digestion procedures and fusion for major element analysis of different standard reference materials |
|-----------------|-----------------|-----------------|
|                  | Digestion (%)   | Fusion (%)      |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
|                  | Recovery (%)    | Recovery (%)    |
|                  | (mg l$^{-1}$)   | (mg l$^{-1}$)   |
|                  | (%)             | (%)             |
digestion blanks of bomb digestion and hotplate digestion were below the detection limits of all elements and therefore the influence of backgrounds can be ignored in major element analysis. Analyte recoveries of the blank spikes are within ±10% of the certified values.

Table 2 lists the results for major elements in two CRMs. Alkali fusion had the best recoveries of all major elements for CRMs, the values being within ±10% of the certified values. It is therefore the best method for major element determination in the lab. However, it should also be noted that some of the major element chlorides are volatile. When carrying out bomb digestion, constantly drying out concentrated HCl matrix sample solutions in PTFE beakers in search of the appropriate concentration of HCl matrix to achieve total digestion can result in volatile chloride evaporation losses and low element recovery, particularly for elements such as Al, Fe and Mg. This is consistent with previous research showing that aluminium chloride (AlCl₃) goes to the gas phase when the temperature reaches 130°C, while iron chloride (FeCl₃) evaporates at a similar rate at this temperature (Lee et al. 2011), and magnesium chloride (MgCl₂) generates evaporation loss at 140°C (Li et al. 2016). While hotplate digestion and ColdBlock™ digestion provide incomplete digestion, the recoveries shown in the table were also not as good as fusion.

Because there were no recommended values for two tungsten tailing samples and one AMD sediment sample, all measured values are listed in Table 3. The data indicate the same trend as the CRM analysis results, i.e., fusion has the best recovery of all elements. The results are also shown in Figure 2 with error bars. From this table and the figures, it seems that the results of fusion are the best decomposition method for analysis by ICP-OES of major elements in tungsten tailing and AMD sediment samples.

**Trace elements**

The trace elements in CRMs, tungsten tailing and AMD sediment samples were determined in the same way as the major elements. As mentioned above, because alkali fusion can introduce interference for trace element analysis, fused samples were not tested for trace elements. All 21 available trace elements of the CRMs were measured using the three different digestion methods, and the recommended values of elements were obtained from the CRM certificates, and GeoReM (Jochum et al. 2005). The results are presented in Table 4.

Most of the trace elements in digestion blanks from the three digestion methods were below the detection limit while the elements detectable were also at very low levels, especially in ColdBlock™ digestion. This indicates that the reagents and digestion vessels did not introduce any significant contamination of these trace elements in the analysis. The analyte recoveries of blank spikes among the three digestion methods were also within ±10% of the certified values through ICP-OES analysis.

According to the CRM analysis results, trace elements from bomb digestion had the best recoveries, while those from hotplate digestion had relatively low recoveries due to incomplete digestion; some elements were even below detection limits. However, loss of volatile chlorides (As, Cd, Cr, Cu) still seemed inevitable from the bomb digestion method, even the ultra-trace elements, because of the long exposure time to air on the hotplate. In ColdBlock™ digestion, aqua regia was the only digestion method for trace element analysis, fused samples were not tested for trace element analysis. The analyte recoveries of blank spikes among the three digestion methods were also within ±10% of the certified values through ICP-OES analysis.

Table 3. Major element concentrations in two tailing samples and one sediment sample using different digestion methods and fusion methods

| Sample | Concentrations (mg kg⁻¹ ± standard deviation) | Fusion | Bomb | Hotplate | ColdBlock™ |
|--------|-----------------------------------------------|--------|-------|----------|------------|
| WT1-4  | Al                                            | 41 ± 3 | 13 ± 2 | 29 ± 2   | 36 ± 2     |
|        | Ca                                            | 15 ± 2 | 20 ± 2 | 14 ± 2   | 16 ± 2     |
|        | Fe                                            | 10 ± 2 | 15 ± 2 | 10 ± 2   | 10 ± 2     |
|        | Mn                                            | 5 ± 2  | 3 ± 2  | 3 ± 2    | 4 ± 2      |
|        | Mg                                            | 3 ± 2  | 3 ± 2  | 3 ± 2    | 3 ± 2      |
|        | Na                                            | 2 ± 2  | 2 ± 2  | 2 ± 2    | 2 ± 2      |

Table 4. Trace element concentrations in two tailing samples and one sediment sample using different digestion methods and fusion methods

| Sample | Concentrations (mg kg⁻¹ ± standard deviation) | Fusion | Bomb | Hotplate | ColdBlock™ |
|--------|-----------------------------------------------|--------|-------|----------|------------|
| WT1-4  | As                                            | 1 ± 0  | 1 ± 0  | 1 ± 0    | 1 ± 0      |
|        | Cd                                            | 1 ± 0  | 1 ± 0  | 1 ± 0    | 1 ± 0      |
|        | Cr                                            | 1 ± 0  | 1 ± 0  | 1 ± 0    | 1 ± 0      |
|        | Cu                                            | 1 ± 0  | 1 ± 0  | 1 ± 0    | 1 ± 0      |
|        | Pb                                            | 1 ± 0  | 1 ± 0  | 1 ± 0    | 1 ± 0      |
|        | Ni                                            | 1 ± 0  | 1 ± 0  | 1 ± 0    | 1 ± 0      |

Concentrations are in mg kg⁻¹ ± standard deviation (n = 3) by ICP-OES
For trace element analysis, 31 trace elements in tungsten tailing and AMD sediment samples were analysed through the three different digestion methods. The results are presented in Table 5 and Figure 3. The analysis results of the tungsten tailing samples indicate that bomb digestion exhibits the highest digestion efficiency for all elements. Hotplate digestion performs in a quite similar way to bomb digestion because the tested samples were completely digested with this method with recoveries as good as with bomb digestion. There were significant underestimations of values of Ba, Cr, Dy, Gd, Nd, Sc, Sn, Tb, Y and Yb through ColdBlock™ digestion, but Bi, Mo and Th had similar digestion efficiencies as bomb digestion.

While the analytical results indicate that tungsten AMD sediment samples behave a little differently from the tungsten tailing samples. ColdBlock™ digestion had the same efficiencies for As, Cu and Zn as bomb digestion. It was also shown that ColdBlock™ had much better efficiencies for Ba, Bi, Cd, Mo, Nd and Ni than hotplate digestion. Therefore, if bomb digestion could not be implemented for tungsten AMD sediment analysis, ColdBlock™ digestion, given that it is a very quick and low reagent-consuming method, should be the best choice for analysis of the above elements. Visible precipitates were observed after hotplate digestion of the tested tungsten AMD sediment sample. According to the results, the precipitates should be rich in Ba, Bi, Gd, Mo, Nd, Ni and Sn. This finding indicates that hotplate digestion would not be suitable for those elements’ analysis because of poor recoveries.

**Tungsten**

Most available CRMs including SARM5 and MESS3 used for major and trace element analysis in this research had little or no tungsten and obviously were not suitable for tungsten analysis. Therefore, one
Table 4. Comparison of digestion procedures and fusion for trace element analyses from different standard reference materials

| Elements | SARM5 Recommended (mg kg\(^{-1}\)) | MESS3 Recommended (mg kg\(^{-1}\)) | Bomb | Hotplate | ColdBlock\(^{TM}\) |
|----------|----------------------------------|----------------------------------|-------|----------|----------------|
|          | Digestion blank (mg l\(^{-1}\)) | Blank spike recovery (%) | SARM5 Recovery (%) | MESS3 Recovery (%) | Digestion blank (mg l\(^{-1}\)) | Blank spike recovery (%) | SARM5 Recovery (%) | MESS3 Recovery (%) | Digestion blank (mg l\(^{-1}\)) | Blank spike recovery (%) | SARM5 Recovery (%) | MESS3 Recovery (%) |
| As       | <2                               | na                               | 80    | <0.01    | 98    | na    | 47    | <0.008   | 101   | na    | 51    |
| Ba       | 46                               | 842                              | <0.008 | 99       | na    | 80    | <0.01  | 98       | na    | 47    | <0.008 | 101   | na    | 51    |
| Cd       | na                               | 0.2                              | <0.001 | 98       | 95    | 96    | <0.001 | 103     | 78    | 93    | <0.001 | 97    | 49    | 41    |
| Ce       | 3                                | 65                               | <0.001 | 96       | 79    | 85    | <0.005 | 101     | na    | na    | 0.004  | 99    | na    | na    |
| Co       | 110                              | 14                               | <0.001 | 96       | 89    | 96    | <0.001 | 104     | 81    | 66    | <0.001 | 95    | 5     | 3     |
| Cr       | 25 200                           | 105                              | <0.001 | 99       | 84    | 76    | <0.001 | 103     | 60    | 45    | <0.004 | 97    | 46    | 36    |
| Cu       | 18                               | 34                               | <0.002 | 99       | 92    | 87    | <0.002 | 98       | 73    | 84    | <0.002 | 99    | na    | 25    |
| Dy       | 0.5                              | 3.2                              | 0.0006 | 97       | na    | 106   | <0.003 | 102     | na    | na    | 0.0001 | 99    | 58    | 75    |
| La       | 1.9                              | 32                               | 0.0005 | 98       | 94    | 94    | <0.001 | 97       | na    | na    | 0.0005 | 101   | 87    | 108   |
| Lu       | 0.06                             | 0.3                              | <0.0005 | 96       | na    | 83    | <0.001 | 102     | na    | na    | <0.001 | 101   | na    | na    |
| Nd       | 1.9                              | 28                               | 0.00005 | 96       | 87    | 80    | <0.003 | 102     | na    | na    | 0.0004 | 100   | 71    | 67    |
| Ni       | 560                              | 47                               | <0.002 | 95       | 78    | 81    | <0.003 | 106     | 70    | 34    | <0.002 | 93    | 86    | 97    |
| Sc       | 29                               | 15                               | <0.0005 | 99       | 100   | 96    | <0.001 | 102     | na    | 42    | <0.001 | 101   | 6     | 34    |
| Sm       | 0.4                              | 5                                | 0.005  | 96       | 103   | 97    | <0.003 | 101     | na    | na    | 0.01   | 100   | 97    | 102   |
| Sr       | 32                               | 129                              | <0.0001 | 100     | 88    | 80    | <0.001 | 100     | 93    | 75    | 0.004  | 100   | 79    | 47    |
| Tb       | 0.08                             | 0.6                              | <0.002 | 97       | 103   | 95    | <0.006 | 102     | na    | na    | <0.002 | 100   | 104   | 102   |
| Th       | 1                                | 12                               | 0.0001 | 98       | 109   | 87    | <0.004 | 101     | na    | na    | <0.002 | 101   | 81    | 62    |
| V        | 230                              | 243                              | <0.002 | 100      | 97    | 81    | 0.04   | 102     | 108   | 90    | 0.02   | 98    | 7     | 43    |
| Y        | 5                                | 23                               | <0.0002 | 98       | 103   | 106   | <0.002 | 101     | na    | na    | <0.0002 | 103   | 5     | 44    |
| Yb       | 0.6                              | 2                                | 0.00005 | 100     | na    | 90    | <0.001 | 102     | na    | na    | <0.00001 | 100   | na    | na    |
| Zn       | 100                              | 159                              | <0.007 | 97       | 107   | 106   | 0.02   | 104     | 114   | 82    | 0.01   | 96    | 15    | 77    |

Concentrations are in mg kg\(^{-1}\) ± standard deviation (1σ) of triple measurements (\(n = 3\)) by ICP-OES.

na: data not available.
Table 5. Trace element concentrations in two tailings samples and one sediment sample by different digestion methods

| Sample Elements | WT1-4 trace elements concentrations (mg kg⁻¹) ± standard deviation | WT7-2 trace elements concentrations (mg kg⁻¹) ± standard deviation | WS5 trace elements concentrations (mg kg⁻¹) ± standard deviation |
|-----------------|---------------------------------------------------------------|---------------------------------------------------------------|---------------------------------------------------------------|
|                 | Bomb Hotplate ColdBlock™ Bomb Hotplate ColdBlock™            | Bomb Hotplate ColdBlock™ Bomb Hotplate ColdBlock™            | Bomb Hotplate ColdBlock™                                      |
| As              | 95.5 ± 1.9 84.3 ± 1.5 50.9 ± 2.2 243 ± 7 260 ± 11 217 ± 2 | 3097 ± 33 3014 ± 40 3051 ± 25                                |                                                               |
| Ba              | 93.2 ± 3.1 97.1 ± 1.5 7.97 ± 0.18 87.5 ± 2.3 79.0 ± 3.1 20.0 ± 0.1 | 68.0 ± 1.3 24.5 ± 0.1 55.4 ± 1.3                             |                                                               |
| Be              | 0.329 ± 0.029 bd bd bd 0.271 ± 0.036 bd bd                      | 0.307 ± 0.023 bd bd                                         |                                                               |
| Bi              | 35.0 ± 0.7 38.2 ± 1.9 33.8 ± 0.6 69.0 ± 0.7 63.6 ± 2 53.8 ± 1.2 | 1218 ± 29 516 ± 6 1081 ± 22                                  |                                                               |
| Cd              | 0.548 ± 0.107 0.429 ± 0.183 bd bd 0.854 ± 0.089 0.692 ± 0.214 0.720 ± 0.080 | 16.7 ± 0.2 12.1 ± 0.1 13.9 ± 0.3                             |                                                               |
| Ce              | 43.4 ± 4.4 39.7 ± 0.4 30.0 ± 3.9 44.3 ± 7.4 39.2 ± 0.9 39.4 ± 2.0 | 454 ± 62 426 ± 12 304 ± 25                                  |                                                               |
| Co              | 0.739 ± 0.243 1.10 ± 0.592 0.460 ± 0.148 1.43 ± 0.12 1.13 ± 0.19 bd | 13.1 ± 0.4 11.4 ± 0.2 6.73 ± 0.16                            |                                                               |
| Cr              | 7.37 ± 0.07 5.53 ± 0.28 2.28 ± 0.06 9.99 ± 0.14 9.68 ± 0.29 8.80 ± 0.25 | 182 ± 3 190 ± 3 129 ± 3                                      |                                                               |
| Cu              | bd bd bd bd bd bd bd 100 ± 2 102 ± 1 107 ± 3                      |                                                               |                                                               |
| Dy              | 7.42 ± 0.95 1.23 ± 0.02 2.07 ± 0.35 6.00 ± 0.46 1.21 ± 0.05 2.53 ± 0.66 | 204 ± 25 158 ± 1 25.0 ± 2.3                                   |                                                               |
| Er              | 1.78 ± 0.22 0.451 ± 0.008 bd bd 0.396 ± 0.045 0.376 ± 0.026 bd | 151 ± 19 147 ± 2 8.00 ± 0.49                                  |                                                               |
| Eu              | bd bd bd bd bd bd bd 0.477 ± 0.063 bd bd                          |                                                               |                                                               |
| Gd              | 11.2 ± 1.6 2.92 ± 0.16 6.33 ± 0.71 12.3 ± 1.1 3.05 ± 0.26 12.4 ± 3.1 | 260 ± 35 84.2 ± 1.1 160 ± 16                                  |                                                               |
| Ho              | 2.08 ± 0.24 2.17 ± 0.04 1.47 ± 0.12 2.50 ± 0.23 2.37 ± 0.02 1.94 ± 0.57 | 83.9 ± 11.1 7.97 ± 0.11 11.4 ± 0.8                            |                                                               |
| La              | 18.1 ± 1.8 14.8 ± 2.2 12.5 ± 1.3 19.9 ± 3.6 14.7 ± 0.9 16.3 ± 1.0 | 155 ± 21 153 ± 2 121 ± 9                                     |                                                               |
| Lu              | 0.351 ± 0.172 bd bd bd bd bd bd                                 | 29.8 ± 7.1 23.2 ± 0.1 4.03 ± 0.04                            |                                                               |
| Mo              | 312 ± 2 316 ± 3 105 ± 3 205 ± 4 194 ± 4 192 ± 8                 | 2432 ± 44 1095 ± 21 1598 ± 26                                |                                                               |
| Nd              | 480 ± 2.9 61 ± 0.1 16.5 ± 1.9 27.7 ± 2.2 20.0 ± 0.2 24.3 ± 4.4 | 261 ± 35 127 ± 1 175 ± 14                                    |                                                               |
| Ni              | 25.2 ± 1.0 26.0 ± 0.2 20.2 ± 2.1 55.0 ± 0.04 57.8 ± 1.6 49.6 ± 0.2 | 54.9 ± 4.9 11.9 ± 0.2 164 ± 0.8                              |                                                               |
| Pb              | bd bd bd bd bd bd bd 698 ± 5 711 ± 6 595 ± 18                 |                                                               |                                                               |
| Pr              | 3.42 ± 0.35 0.362 ± 0.005 1.26 ± 0.14 3.16 ± 0.23 0.381 ± 0.006 2.10 ± 0.43 | 62.1 ± 8.8 67.6 ± 1.0 22.5 ± 2.1                              |                                                               |
| Sc              | 7.38 ± 0.94 3.29 ± 0.02 5.21 ± 0.70 7.88 ± 0.07 3.02 ± 0.21 4.59 ± 0.93 | 48.3 ± 6.5 31.2 ± 4.6 31.0 ± 12                                 |                                                               |
| Sm              | 27.5 ± 2.3 24.8 ± 2.0 4.23 ± 0.36 44.5 ± 2.0 42.2 ± 1.8 54.5 ± 0.17 | 32.9 ± 6.2 16.5 ± 1.8 7.95 ± 0.94                             |                                                               |
| Sn              | 5.13 ± 0.13 4.99 ± 0.03 2.09 ± 0.01 4.25 ± 0.05 5.73 ± 0.04 3.12 ± 0.01 | 5.60 ± 0.04 5.48 ± 0.02 1.49 ± 0.01                             |                                                               |
| Sr              | 1.07 ± 0.83 0.604 ± 0.053 0.272 ± 0.072 0.276 ± 0.043 0.640 ± 0.048 0.083 ± 0.017 | 2.70 ± 0.50 bd bd                                           |                                                               |
| Tb              | 21.2 ± 1.6 21.2 ± 0.2 18.7 ± 1.6 33.8 ± 6.3 21.1 ± 0.4 29.1 ± 1.3 | 238 ± 28 240 ± 8 175 ± 13                                   |                                                               |
| Th              | bd bd bd bd bd bd bd 248 ± 3.2 bd bd                         |                                                               |                                                               |
| Y               | 38.2 ± 4.2 6.72 ± 0.17 6.74 ± 0.77 26.2 ± 1.8 6.77 ± 0.09 8.90 ± 1.65 | 1039 ± 54 1015 ± 11 58.2 ± 5.4                               |                                                               |
| Yb              | 4.90 ± 0.50 0.940 ± 0.001 0.635 ± 0.066 3.26 ± 0.17 0.970 ± 0.008 0.941 ± 0.121 | 233 ± 33 232 ± 3 22.9 ± 2.0                                  |                                                               |
| Zn              | 75.8 ± 1.8 67.3 ± 1.9 67.7 ± 3.6 60.8 ± 1.5 59.6 ± 2.0 46.4 ± 1.3 | 261 ± 3 265 ± 5 265 ± 6                                    |                                                               |

Concentrations are in mg kg⁻¹ ± standard deviation (1σ) of triple measurements (n = 3) by ICP-OES.
bd: element concentration below detection limits.
granite rock powder CRM (JG2) and one greywacke rock powder CRM (OREAS42P) with known tungsten concentration values were analysed for comparison. The results are presented in Table 6.

The digestion blanks of bomb and hotplate digestion were below the detection limit, and the ColdBlock™ digestion blank was at a relatively low level (0.9 mg l$^{-1}$). This result indicates that tungsten...
Table 6. Tungsten concentrations and blank spike recoveries in CRMs, two tungsten tailing samples, and one tungsten AMD sediment sample using different digestion methods

|            | WT1-4 tungsten concentrations (mg kg⁻¹) | WT7-2 tungsten concentrations (mg kg⁻¹) | WS5 tungsten concentrations (mg kg⁻¹) |
|------------|----------------------------------------|----------------------------------------|--------------------------------------|
|            | ±standard deviation                     | ±standard deviation                     | ±standard deviation                   |
| OREAS42P   |                                         |                                         |                                      |
| JG2        | Recommended tungsten concentration (mg kg⁻¹) | 169 ± 8                                | 571 ± 14                             | 21 978 ± 574                        |
| WT1-4      | Blank digestion (mg l⁻¹)                | Blank spike recovery (%)                | JG2 Recovery (%)                      |                                      |
|            | Digest blank (mg l⁻¹)                   | Blank spike recovery (%)                |                                     | OREAS42P Recovery (%)               |
|            | 32                                      | 23                                     | 101                                  | 105                                  |
|            | 106                                     | 105                                    | 169 ± 8                              | 571 ± 14                             |
|            | 0.9                                     | 97                                     | 118 ± 3                              | 311 ± 2                              |
|            | 0.01                                    | 96                                     |                                      |                                      |
|            | 52                                      | 67                                     |                                      |                                      |
|            | 0.9                                      | 36                                     |                                      |                                      |
| ColdBlock™| Digestion blank (mg l⁻¹)                | Blank spike recovery (%)                |                                      |                                      |
|            | 0.9                                     | 36                                     |                                      |                                      |

Concentrations are in mg kg⁻¹ ± standard deviation (1σ) of triple measurements (n = 3) by ICP-OES.

Table 7. Comparison of trace element concentrations analysed by ICP-OES and ICP-MS after bomb digestion

| Sample     | Ba  | Be  | Bi  | Cd  | Ce  | Co  | Cr  | Cu  | Dy  | Er  | Eu  | Gd  | Ho  | La  | Lu  | Mo  | Nd  | Ni  | Pb  | Pr  | Sc  | Sm  | Sn  | Sr  | Tb  | Th  | Tm  | V  | W  | Y  | Yb  |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| WT1-4 (mgkg⁻¹) | ICP-MS | 96.5 ± 1 | 0.228 ± 0.014 | 37.0 ± 0.4 | 0.525 ± 0.034 | 41.6 ± 0.3 | 0.804 ± 0.082 | 7.25 ± 0.09 | 10.0 ± 0.1 | 7.78 ± 0.19 | 1.88 ± 0.05 | 0.132 ± 0.010 | 14.7 ± 0.3 | 2.21 ± 0.05 | 17.3 ± 0.3 | 0.720 ± 0.032 |
|            | ICP-OES | 93.2 ± 3.1 | 0.329 ± 0.029 | 35.0 ± 0.7 | 0.548 ± 0.107 | 43.4 ± 4.4 | 0.739 ± 0.243 | 7.37 ± 0.07 | bd | 7.42 ± 0.95 | 1.78 ± 0.22 | bd | 11.2 ± 1.6 | 2.08 ± 0.24 | 18.1 ± 1.8 | 0.351 ± 0.172 |
| WT7-2 (mg kg⁻¹) | ICP-MS | 87.5 ± 0.9 | 0.280 ± 0.018 | 63.2 ± 0.4 | 0.853 ± 0.067 | 47.3 ± 0.4 | 1.52 ± 0.18 | 9.36 ± 0.36 | 18.2 ± 0.5 | 5.77 ± 0.12 | 0.347 ± 0.009 | 0.0957 ± 0.0082 | 13.6 ± 0.3 | 3.03 ± 0.08 | 16.1 ± 0.1 | 0.151 ± 0.005 |
|            | ICP-OES | 87.5 ± 2.3 | 0.271 ± 0.036 | 69.0 ± 0.7 | 0.854 ± 0.089 | 44.3 ± 7.4 | 1.43 ± 0.12 | 9.99 ± 0.14 | 6.00 ± 0.46 | 0.396 ± 0.045 | bd | 12.3 ± 1.1 | 2.50 ± 0.23 | 19.9 ± 3.6 | bd |                                      |
| WS5 (mg kg⁻¹) | ICP-MS | 64.8 ± 0.3 | 0.301 ± 0.019 | 1236 ± 9 | 16.0 ± 0.5 | 431 ± 4 | 13.2 ± 0.5 | 181 ± 3 | 96.0 ± 1.0 | 199 ± 2 | 152 ± 2 | 1.00 ± 0.06 | 296 ± 4 | 80.0 ± 2.4 | 144 ± 1 | 31.7 ± 0.6 |
|            | ICP-OES | 68.0 ± 1.3 | 0.307 ± 0.023 | 1218 ± 29 | 16.7 ± 0.2 | 454 ± 62 | 13.1 ± 0.4 | 182 ± 3 | 100 ± 2 | 204 ± 25 | 151 ± 19 | 0.477 ± 0.063 | 260 ± 35 | 83.9 ± 11.1 | 155 ± 21 | 29.8 ± 7.1 |
| ICP-OES   | Mo  | Nd  | Ni  | Pb  | Pr  | Sc  | Sm  | Sn  | Sr  | Tb  | Th  | Tm  | V  | W  | Y  | Yb  |
| 110 ± 1   | 26.7 ± 0.4 | 0.721 ± 0.077 | 31.6 ± 0.4 | 4.55 ± 0.25 | 3.63 ± 0.28 | 7.08 ± 0.23 | 25.7 ± 0.6 | 5.64 ± 0.19 | 0.782 ± 0.033 | 21.9 ± 0.2 | 0.00653 ± 0.00030 | 1.51 ± 0.04 | 172 ± 12 | 39.6 ± 0.6 | 5.00 ± 0.15 |
| 112 ± 2   | 28.8 ± 2.9 | bd | 25.2 ± 1.0 | 1.0 | 3.42 ± 0.35 | 7.38 ± 0.94 | 27.5 ± 2.3 | 5.13 ± 0.13 | 1.07 ± 0.83 | 21.2 ± 1.6 | bd | 169 ± 8 | 38.2 ± 4.2 | 4.90 ± 0.50 |
| 228 ± 3   | 31.4 ± 0.5 | 12.9 ± 0.6 | 55.6 ± 0.7 | 3.33 ± 0.12 | 3.90 ± 0.71 | 7.53 ± 0.13 | 44.7 ± 0.8 | 5.03 ± 0.09 | 0.127 ± 0.003 | 30.2 ± 0.3 | 0.503 ± 0.016 | 5.02 ± 0.09 | 557 ± 14 | 27.5 ± 0.4 | 3.75 ± 0.22 |
| 206 ± 4   | 27.7 ± 2.2 | 12.9 ± 0.3 | 55.0 ± 0.4 | bd | 3.16 ± 0.23 | 7.88 ± 0.07 | 44.5 ± 2.0 | 4.25 ± 0.05 | 0.276 ± 0.043 | 33.8 ± 6.3 | bd | 571 ± 14 | 26.2 ± 1.8 | 3.26 ± 0.17 |
| 2622 ± 12 | 242 ± 6 | 53.2 ± 2.2 | 685 ± 5 | 37.2 ± 0.9 | 66.7 ± 5.8 | 46.4 ± 0.8 | 31.6 ± 0.9 | 5.74 ± 0.12 | 2.03 ± 0.41 | 236 ± 2 | 25.0 ± 0.5 | 6.72 ± 0.24 | 21 708 ± 884 | 1103 ± 14 | 217 ± 2 |
| 2432 ± 44 | 261 ± 35 | 54.9 ± 4.9 | 698 ± 5 | bd | 62.1 ± 8.8 | 48.3 ± 6.5 | 32.9 ± 6.2 | 5.60 ± 0.04 | 2.70 ± 0.50 | 238 ± 28 | 24.8 ± 3.2 | bd | 21 978 ± 574 | 1039 ± 54 | 233 ± 33 |

Concentrations are in mg kg⁻¹ ± standard deviation (1σ) of triple measurements (n = 3) by ICP-OES and ICP-MS.
contamination was not significant in bomb and hotplate digestion and was acceptably low in ColdBlock™ digestion. Independent single tungsten element blank spike samples were in 1 mg l⁻¹ tungsten concentration, which is diluted from the 1000 mg l⁻¹ tungsten NIST-traceable standard. The tungsten blank spike sample recoveries were within ±10%.

The CRM analytical results showed bomb digestion had the best tungsten digestion efficiency, while ColdBlock™ digested the least tungsten from the CRMs. This trend is consistent with most major and trace element digestion efficiencies using the three methods.

The analytical results for the tungsten tailing samples showed that bomb and hotplate digestion achieved total tungsten mineral digestion when the tailing sample had a relatively low tungsten concentration (WT1-4). However, tungsten recovery decreased when its concentration increased (WT7-2), as evidenced by the presence of a trace amount of tungsten precipitate.

Because the AMD sediment sample (WS5) had a very high tungsten concentration (c. 2.2%), the 5% HNO₃ matrix could not fully dissolve this sample after multiple digestions. Yellowish H₂WO₄ precipitates were observed in the bottom of beakers when 5% HNO₃ was applied as a matrix as usual after bomb digestion and capped and heated for a long time (c. 7 hours) at 140°C. During bomb digestion, a high concentration of HF totally dissolved the sediment sample, but it could not be used as the matrix for ICP-OES and ICP-MS analysis. Aqua regia and a high concentration of nitric acid were also tried as the matrix to totally dissolve the tungsten precipitate, but they also were not successful.

However, recent research has demonstrated that the dissolution of tungsten, in the form of H₂WO₄, in NaCl-bearing fluids at low pH could be greatly improved because salinity can increase the ionic strength of the solutions (Wang et al. 2019). As sodium was a major element in the test tungsten tailing and AMD sediment samples, when HCl was introduced into the matrix, low pH and NaCl-bearing solutions formed easily, which would improve the dissolution of tungsten minerals in the samples. Several HCl concentrations were tested in the experiments. Eventually, a relatively high concentration (20%) of HCl completely dissolved the H₂WO₄ precipitates, and it was used as the matrix for ICP-OES and ICP-MS analyses. The results also clearly showed bomb digestion with a 20% HCl matrix achieved the best tungsten recovery when the concentration was very high in the AMD sediment sample. The tungsten concentration was almost 10 times higher than the hotplate digestion result. ColdBlock™ digestion was even worse than hotplate digestion in extracting tungsten from the samples. In conclusion, bomb digestion with a 20% HCl matrix was a better digestion method for high tungsten concentration tailing and AMD sediment samples, as indicated in the literature.

**ICP-OES and ICP-MS analysis comparison**

The two tungsten tailing samples and the AMD sediment sample were also analysed by both ICP-OES and ICP-MS for quality control purposes after bomb digestion (Table 7). Based on the analysis results, as expected, ICP-MS was obviously more sensitive and accurate than ICP-OES; results using ICP-MS had smaller errors, except for very few elements. Some ultra-trace and trace concentration elements, like Eu, Pr and Tm could be detected by ICP-MS, but not by ICP-OES. The data achieved by ICP-OES were in good agreement with ICP-MS data. This indicates that the data analysed through ICP-OES were reliable.

Conclusions

Three different digestion methods for tungsten tailing and AMD sediment samples were described and tested in this research. For major element analysis, alkali fusion was also tested. For the major elements, fusion is the most accurate and time-saving method. For trace elements, bomb digestion is the best method for extracting all elements, because it is a total digestion method. However, the potential loss of volatile chlorides of some elements during bomb digestion should be noted. ColdBlock™ digestion, even though a faster and safer method, did not perform well for rock and marine sediment CRMs, only very few elements having achieved good recoveries. However, in the results for the tungsten tailing and AMD sediment samples, several elements including Bi, Mo and the REEs achieved recoveries as good as with bomb digestion. For the analysis of those elements, ColdBlock™ digestion is a good choice. For tungsten element analysis, bomb digestion with a 20% HCl matrix is the best method for achieving total digestion of tungsten minerals. This was proved in the sample with high tungsten concentration, and this method has the highest tungsten digestion efficiency. Hotplate digestion is not recommended in any analysis of tungsten tailings and AMD samples. It is time-consuming, similar to bomb digestion, but for some elements the digestion efficiency was not even as good as with ColdBlock™ digestion.

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**Data availability** All data are provided in full in the results section of this paper.

**Author contributions** ZH: conceptualization (lead), data curation (lead), formal analysis (lead), investigation (lead), methodology (lead), writing – original draft (lead), writing – review & editing (lead); ME: conceptualization (supporting), investigation (supporting), methodology (supporting), project administration (leading), writing – review & editing (supporting); AN: formal analysis (supporting), methodology (supporting), writing – review & editing (supporting); MM: writing – review & editing (supporting)

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