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Enhanced flow injection leaching of rocks by focused microwave heating with in-line monitoring of released elements by inductively coupled plasma mass spectrometry

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Abstract

A focused microwave digestion system was used to heat a mini-column of sample of crushed rock (hematite) during its successive leaching by repeated 250-μL injections of water, HNO_3 1%, 10% and 30% (v/v). The mini-column was connected to the nebulizer of an inductively coupled plasma mass spectrometry instrument, which allowed a continuous monitoring of the progressive release of elements by a given leaching reagent. Quantitation of the accessible fraction of Mg, V, Cr, Mn, Co, Ni, Cu, Zn, Mo, Sb and Pb was done by calibration using 250-μL injections of standard solutions prepared in the leaching reagent matrices. Total digestion of the sample residue was also done to verify mass balance. With the exception of Mg, V and Co, where the same total amount was released with or without microwave heating, an increased release resulted from focused microwave heating, by up to an order of magnitude. Furthermore, mass balance was verified for more elements using microwave heating, presumably because of a lower relative proportion of spectroscopic interference as a result of an increased release of analytes. Using microwave energy in general resulted in the dissolution of additional phases, as evidenced by significantly different $^{208}Pb/^{206}Pb$ ratios as well as the increased release of elements with milder reagents. In fact, in the case of Pb, leaching with 30% HNO_3 was no longer necessary as all the Pb was released in the first three leaching reagents. Microwave heating could therefore be used advantageously in on-line leaching for exploration geochemistry and environmental monitoring.

Keywords: On-line leaching; Microwave heating; Inductively coupled plasma mass spectrometry (ICPMS); Rock samples

1. Introduction

Many methods have been devised in an attempt to evaluate the distribution and fractionation of elements in solid matrices. Most of them involve sequential extraction schemes that are based on operationally or functionally defined species characterization [1–4]. They may provide information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals [5]. However, despite their wide application, sequential extraction procedures have some disadvantages such as lack of selectivity, being tedious and time consuming [6,7].

While most of the sequential extractions have been carried out in batch systems, some dynamic flow-through extraction techniques have been proposed to better mimic environmental conditions [7–14]. Reduction in error associated with repeated centrifugation, filtration and washing is one of the features in favor of dynamic systems. Additionally, they are faster than batch extractions and lessen re-adsorption problems [7,8], which they can also help study.

The main approaches that have been implemented so far, namely those using a rotating coiled column, a stirred flow-cell, a packed mini or micro-column or microdialysis sampling, were recently reviewed [7]. The microdialysis approach is still in its infancy and has only been applied to in situ microsampling of interstitial/pore soil water [13]. Of the other three approaches, the flow-through mini-column approach is the simplest to implement, and provides the most versatility because different extraction modes (continuous leaching, static extraction, recirculation,

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etc.) can readily be implemented using flow injection (FI), which moreover allows in-line detection of the released analytes [7].

An example of a simple mini-column approach is the continuous on-line leaching method that was developed by Beauchemin et al. [10]. It involves either continuous leaching of a mini-column containing the soil sample by leaching reagents of increasing acid concentration, or using a simple FI manifold to repeatedly inject the same leaching reagents, which are then pumped through the sample, while continuously monitoring the released analytes by inductively coupled plasma mass spectrometry (ICPMS). The combination of this on-line leaching approach with ICPMS allowed a measurement of the mobility and fractionation of elements in real time. Indeed, it simultaneously provided data on what elements were released and what phases were breaking down, enabling the reliable assignment of trace elements to host phases [15,16]. This is in contrast to conventional sequential extractions methods where certain reagents are assumed to dissolve specific phases, based on previous work on other samples, but this is usually not verified. In any case, this on-line approach allowed the acquisition of a huge amount of data within 20 min if a quadrupole (Q) or time-of-flight (TOF) ICPMS instrument was used, or 1.5 h if a high-resolution (HR) sector field instrument was used (the slower scanning rate of the latter requiring the use of a micronebulizer) [10].

Although ICPMS allows very sensitive detection, it is susceptible to numerous spectroscopic interferences arising from the plasma, sample matrix and reagents. For this reason, the well-established sequential extraction schemes were avoided in the above study to eliminate spectroscopic interferences arising from the various reagents needed. Instead, sequential leaching was done with water, 1%, 10% and 30% (v/v) HNO_3, which, without adding any additional feature to the background mass spectrum, was found to be equivalent to a single 2-h batch extraction with 2% HNO_3 in terms of the total amount of analyte released [10]. Others [17–19] have also been using increasing concentrations of HNO_3 for extraction, and have in fact found that HNO_3 was a better extractant than *aqua regia* [17]. In these other studies, which involved centrifugation of the extractant through the sample in a batch mode, the highest HNO_3 concentration was 5 M, which is equivalent to 30% (v/v) HNO_3; hence, the range covered was the same, except that six different concentrations (from 0.01 to 5 M HNO_3) were used for the extractions of soils and sediments [16–18], instead of the three (1% i.e. about 0.15 M, 10% i.e. about 1.5 M, and 30% i.e. about 5 M) used for crushed rock samples [10,14,15]. It is interesting to note that these two different approaches, which were developed completely separately but nonetheless yielded the same range of concentration (i.e. from water to 5 M HNO_3), were initially published the same year (in 2002).

The approach of Beauchemin et al. was developed in view of application to exploration and environmental geochemistry [16]. It would also be invaluable for monitoring of the mobility of elements in the environment. To further improve it, it should be kept simple but with an increase in accuracy and sample throughput, so that it can effectively be used, for example, to identify pathfinder elements i.e. indicative of an ore [16]. One possibility is through the application of microwave heating, which has been used advantageously in on-line systems for solid sample digestion, since it reduces the time delays between sample delivery and analysis, while improving personal safety [20]. When applied to batch extractions, microwave heating not only substantially reduced the extraction time but it also led to better precision as a result of the operating conditions being more stable and easily controlled than conventional procedures [21]. On the other hand, the results were not necessarily equivalent to those obtained by conventional procedures, at least not for all the analytes [22]. Still, microwave-based extractions have been proposed as fast screening methods for risk assessment, i.e. the quick evaluation of the accessibility of toxic elements to the environment. The purpose of this work was to verify if the application of microwave heating to on-line leaching would be similarly advantageous.

2. Experimental

2.1. Instrumentation

Although some of the preliminary work was carried out on a Leco Renaissance ICP-TOFMS instrument, most of this work was done using a Varian UltraMass 700 ICP-QMS instrument (Mulgrave, Victoria, Australia) with a Sturman–Masters spray chamber and a concentric nebulizer. Some of its operating conditions were kept constant. Indeed, the RF power was maintained at 1.2 kW while the Ar plasma, auxiliary and aerosol gas flow rates were kept, respectively, at 15, 1.05 and $0.91\ \mathrm{L\,min^{-1}}$. The sampling depth was optimized daily and ranged between 6.5 and 7 mm. The sample uptake rate, which was dependent on back-pressure through the mini-column of rock, was $0.8–0.9\ \mathrm{mL\,min^{-1}}$. The maximum uptake rate that back-pressure would allow was selected to maximise sample throughput, as lower uptake rates only resulted in broader peaks that were not taller. Except where otherwise indicated, the most abundant isotope of several analytes was monitored: Co, Cr, Cu (*m/z* 63 and 65), Mg (*m/z* 24 and 25), Mn, Mo, Ni, Pb (*m/z* 204, 206-208), Sb, V and Zn (*m/z* 64 and 68). The measurement time was 399 ms. Data acquisition was done in time-resolved, peak-hopping mode with 1 point per peak, 1 scan per replicate, a dwell time of 1 ms (except for masses 204–207 where 10 ms was used), and 0.025 amu spacing. The raw data were then treated with in-house QBASIC software for smoothing (using a 7-point Savitzky–Golay polynomial moving window) and determination of peak area. When continuous nebulization was used, data acquisition was performed in the steady-state mode (peak-hopping mode with the same dwell time indicated above, 3 points per peak, 5 scans per replicate, 10 replicates per sample, 2 s replicate time and 0.025 amu spacing).

2.2. Packing of mini-column

During previous studies from this group, 20–50 mg of rock or mineral sample (with a particle size of 0.2–1 mm) was packed in mini-columns. Since the goal is to assess the mobility of analytes and that, by crushing the soil finer than 0.2 mm, normally inaccessible phases would become exposed, the same particle size