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Comparative study of optimised BCR sequential extraction scheme and acid leaching of elements in the certified reference material NIST 2711

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Abstract

The optimised BCR sequential extraction procedure and a 4 h 1 mol L^{-1} HCl partial extraction have been performed on the NIST 2711 reference material for a suite of 12 elements (Cd, Sb, Pb, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, As) using magnetic sector ICP-MS. A pseudo-total aqua regia digest of NIST 2711 has also been undertaken for quality assurance purposes, and comparison of the sum of the four BCR fractions, which included an aqua regia digest on the residue, with the pseudo-total aqua regia digest has been used to assess the accuracy of the BCR partitioning approach. As a result of this work, discrepancies between previous studies about BCR partitioning of elements in NIST 2711 have been discussed and an increase in confidence about the use of BCR partitioning scheme on seven elements (Cd, Pb, Al, Mn, Fe, Cu, Zn) in this standard material has been obtained. On the other hand, BCR partitioning for Sb, Cr, Co, Ni and As has been provided for the first time. Partial extraction results are also reported for the same 12 elements analysed by the optimised BCR procedure, with the partial extraction results exhibiting a strong correlation with the sum of the three labile steps of the BCR procedure.

Keywords: NIST 2711; Sequential extraction; BCR sequential extraction; Partial extraction; ICP-MS

1. Introduction

The shift away from simply measuring total contaminant levels in sediments to a risk-based approach to determine sediment quality (as is the case for the Australian and New Zealand Environment and Conservation Council, ANZECC, Water Quality Guidelines, 2000) has stimulated the need for alternative methods of assessing sediment quality [1]. Under the ANZECC risk-based approach, if a total metal analysis on a sediment sample exceeds the sediment guideline value, further testing would be undertaken to determine the factors controlling bioavailability of the contaminant metal. For example, sulfide and organic content of the sediment, and contaminant speciation within the sediment, are critical in controlling whether or not contaminants will be readily available within the sediment porewater. Partial (single) and sequential extraction procedures are two techniques that have been used for determining the extractable forms of metals within sediments [2].

Partial extractions unselectively target labile metals with the degree of extraction dependent upon the severity of the reagent [3]. In contrast, sequential extraction procedures have been applied to soils and sediments to characterise their respective metal fractions, by selectively targeting and releasing metals bound in certain geochemical phases, such as carbonate, iron and manganese oxide/hydroxide, sulfidic, organic, and silicate [4].

Several problems have been identified with the use of sequential extraction procedures, including non-selectivity and readsorption [5–8]. Consequently, fractionation of metals is operationally defined in terms of the extraction mechanism used to release the metals rather than in terms of the discrete geochemical phases. One of the more commonly used sequential extraction procedures is the BCR (Community Bureau of Reference of the European Commission, now the Standards, Measuring and Testing Programme) procedure [9]. The BCR procedure aims to fractionate metals into the operationally defined phases of acid

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extractable, reducible, oxidisable and residual, with the steps targeting exchangeable and carbonate bound metals, iron and manganese oxide/hydroxide associated metals, metals bound to sulfide and organic phases, and mineral phases, respectively. Due to the many schemes and variations in use, the BCR procedure was originally developed to try to standardise sequential extraction schemes. The original procedure has since been modified [10], including changes to the concentration of the reagent and pH of the second step, which has resulted in better precision between laboratories for the extraction of reducible metals. The addition of a fourth step, an aqua regia digest on the solid residue remaining after Step 3, has provided the opportunity for quality assurance by comparison of the sum of the four BCR steps to an independent aqua regia analysis on a second portion of sample [10].

In contrast to sequential extraction schemes, partial extractions are a simple and cost effective way to investigate the labile metals in sediments. Although there are numerous methods for partial extractions, they generally fall into three groups: (i) dilute solutions of strong mineral acids, (ii) weak acids and (iii) solutions of complexing or reducing agents [11,12].

Dilute HCl is one of the more common partial extractants used [3,12–14]. It extracts labile metals, but has little effect on breaking up the silicate lattice and residual phase metals [3], hence leaving metals bound to these phases untouched. Partial extractions have also been shown to correlate better with trace metal levels in benthic organisms than total digests [15–17].

The application of partial (single) and sequential extractions as a means of assessing sediment quality has also resulted in the development and certification of new reference materials, such as BCR 483 and BCR 484 (sewage sludge amended soils certified for EDTA and acetic acid extractions) [18], and BCR 701 (lake sediment certified for BCR 3-step sequential extraction) [19,20]. A number of other reference materials, including NIST 2711 (soil certified for total metals and non-certified EPA Method 3050 leachable concentrations), have been used for assessing sequential extraction procedures. NIST 2711 is a moderately contaminated soil intended for quality assurance of analysis of soils and sediments, and although no certified values exist for sequential extractions performed upon NIST 2711, a variety of sequential extraction procedures have been applied to this reference material [21–25].

This paper investigates the partitioning and accuracy of 12 elements (Cd, Sb, Pb, Al, Cr, Mn, Fe, Co, Ni, Cu, Zn and As) in NIST 2711 using the optimised BCR sequential extraction procedure [10] and a dilute acid single step partial extraction with multi-element analysis by magnetic sector ICP-MS. Multi-element determination by ICP-MS has not been previously used for partitioning of elements in NIST 2711 using the optimised BCR procedure.

Whilst results have previously been reported for Pb, Al, Mn, Fe, Cu and Zn using the optimised BCR procedure [24,25], discrepancies existed between those studies for Pb, Al and Mn. This work clarifies those discrepancies, and provides partitioning results for Cd, Sb, Cr, Co, Ni and As under the optimised BCR procedure. Pseudo-total (aqua regia) metal analyses are also reported for NIST 2711 and have been compared with the sum of the four BCR steps for quality assurance purposes. Partial extraction (4 h 1 mol L^{-1} HCl) results are also reported for the 12 elements analysed, and a comparison of the partial extraction results has been made with the non-residual, labile metals released using the BCR procedure. The metals partitioning data reported here for NIST 2711 will be valuable for further environmental studies and for inter-laboratory comparisons.

2. Experimental

2.1. Standard reference material NIST 2711

NIST 2711 is a moderately contaminated Montana soil produced by National Institute of Standards and Technology (NIST) [26]. The original sample was collected from the till layer of a wheat field, where it was subsequently air dried, sieved to 2 mm and ground to pass through a 74 μm screen [26]. Three 1 g samples were dried at 105 °C for 24 h to calculate moisture content. This enabled concentrations to be reported on a μg g^{-1} dry weight basis.

2.2. BCR sequential extraction procedure

The optimised BCR procedure was followed according to the procedure described fully in Rauret et al. [10]. A brief summary of the method is shown in Table 1. Each extraction step was performed in triplicate, starting with 1 g of original material. All reagents were of analytical grade quality or better, with all solutions and dilutions prepared in Milli-Q water (resistance = 18.2 MΩ cm^{-1}). The aqua regia residual step performed on the residue from Step 3 was based on Australian Standard AS 4479.2, rather than the recommended ISO 11466 method,

Table 1
Reagents and conditions employed for the modified BCR sequential extraction procedure

Step	Fraction	Reagent and conditions
1	Acid extractable	1 g NIST 2711, 40 mL 0.11 mol L^{-1} CH_3COOH, shaken 16 h at room temperature, centrifuged 3000 × *g* for 20 min
2	Reducible	40 mL 0.5 mol L^{-1} $NH_2OH \cdot HCl$, pH ~ 1.5, shaken 16 h at room temperature, centrifuged as in Step 1
3	Oxidisable	Digested with 10 mL 8.8 mol L^{-1} H_2O_2, 1 h at room temperature, 1 h at 85 °C, 10 mL 8.8 mol L^{-1} H_2O_2 added, 1 h at 85 °C, reduced volume, extracted with 50 mL of 1 mol L^{-1} NH_4COOCH_3, shaken 16 h at room temperature, centrifuged as in Step 1
4	Residual	7.5 mL 12 mol L^{-1} HCl, 2.5 mL 16 mol L^{-1} HNO_3, 16 h at room temperature, 2 h gentle reflux, cool, filtered through Whatman 540