



# ICP-OES assessment of heavy metal contamination in tropical marine sediments: A comparative study of two digestion techniques

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## ABSTRACT

A closed vessel microwave assisted aqua regia digestion and an alkaline fusion dissolution technique were compared and utilised for heavy metal determination in sediments. Ten metals (Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). The precision and accuracy of the digestion procedures were verified using a reference material (RM) for sediment. The results of the analysis were statistically treated by means of Student's *t*-test ( $p < 0.05$ ) and regression analysis. A comparison of the two digestion methods showed no statistically significant difference in metal concentrations in the RM except for Al and As. Recovery values for all metals were nearly quantitative (>82%) for both digestion methods, except for Al and As, which were underestimated using the acid digestion (AD) method and the alkaline fusion (AF) method, respectively. The average relative standard deviations for both digestion methods were less than 6%, indicating good method precision. The application of the two methods for the determination of ten heavy metals in ten sediment samples showed significant correlation between results achieved by both digestion methods for all the metals studied except for As. This study has demonstrated that the microwave-assisted aqua regia digestion is more suitable for the determination of minor and volatile elements such as As, while the alkaline fusion technique is more suitable for the determination of silicate bound and refractory metals. Application of the proposed methods to sediments from a coastal environment in Fiji showed that the sediments were highly contaminated with metal levels as much as  $345 \text{ mg kg}^{-1}$  As,  $519 \text{ mg kg}^{-1}$  Cr,  $530 \text{ mg kg}^{-1}$  Cu,  $1387 \text{ mg kg}^{-1}$  Ni,  $800 \text{ mg kg}^{-1}$  Pb and  $1720 \text{ mg kg}^{-1}$  Zn, as a consequence of improper industrial waste management.

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## 1. Introduction

Of the many environmental chemical contaminants, heavy metals are prominent environmental pollutants due to their non-degradable, bioaccumulative and toxic nature [1–5]. The accumulation of heavy metals in the aquatic environment such as sediments causes a potential risk to human health due to the transfer of these elements in aquatic media, uptake by plants and their subsequent introduction in the food chain [5]. The biohazard in sediments is further aggravated by the presence of a mixture of several heavy metals and metalloids introduced through anthropogenic activities.

Heavy metal contamination in the aquatic environment has often been assessed by the determination of their total element contents in sediments and comparison with established national guidelines [5,6]. Total sediment element contents reflect the geological origins of soils as well as the anthropogenic inputs. Sediment Quality Guidelines (SQG), based on total metal contents and concerning maximum allowable total trace element concentrations in sediments, are currently in use in various countries [5,6]. Therefore, in an environmental

monitoring activity, it is important to determine whether the total metal content is within the range of background levels or over the concentration limits according to the national legislation [7,8]. These kinds of studies allow the identification of metal “hot spots” and can be used to classify polluted sites [9,10]. However, achieving a total decomposition of the sediment sample is a major requirement, especially where normalisation of trace element concentrations to those of a conservative lithogenic reference element, such as Al, is performed for the purpose of determining elemental enrichment factors [11]. The actual total metal concentrations may also be required for mass balance studies from the sequential extractions which determine trace element partitioning and mobility [12–14]. Total heavy metal concentrations in sediments thus, require to be being accurately determined for many purposes.

Highly sensitive spectroscopic techniques, including atomic absorption spectrometry (AAS), inductively coupled plasma-optical emission spectrometry (ICP-OES) and inductively coupled plasma-mass spectrometry (ICP-MS), have great advantages for the determination of heavy metals. The limitation of these techniques is that the solid sample needs to be transformed into a solution which requires more than 60% of the total time to complete the analysis [3]. Hence, sample preparation is often regarded as the weak link in heavy metal analysis where much

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scope for improvement is required [9,12], so that the analytes are completely released and solubilised, *i.e.* total decomposition of the sample is achieved. Sample digestion is mainly carried out by a fusion or a wet procedure based on an acid digestion with a heated mixture of mineral acids. In this regard, various types of acid mixtures using HCl, HNO<sub>3</sub>, HF, HClO<sub>4</sub>, HBO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub>, with suitable digestion equipment have continuously been investigated to dissolve soil and sediment samples [6,9,10,15]. However, the use of several types of hazardous and incompatible acids (*e.g.* HF, HClO<sub>4</sub>) has been highly recommended [16] because the total decomposition of the siliceous and organic based matrix samples has still been difficult without the use of HF and HClO<sub>4</sub> [3,10,17]. In addition, use of HF has adverse effects on apparatus and equipment, while HClO<sub>4</sub> requires specialised laboratory conditions for its use [3]. Also, an additional treatment step with the addition of saturated boric acid solution to digests before analysis is necessary to destroy any excess HF in order to avoid glassware erosion and torch damage in ICP instrument [18]. It has also been found that when HF is present, metal fluoride species are produced which are quite insoluble in the aqueous solution [19].

Most studies on the evaluation of digestion procedures for heavy metal analyses are also limited to standard reference materials which do not give enough information regarding real samples [1,10,17,20–22]. It has also been shown that elemental recovery may vary from soil to sediment and other material, even using the same digestion procedure [14,23,24], or even using different standard methods on the same samples [2,25]. As such it is fairly difficult to harmonise and recommend a standard total metal extraction procedure for environmental solid matrices such as sediments and research has indicated the need of a detailed study of metal extraction capability of digestion methods in specific sediments of the ecosystem under study. Few methods have frequently been used as standard total extraction methods [25] without an explanation or experimental verification, despite the fact that they do not totally transform some components of many types of sediments into aqueous solution [2].

Therefore, with this effort, less aggressive and hazardous methods need to be investigated for heavy metal determination in environmental solid matrices *i.e.* sediments, which should show good comparability with the HF-HClO<sub>4</sub> methods [3,13,15,26,27]. It has been shown that alternative safer digestion methods can effectively extract metals in samples and thus the complete decomposition of silicate matrix by HF is not necessary [19]. In this respect, aqua regia extraction is one of the more widely used acid leaching methods which is rapid and easy to perform, and avoids handling hazardous HF solutions. The aqua regia (3:1, v/v, HCl:HNO<sub>3</sub>) digestion procedure is considered adequate for analysing the total-recoverable heavy metals in sediments, while the microwave-assisted acid solubilization has proved to be the most suitable method for the digestion of complex matrices *i.e.* sediments containing oxides, clay, silicates and organic substances [5]. Based on the considerations of minimising working time as well as volatile loss of analytes, closed vessel microwave-assisted digestion has been employed with increasing success, and thus, is state-of-the-art for wet digestion [12,13,27,28]. On the other hand, sample dissolution by fusion procedures is fast, does not require expensive laboratory equipment and above all, is not sensitive to the different mineral natures of the samples [29]. Therefore, herein, we have attempted to investigate the applicability of a simple alkaline fusion procedure against a modern state-of-the-art microwave aqua regia digestion procedure to determine the heavy metals in standard reference and environmental sediment samples using ICP-OES. Our first step was to validate the methods using a sediment reference material (RM) and suggesting the most appropriate procedure for sediment digestion depending on the element considered, in terms of data quality control and digestion efficiency. A secondary aim was to apply the methods in a number of sediment samples in which the concentrations of these elements varied widely from a

contaminated estuary in Fiji [30,31]. Based on the above consideration and in continuation of our studies [30,31], herein, we report the comparison of a microwave-assisted aqua regia digestion extraction for sediments with a lithium tetraborate fusion method for the determination of some trace (As, Co, Cr, Cu, Mn, Ni, Pb and Zn) and major (Al and Fe) element concentrations in sediment samples.

## 2. Experimental

### 2.1. Sampling of sediments

To assess contamination in an environmental monitoring perspective, the sediment samples were taken from the Lami coastal environment, an industrialised area of eastern Viti Levu, the main island of Fiji. The sediment sampling sites selected for these investigations were diverse in terms of depositional environment *i.e.* samples of marine, estuarine and riverine origin were taken. The choice of these diverse samples subjected the methods to different types of sediment samples and to samples with highly varying concentrations of metals. Approximately 500 g of superficial soil or sediment was collected by hand (with latex gloves and plastic spatula), put into cleaned ziplock plastic bags and taken to the laboratory in cool boxes. In the laboratory, coarse particles, leaves or large material were removed. The samples were then subsampled and frozen in the refrigerator at  $-20\text{ }^{\circ}\text{C}$  for 24 h. Extreme care was taken to avoid sample contamination at every stage of the sampling procedure and verified using field blanks, which were subjected to the same sampling procedure.

### 2.2. Reagents

Reagents used in this study were of the highest available quality *i.e.* analytical grade, unless stated otherwise. All solutions and dilutions were prepared in doubly distilled deionised (Milli-Q Millipore 18.2 M $\Omega$ .cm resistivity) water. High purity HCl and HNO<sub>3</sub> were used after purifying using quartz sub-boiling distillation unit. Commercially available mono element standard solutions (C.P.A. Ltd., Bulgaria) were used to prepare a series of composite calibration standard solutions for all metals using serial dilutions. 1000 mg L<sup>-1</sup> of As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn was used to prepare multielement standards ranging between 0.003 and 10 mg L<sup>-1</sup> for As, Co, Cr, Cu, Ni and Pb, while 0.003 and 30 mg L<sup>-1</sup> for Mn and Zn. 10,000 mg L<sup>-1</sup> of Al and Fe was used to prepare 0.3–3000 mg L<sup>-1</sup> of Al and Fe standards. All multielement standards were prepared in matrix solutions which included a mixture of 0.5% Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> and 4.3% HCl solution for the alkaline fusion method and a mixture of 16% HCl and 8% HNO<sub>3</sub> solution for the microwave digestion method, respectively, for matrix matching. A 1 mg L<sup>-1</sup> multielement quality control standard was also prepared by diluting 100 mg L<sup>-1</sup> multielement commercial standard (C.P.A. Ltd., Bulgaria) using the appropriate matrix solution. A linear calibration with up to seven multielement standards was prepared. The reference material (RM) Buffalo River Sediment (RM 8704 – NIST, USA) was used to verify the repeatability and accuracy of the whole analytical procedure.

### 2.3. Equipment

All sample containers, autosampler cups, reagent bottles and glassware were acid washed with 10% v/v nitric acid before rinsing with copious amounts of ultrapure water and drying in air before use. Analysis of all sample digests and extractions was performed using an Optima 3200DV inductively coupled plasma-optical emission spectrometer (Perkin-Elmer). The ICP-OES instrumental conditions used for the metals determination are given in Table 1.

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