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# 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.

**Table 1**

(i) ICP-OES instrumental parameters for the analysis of Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in sediment CRM and samples and (ii) ICP-OES analytical parameters for Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn analysis in sediment CRM and samples.

(i)			
Parameter	Value	Parameter	Value
Nebuliser type	Low-flow Gem-cone	Read delay	30 s
Spray chamber type	Cyclonic	Calibration type	Zero intercept, linear
RF power	1300 W	Purge	Normal
Plasma gas flow	15 L min <sup>-1</sup>	Resolution	Normal
Auxiliary gas flow	0.8 L min <sup>-1</sup>	Rinse	20 s
Plasma viewing	Axial/radial	Background correction	2 points
Sample flow rate	2 mL min <sup>-1</sup>	Replicates	3
Nebuliser gas flow	0.8 L min <sup>-1</sup>	Carrier solution	1% HNO <sub>3</sub>
Auto integration	1 s min–2 s max	Rinse solution	5% HNO <sub>3</sub>
Processing mode	Area	Acidity of standards/samples	Variable
(ii)			
Analyte	Emission line (nm)		Limits of detection (LODs)
	Main	Alternate	
			Dry weight sediment (mg kg <sup>-1</sup> )
			AF AD
Al	308.215	394.401	20.0 2.0
As	193.696	197.197	10.0 1.0
Co	228.616	238.892	3.0 0.3
Cr	267.716	205.560	2.0 0.2
Cu	324.752	327.393	0.9 0.1
Fe	259.939	234.349	4.0 0.4
Mn	257.610	259.372	1.0 0.1
Ni	232.003	341.476	3.0 0.3
Pb	220.353	217.000	3.0 0.3
Zn	213.857	206.200	2.0 0.2

#### 2.4. Sample preparation and analysis

Soil and sediment samples were oven-dried at 60 °C to constant weight and fractions of <2 mm were obtained using nylon sieves. The 2 mm fraction was then ground in a mill (Fritsch Pulverisette, Germany) and sieved to ensure a maximum particle size of 100 µm. This was done in order to minimise the variability due to grain size composition. Finally, samples were preserved in the refrigerator at 4 °C until analysis. The reference material was not oven-dried prior to digestion to prevent loss of volatile compounds and possible contamination. The element concentrations measured were based on dry weight after correcting for moisture content determined from separate subsamples dried in an oven for 48 h at 60 °C. Digestates that could not be immediately analysed were stored at 4 °C until analysis.

##### 2.4.1. Digestion methods and metal determination with ICP-OES

For the determination of heavy metal concentrations, the sediment samples were digested by two methods: (1) an alkaline fusion (AF) technique involving lithium tetraborate and (2) a microwave-assisted aqua regia digestion (AD), which was chosen as such that the minimum amount of acids could be used with the microwave apparatus. Optimum digestion conditions are given in sections 2.4.1.1 and 2.4.1.2. A blank reagent and quality assurance solution were run with each of the sample batches. All measurements were made at two wavelengths. If one wavelength was affected by interferences, then the other one was considered. The element concentration was given as the mean of three measurements. In the case of both wavelengths being chosen, concentration was calculated as the mean of the two results.

**2.4.1.1. Lithium tetraborate fusion technique (AF).** This method involved thoroughly mixing 0.1 g of accurately weighed sediment sample with 0.5 g of lithium tetraborate in a graphite crucible. The

mixture was then fused for 15 min at 1100 °C in a muffle furnace (Heraeus Instruments, Germany). The melt was then quenched into Teflon cups containing 4 mL conc. HCl in 46 mL ultrapure water and subjected to magnetic stirring using small Teflon-coated stirring bars for 30 min to aid dissolution. The mixture was then filtered, quantitatively transferred and made up to 100 mL in a volumetric flask. A reagent blank was prepared similarly. These samples were then transferred to the ICP-OES autosampler tubes and analysed under the conditions shown in Table 1. After each extraction, the graphite crucibles were decontaminated by soaking in nitric acid (10% v/v) for 24 h and rinsed with ultrapure water.

**2.4.1.2. Aqua regia with closed-vessel microwave digestion technique (AD).** This method involved taking 0.25 g of accurately weighed sample in polytetrafluoroethylene-tetrafluoromethane (PTFE-TFM) vessels, to which 6 mL conc. HCl and 2 mL conc. HNO<sub>3</sub> were added. The medium pressure vessels were then capped, and subjected to micro-wave exposure for complete digestion using a Anton Paar® GmbH Multiwave 3000 microwave digestion system equipped with the Rotor 16MF100 (Graz, Austria) for 30 min. An immersed temperature sensor in a reference vessel provided accurate reaction temperature control. The lip-type seal, made of chemically inert TFM, allowed for hermetic closure of the reaction vessels. The microwave oven specifications are given in Table 2(i) while the digestion programme used is listed in Table 2(ii). The total digestion time was 45 min, which included a 30 min cooling time in the microwave digester. After the automatic vessel built-in forced air cooling, the samples were filtered, quantitatively transferred and made up to 25 mL in a volumetric flask with ultrapure water. These samples were then transferred to the ICP-OES autosampler tubes and analysed using the conditions as shown in Table 1. After each digestion, concentrated nitric acid was placed in the Teflon vessels which underwent a cycle of decontamination in the microwave oven with the same programme as for the samples.



**Table 2**

(i) Microwave digestion system parameters and (ii) microwave digestion programme used in this study.

(i)			
Parameter	Value		
Vessels	MF100		
No. of vessels	16		
Liner material	PTFE-TFM		
Pressure jacket	Fibre-reinforced PEEK (poly-ether-ether-ketone resin)		
Volume	100 mL		
Controlled pressure	20 bar (290 psi)		
Max. pressure	70 bar (1000 psi)		
Test pressure	140 bar (2000 psi)		
Max. temperature	200 °C		
Reaction control	One reference vessel with immersed temperature probe and pressure sensor		

(ii)			
Step	Power (W)	Hold time (min)	Fan speed
1	200	5	1
2	500	5	1
3	1000	15	1
4	0	15	2

### 3. Results and discussion

#### 3.1. Quality control in analysis

All calibration curves for heavy metals had a correlation coefficient of  $R > 0.999$ . Quality assurance throughout the analytical process was maintained by the routine inclusion of a reference material and reagent blanks in each AF batch of fifteen samples as well as in AD batch of fifteen samples. Sample replicates were also regularly analysed after every ca. 10 samples. Accuracy was determined by comparing the measured concentration with the certified value and was expressed as percentage recovery (Rec. %). Satisfactory precision and accuracy were required to be within <20% and 80–120% for all elements, respectively, which corresponded to the uncertainty of the NIST-certified values, according to a 95% confidence interval for the true values [23]. The limits of detection (LOD) of each analyte were calculated as the analyte concentration that corresponded to three times the standard deviation of ten independent measurements of the blank, divided by the slope of the calibration curve [32]. Heavy metal content in the blanks was close to or below the detection limit, indicating a null contamination effect in both digestion methods. Analysis of variance was used to assess significant differences between treatments using a simple paired *t*-test at a confidence level of  $\alpha = 0.05$ . Simple correlation analysis was used to determine method correlation coefficients for each element at probability levels of  $\alpha = 0.5, 0.01$  and  $0.001$ . Percent biases were used to compare magnitude and consistency of these methods for analysing individual metals. The bias between AF and AD methods was defined as the concentration difference between the two methods divided by the concentration of the AD method. As such, a positive bias between the two methods implied that the concentration obtained from the AF method was greater than that from the AD method.

#### 3.2. Heavy metal concentrations in the sediment in NIST Reference Material 8704

Sakan et al. [5] reported variable recoveries ranging from 81.8 to 117% for Co, Cr, Cu, Fe, Mn, Pb, Ni and Zn analysis in CR-143R 'Sewage sludge amended soil' and BCR-146R 'Sewage sludge from industrial origin' certified reference materials using microwave aqua regia digestion and ICP-OES analysis, where the high variability was attributed to the

complex matrix of materials. Therefore, the analysis of the RM 8704 for ten elements (Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) was undertaken largely to investigate the validity of the fusion procedure against an acid digestion procedure and to investigate concentrations of several heavy metals in marine sediment samples from a contaminated environment. The percentage recovery of each heavy metal was obtained as [(measured concentration in  $\text{mg kg}^{-1}$ /mean certified value for RM 8704 in  $\text{mg kg}^{-1}$ )  $\times 100$ ]. Five replicate measurements were made for the RM, and the precision of replicate analyses of RM 8704 was defined as relative standard deviation (RSD). The concentrations of ten elements (Al, As, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) determined in sediment samples according to the two digestion procedures are summarised and compared with certified values in Table 3.

#### 3.3. Precision of two digestion methods

For both methods compared, precision was assessed as percentage relative standard deviation (RSD), with RSD <20% being deemed acceptable [24]. Average precision values and concentrations for elements for each method are presented in Table 3. Both AF and AD digestions achieved precise analysis using the RM 8704 which were within the target precision range of 20% for all elements except As by AF method.

Generally, the RSD values obtained by AD method were generally lower than the values obtained by AF method. AD method produced higher precision for As, Co, Cr, Cu, Mn, Pb and Zn than AF method, which is expected because these trace metals are relatively volatile. The mean elemental concentrations determined by AD method ( $n = 5$ ) were of satisfactory precision (RSD <3.4%), as demonstrated by the agreement with certified values for RM 8704. As a result of closed environment in AD method, the loss of analytes is minimised. The precision for the two techniques may also be different probably due to the different sample masses adopted in this work (0.1 g for AF and 0.25 g for AD method). Hence, the precision of the fusion procedure could be improved by using larger sample masses than those actually used here.

Normally, the precision for heavy metal analysis, such as Co, Cr, Cu, Mn, Ni, Pb and Zn, is below 20% for microwave aqua regia digestion with ICP-OES analysis [14,33]. Recently, Sakan et al. [5] reported a microwave aqua regia digestion technique combined with ICP-OES for Co, Cr, Cu, Fe, Mn, Pb, Ni and Zn analysis in CR-143R 'Sewage sludge amended soil' and BCR-146R 'Sewage sludge from industrial origin' certified reference materials, for which the precision was within 10%. Our results are also consistent with those of Melaku et al. [18] where the precision of the aqua regia digestion procedures was lower than 6% for Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn in BCR CRM 277 Estuarine sediment and BCR CRM 320 River Sediment using ICP-MS. Tam and Yao found excellent recoveries for Zn, Ni, Cr, Cu, Mn, Fe and Al in Standard Reference Material, SRM-GBW 07313 (marine sediments from the People's Republic of China) using microwave aqua regia digestion [11] while Nieuwenhuize et al. [27] obtained an extraction efficiency of Cr, Cu, Fe, Mn, Pb and Zn in a river sludge sample with RSD <12% using AD method with ICP-OES.

The AF produced higher precision for Al, Fe and Ni for the RM, because Al and Fe are refractory metals, which were completely digested from the silicate-aluminosilicate matrix. Bettinelli et al. [22] reported good precision for the refractory and silica bound elements such as Al with high temperature lithium tetraborate fusion of NBS River (1645) and Marine sediment (1646) CRMs using ICP-OES. Other trace elements (Mn, Cr, Ni, Cu, Zn and Co) were also determined within a precision of 1–10% in the two CRMs using the alkaline fusion procedure. Satisfactory precision was also obtained through AF method by Marques et al. [34] in the ICP-MS analyses of As, Co, Cu, Fe, Mn, Ni, Pb and Zn in the NIST SRM 1646a Estuarine Sediment which was dry-ashed at 550 °C and then fused at 1100 °C for 30 min with lithium metaborate. These studies, as well as the present

**Table 3**

Precision and accuracy of the two digestion procedures for the determination of ten metals in NIST Reference Material 8704.

Metal	Certified value (mg/kg) <sup>a</sup>	This work (AF) (mean, n = 5) (mg/kg) <sup>a</sup>	RSD (%)	Rec. (%)	This work (AD) (mean, n = 5) (mg/kg) <sup>a</sup>	RSD (%)	Rec. (%)	Bias (%) (AF vs AD)
Al	61	59.6 ± 0.9	1.5	97.7	44.5 ± 1.0	2.2	73.0	34
As	17 <sup>b</sup>	<DL	–	0	14.5 ± 0.7	4.8	85.3	–100
Co	13.6	11.2 ± 0.5	4.5	82.4	11.6 ± 0.5	4.3	85.3	–3
Cr	121.9	121.9 ± 5.6	4.6	100.0	118.6 ± 3.1	2.6	97.3	3
Cu <sup>c</sup>	N/A	105.7 ± 2.6	2.5	N/A	104.4 ± 2.3	2.2	N/A	4
Fe	39.7	39.2 ± 0.7	1.8	99.7	38.8 ± 0.9	2.3	97.7	1
Mn	544	544.4 ± 13.8	2.5	100.1	553.1 ± 3.7	0.7	101.7	–2
Ni	42.9	44.1 ± 2.0	4.5	102.8	44.6 ± 2.1	4.7	104.0	–1
Pb	150	143.3 ± 18.8	13.1	95.5	146.0 ± 6.0	4.1	97.3	–2
Zn	408	353.2 ± 7.8	2.2	86.6	402.3 ± 7.4	1.8	98.6	–12
Average			3.7	85.0		3.3	93.4	

Rec.: recovery.

<sup>a</sup> Al and Fe concentrations are g kg<sup>–1</sup>.<sup>b</sup> The concentration of As provided in the RM is not a certified value, but for information purpose only.<sup>c</sup> The certified concentration of Cu was not given for the RM.

one, support the idea that alkaline fusion is generally an effective dissolution method for most sediment reference materials for heavy metal analysis.

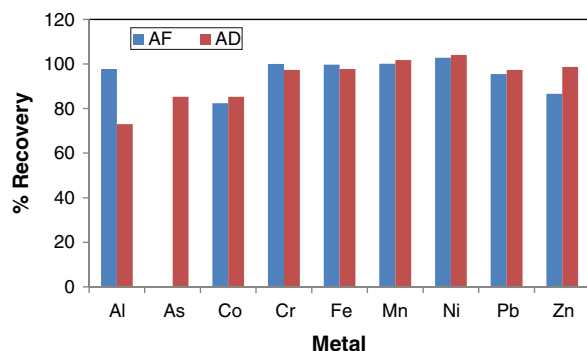
According to Scancar et al. [35], the proportion of the heavy metals dissolved during digestions depends on the matrix and on the metal to be analysed. Low As precision in the AF procedure may be explained by the loss of analyte during the heating step rather than by incomplete dissolution of the sample [22]. Similar explanation could be offered for the relatively lower precision obtained for Pb (13%) using AF because of loss of Pb through volatilization during the fusion step. Nam et al. [36] showed that method reproducibility can be a major problem when analysing heavy metals in sediments using standard established methods. The AD method of extraction seemed to be a highly reproducible method for the determination of heavy metals in sediment samples studied in the present case. However, when based on the average precision of the two digestion methods over ten elements using the RM, the AD method (3.3%) was quite comparable with the AF digestion (3.7%). This implies that the two digestion procedures generally achieved comparable and acceptable precision in analysing all the heavy metals except As.

#### 3.4. Accuracy of two digestion methods

Recoveries of elements were calculated as the percent of certified elemental concentration extracted from the RM 8704, with recoveries 80–120% being deemed acceptable [23]. Generally, accurate results were obtained for all heavy metals using both methods except for Al by the AD method and As by the AF method, which is illustrated as Fig. 1. It can be seen from the data presented in Table 3 and Fig. 1 that most metals quantitatively leached after AD method in the RM analysed. Successful leaching was achieved for Co, Cr, Cu, Fe, Pb,

Mn, Ni and Zn (85.3–104%), but a significantly lower efficiency of leaching was found for Al (73.0%). The low recovery for Al obtained with microwave aqua regia digestion has also been observed by other researchers, which is due to the great complexity of the dissolved matrix affecting the recovery of refractory elements like Al [13,23]. It has been reported that either HF or HClO<sub>4</sub> or a combination of both acids be used in the digestion step to completely release Al from the aluminosilicate phase [17]. Similar results for Al from NIST SRM 2704 were reported using microwave HNO<sub>3</sub>–HF–HClO<sub>4</sub> digestion [37]. Vojtekova et al. [38] showed that most Al in sediments is found in the residual phase, which required using the acid mixture HF–HNO<sub>3</sub>–HClO<sub>4</sub> for extraction. Landajo et al. [39] analysed a certified material RTC 008-050 (soil/sediment) using microwave digestion for 17 min, 5:1 HCl:HNO<sub>3</sub> ratio solvent, 70% microwave power and 25 mL solvent volume, and found highly variable recoveries for the following heavy metals: As (102%), Cr (120%), Cu (76%), Fe (70%), Mn (80%), Ni (106%), Pb (98%) and Zn (107%). Florian et al. [1] investigated certified estuarine sediment using AD method and found recoveries of 90–120% of the total concentrations for Cr and Pb, with an average precision of 3%, while Relic et al. [14] obtained 82–113% recovery for Ba, Ca, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and V in BCR 143R and BCR 146R reference materials using microwave aqua regia digestion and ICP-OES determination. Eight investigated heavy metals (Cr, Cd, Cu, Fe, Mn, Ni, Pb and Zn) in four sediment CRMs exhibited highly variable recoveries (21–99%) with respect to the certified values using the AD method [15] while Melaku et al. [18] showed good microwave aqua regia digestion efficiency with CRM 277-Estuarine Sediment reference material for Co, Cr, Cu, Mn, Ni, Pb and Zn (86.4–101.4%) but unsatisfactory results for CRM-320 River Sediment reference material (63.8–104.1%).

Overall, when compared with the AF method, the AD method had either increased or comparable elemental recovery for all elements except Al (Fig. 1). The average recovery over ten heavy metals for the AD method (93%) was significantly greater than that of the AF (85%) digestion procedure. The high efficiency of the sample digestion using the microwave method has been attributed to the fragmentation of the solid materials due to the high pressures, which exposes fresher and finer portions of the sample to acid attack [40]. Chromium has usually been reported by researchers to be underestimated by microwave aqua regia digestion in sediment samples [13,16,23]. However, Cr was effectively extracted by AD method in the present case for the certified sediment. The digestion power of aqua regia arises from the reactivity of nitrosyl chloride (NOCl) and/or free chlorine formed in freshly prepared aqua regia solution [15,23], thus should be a better extracting agent for the refractory metal such as chromium, and the same was shown in the present study. Copper is not certified for RM 8704 but the two sets of results for both methods are in close agreement. Hence Cu can be said to be quantitatively recovered with both



**Fig. 1.** A comparison of the metal recovery from NIST Reference Material 8704 using the alkaline fusion and acid digestion methods.

methods. The total Cu value of  $98.6 \pm 5.0 \text{ mg kg}^{-1}$  provided for SRM 2704 (which is similar in composition to RM 8704) is intermediate between our  $105.7 \pm 2.6 \text{ mg kg}^{-1}$  (AF method) and  $104.4 \pm 2.3 \text{ mg kg}^{-1}$  (AD method) values. A value of  $95.9 \pm 5.5 \text{ mg kg}^{-1}$  for Cu has been recently reported for RM 8704 by Divrikli et al. [41]. Hence the experimental values from both digestion methods are quite satisfactory.

Recoveries for elements in the sediment RM for AF method varied from 82 to 103%, except for As which was not detected at all (Table 3). The total Al recovery obtained by the AF method (97.7%) was clearly higher than the acid-extractable method (73.0%), reflecting the requirement for fusion to completely dissolve the aluminosilicates present in the sediments. Aluminium is quantitatively recovered using AF method because hard lattices of Al minerals (e.g. silicates) can be broken, which is not achieved by aqua regia [16]. Quantitative results were also obtained for Al, Fe, Mn, Cr, Ni, Cu, Zn, and Co by Bettinelli et al. [22] using lithium tetraborate fusion in two NIST Standard Reference Materials, River Sediment 1645 and Marine Sediment 1646 [28,42]. In environmental analysis, low recoveries for elements such as As and Pb by fusion methods have often been attributed to their volatilisation losses [22,28,42]. However in the present study Pb was quantitatively recovered (95.5%), albeit with a relatively lower precision (13%).

The use of  $\text{HNO}_3\text{--HCl--HF--H}_3\text{BO}_3$  acid mixtures for complete dissolution and determination of the Co, Cr, Cu, Mn, Ni, Pb and Zn in sediments has been recommended [18,21]. Using very intensive conditions, Sun et al. [10] compared recoveries of nine heavy metals in sediment (NIST SRM 2704) using microwave assisted  $\text{HNO}_3\text{--HCl--HF}$  and  $\text{HNO}_3\text{--HClO}_4\text{--HF}$  digestion methods, which were found to be 86–113% for Ag, Cr, Cu, Fe, Mn, Ni, Pb and Zn. However, the use of HF and  $\text{HClO}_4$  is not recommended for routine analyses since they involve long, hazardous and cumbersome procedures as well as the need for specialised laboratory equipment (e.g. perchloric acid hood, with appropriate wash down facility) due to their highly explosive and corrosive nature [3]. In addition, HF also has adverse effects on the life of laboratory equipment and apparatus. Therefore, the alkaline fusion method used here for total metal extraction from sediments is a very good alternative to the hazardous acid procedures.

### 3.5. Heavy metal concentrations in marine sediment samples

The environmental sample, being less homogeneous than reference materials, can provide highly variable recovery values for metals due to different matrix effects [13]. Hence, depending on the sample,

in the Cu, Ni and Pb contamination assessment in marine sediments by Pena-Icart et al. [2], the EPA 3050B and ISO 11466.3 methods extract the total metal content or a fraction (10–100%) of it. Therefore, the two digestion procedures in the present work were tested for their precisions and recoveries using ten sediment samples as their matrix differed from that of the reference material. Therefore to assess environmental contamination, the validated AF and AD methods were applied to real sediment samples from Lami coastal environment, adjacent to an industrialised area of eastern Viti Levu, the main island of Fiji [30,31]. The summary of the results with statistics is given in Table 4. The paired-samples *t*-test was used to compare heavy metal content obtained by both methods. A low significance value ( $p < 0.05$ ) indicates that there is a significant difference between results achieved by both digestion methods for a given element.

Firstly, as per the results shown in Table 4, the differences between the minimum and maximum values for all the elements are quite large, showing the wide diversity in the study sites. The regression analysis indicated significant positive correlation between AF and AD methods for all the metals except for As. The linear regression showed a good correlation between AF and AD methods for Al, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn ( $r > 0.87$ ). In fact, samples with very high as well as very low concentrations of heavy metals generally show a good correlation between the results from the two methods. This suggests that similar biases between these methods would be expected if they were used to determine concentrations of these nine elements in other sediments taken from other study sites. However, As ( $r = 0.47$ ) presented a low determination coefficient indicating a slight difference between the methods. The discrepancy in elemental recovery of As among the two methods may be attributed to loss due to volatility, as described in the previous sections 3.3 and 3.4, since only  $33.1 \text{ mg kg}^{-1}$  As was detected by the AF method as compared to  $345.2 \text{ mg kg}^{-1}$  by the AD method for the same sediment sample (Table 4).

The RSD values recorded for AF method for most metals were lower than values found for AD method. All heavy metals studied here except for As and Zn behaved in this manner, with AF method being more precise than the AD method. A greater variability with the AD method is expected as compared to the AF method since complete digestion and solubilization is carried out by AF method, especially in the case of Al. The lower precision obtained for As and Zn by AF method may be explained by the loss of these elements during the fusion step rather than incomplete dissolution.

Application of the paired-samples *t*-test demonstrated that there was a significant difference for these metal concentrations when

**Table 4**  
Analytical results for the analysis of metals in ten sediment samples (as  $\text{mg kg}^{-1}$  or  $\text{g kg}^{-1}$  on dry sediment basis).

Metal	Mean ( $\text{mg kg}^{-1}$ ) <sup>a</sup> (n = 10)		Bias (%)	SD ( $\text{mg kg}^{-1}$ ) <sup>a</sup>		Min. ( $\text{mg kg}^{-1}$ ) <sup>a</sup>		Max. ( $\text{mg kg}^{-1}$ ) <sup>a</sup>		RSD (%)		AF vs AD	
	AF	AD		AF	AD	AF	AD	AF	AD	AF	AD	Corr. (r)	<i>t</i> -Test <sup>b</sup>
Al	70.8	56.0	26	9.3	13.0	55.1	37.4	85.8	72.5	13.1	23.2	0.87*	**
As	2.7	43.1	−94	8.3	103.9	0.0	0.0	33.1	345.2	308.8	241.2	0.47	NS
Co	29.9	23.2	29	4.7	3.9	20.5	15.0	37.8	28.9	15.6	16.7	0.93*	**
Cr	136.5	81.1	68	155.7	101.1	39.0	20.0	518.7	373.3	114.1	124.7	0.89*	**
Cu	159.5	168.4	−5	167.6	178.2	10.4	14.5	504.9	530.4	105.1	105.8	1.00*	NS
Fe	60.8	56.1	8	12.7	13.1	36.0	29.8	77.3	75.0	20.9	23.3	0.98*	**
Mn	877.6	755.1	16	281.0	249.2	409.8	350.0	1456.0	1366.0	32.0	33.0	0.97*	**
Ni	28.9	26.1	11	10.4	9.9	12.4	11.5	42.6	42.1	36.0	37.9	0.98*	NS
Pb	166.5	189.9	−12	175.0	253.3	8.0	12.0	747.2	799.6	105.1	133.4	0.98*	NS
Zn	405.8	426.4	−5	455.6	473.9	99.0	100.6	1613.0	1720.0	112.3	111.1	1.00*	NS

\* Significant at the 0.001 probability level.

\*\* Significant at the 0.05 probability level. NS = not significant. AF = alkaline fusion method. AD = microwave aqua regia digestion method.

<sup>a</sup> Al and Fe are  $\text{g kg}^{-1}$ .

<sup>b</sup> Paired-samples *t*-test (least significant difference) at  $\alpha = 0.05$ .

results were analysed sample by sample. Thus, significant improvement in the digestion efficiency was observed for Al, Co, Cr, Fe and Mn when using a simple *t*-test at  $\alpha = 0.05$  with the AF method, as compared to the AD method. This indicates that the AF method was more effective in dissolving these elements from sediment samples than the AD method. This can be attributed to the efficient decomposition of the sediment matrix containing Mn/Fe oxides, aluminosilicates and clay minerals. The most notable was Cr as reflected by its large positive bias (68%) i.e. on average, 68% more Cr was released by the AF method than the AD method for sediments. Some researchers have reported that microwave acid digestions give lower values for Cr in sediments due to its associations with certain matrices such as chromite, aluminosilicate minerals and organic matrix, which cannot be decomposed by either aqua regia or even aqua regia-HF [11,15,17,22,36,42]. However, further investigation on the mineralogical composition of the sediments is needed to identify the possible sediment matrices that exist in samples taken from the present location.

The biases for concentrations of Cu, Fe and Zn between the two digestion procedures were negligible (<10%), while concentrations of Ni, Pb and Mn were comparable (with bias <20%) using the two digestion methods (Table 4). The similarities in Cu, Fe, Mn, Ni, Pb and Zn extraction between AF and AD methods show that at high temperatures volatilization does not occur to a significant extent and both methods extract these elements in almost similar efficiency. As shown in Table 4, greater biases were obtained between the two methods for Al, As, Co and Cr in the ten sediment samples than in the RM (Table 3) due to inefficient extraction or loss due to volatility (*vide supra*). The very high and variable level of heavy metal contamination in the sediments would also have affected the bias, recovery and hence overall precision of the analysis for these samples. Since three different types of sediments (coastal, estuarine and riverine) were used in the present study, high biases would be expected [2]. Therefore biases between different digestion procedures in NIST RM and real sediments for most metals are difficult to compare. From

the data of Table 4 it can also be concluded that the proportion of metals dissolved is variable and that it depends on the sediment matrix and on the element analysed, reinforcing the conclusions of similar studies done elsewhere [18,23]. Therefore, the present study underlines the importance of validating sample digestion procedures using standard reference materials and some representative field samples before actual environmental analyses.

### 3.6. Distribution of the heavy metals in the study sites

Overall heavy metal concentrations were calculated for the studied sites as the mean with standard deviation (SD) of ten sediment samples and the results illustrated as Fig. 2. The lowest concentrations of metals in samples were found in the upper stream of the Lami River, which is free of any industrial activity [30,31], and hence served as background values (Table 4). Apart from Fe, Al and Mn, the three main components of the sediments, the concentrations of Cr, Cu, Pb and Zn were highly elevated in most of the samples, with average concentrations of 136.5, 168.4, 189.9 and 426.4 mg kg<sup>-1</sup> respectively, for the ten samples. There are huge differences between the minimum and maximum values of As, Cr, Cu, Ni, Pb, and Zn concentration observed in the ten sediment samples (Fig. 2). Table 4 clearly shows that the highest concentrations of As, Cr, Cu, Ni, Pb, and Zn were found to be 345.2, 518.7, 530.4, 1387, 799.6 and 1720 mg kg<sup>-1</sup>, respectively. Moreover, these metal concentrations greatly exceed international SQG values, which are used as thresholds for metal concentrations above which sediments are considered to be contaminated and harmful to biota [6]. High metal concentrations suggest a significant input from the surrounding industries, especially paint and battery manufacturers and through urban waste discharge in the Lami industrial environment. The entire data were also subjected to a statistical analysis and correlation matrices were produced to examine the inter-relationship among the investigated metal concentrations. The values of Pearson

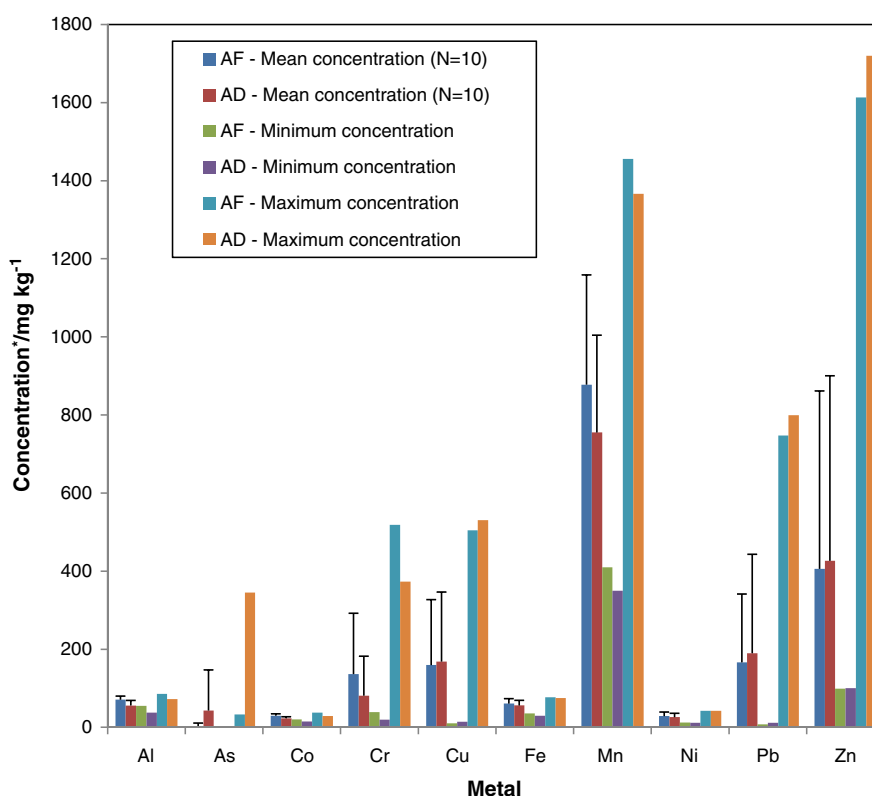


Fig. 2. Comparison of the mean, minimum and maximum concentrations of metals in ten sediment samples from the Lami (Fiji) coastal environment, using the AF and AD techniques. \*Al and Fe concentrations are indicated as g kg<sup>-1</sup>.



**Table 5**

Correlation matrix of analysed parameters in ten sediment samples from the Lami coastal environment showing Pearson correlation coefficients ( $r$ ) between metals.

Metal	Al	As	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Al	1.00									
As	0.01	1.00								
Co	0.25	0.29	1.00							
Cr	0.02	<b>0.87</b>	0.26	1.00						
Cu	0.00	<b>0.94</b>	0.33	<b>0.88</b>	1.00					
Fe	0.29	0.33	0.52	0.30	0.44	1.00				
Mn	0.13	0.00	0.02	0.01	0.00	0.00	1.00			
Ni	0.06	0.00	0.00	0.00	0.03	0.04	0.00	1.00		
Pb	0.01	0.01	0.01	0.44	0.00	0.08	0.00	0.00	1.00	
Zn	0.02	<b>0.94</b>	0.33	<b>0.93</b>	<b>0.92</b>	0.29	0.00	0.00	0.00	1.00

All  $r$  values indicated in bold are significant at the 0.001 probability level.

correlation coefficients ( $r$ ) between metal concentrations are given in Table 5. According to the literature, Al, Fe and Mn are variables usually linked to the geochemical matrix of sediments, while the trace metals would indicate an overall pattern of the sediment contamination [37,39]. There are significant positive correlations of As with Cr, Cu and Zn with corresponding  $r$  values of 0.87, 0.94 and 0.94, respectively. Chromium has significant positive relationships with Cu and Zn with corresponding  $r$  values of 0.88 and 0.93, respectively, while Cu is also correlated with Zn ( $r > 0.92$ ). The weak correlation of As with Al, Fe and Mn while strong association with Cr, Cu and Zn may be due to anthropogenic contamination of the sediments [11,39]. The significant positive correlations between As–Cr, As–Cu, As–Zn, Cr–Cu, Cr–Zn and Cu–Zn show that the sediments with significant correlations among the concentrations of the elements are from the same pollution sources in the coastal environment.

#### 4. Conclusion

The results of this study indicate that alkaline fusion or microwave aqua regia dissolution combined with ICP-OES determination is a very rapid and accurate method for analysing sediments for several heavy metals. Application of alkaline fusion and microwave aqua regia digestion methods to a certified sediment sample showed good similarity for Cr, Cu, Fe, Mn, Ni, Pb and Zn determination by ICP-OES. In particular, AF method improved digestion efficiency for Al, Co, Cr, Fe and Mn while the microwave aqua regia method improved extraction results for As, Cu, Pb and Zn. According to the obtained digestion efficiency in ten different sediments, both methods can be satisfactorily used to estimate the total concentration of Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in sediments from contaminated environments. Except for the determination of the volatile analytes such as As, the AF method can be proposed as alternative to the microwave aqua regia method for the determination of the total Al, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn levels in sediment samples. This study underlines the importance of validating sample digestion procedures using reference and some real sediment samples before actual environmental analyses. The sediment data obtained suggest that there is significant discharge of heavy metal from the urban industrial activities to the estuary under study, though further analysis is necessary to obtain the actual ecological impact of this pollution on the immediate environment.

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