

Comparison of Acid Digestion Techniques To Determine Heavy Metals In Sediment And Soil Samples

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ABSTRACT

Four acid digestion procedures were applied to certified samples to offer a proper method for determination of Cr, Cu, Pb and Zn in soils and sediments. EPA's Acid Digestion Procedure 3050B and three low pressure microwave heating programmes modified in this study were tested by using two standard referencematerials; Estuarine Sediment-1646a and San Joaquin Soil-2709. Short digestion time, less acid consumption, and high extraction efficiency were noted as the advantages of microwave digestion procedures. According to the results, San Joaquin Soil was efficiently extracted with the second microwave heating programme named as P2 (84.4% Cr, 96.9%Cu, 102.3% Pb, 90.1% Zn) where Estuarine Sediment gave the most accurate results (99.8% Cr, 103.9% Cu, 97.4% Pb, 96.3% Zn) with the third microwave extraction procedure (P3).

Key Words: Acid digestion, Heavy metal, Microwave extraction, Sediment, Soil

1. INTRODUCTION

Heavy metals are considered to be one of the main sources of pollution in the environment, because of their significant effect on the ecological quality [1]. The main sources of heavy metal pollution in the environment are man-made effects, including combustion of fossil fuels, mining activities, wastewater discharges of manufacturing industries, and waste disposal [2]. High levels of heavy metals in the sediments and soils may pass to the aquatic environment, groundwater, and plants through the transfer processes and reach to the animals and humans. Therefore, the use of simple and accurate methods for monitoring heavy metals has a great importance among the environmental studies.

Analytical instruments and techniques have been developed over the past 30 years to determine the

concentrations of metals in our ecosystem; atmosphere, water, soils and sediments [3]. Highly sensitive spectroscopic techniques such as flame or electrothermal atomic absorption spectroscopy (FAAS, ETAAS) and inductively coupled plasma-optical emission spectrometry and inductively coupled plasma mass spectrometry (ICP- OES and ICP-MS) are the most widely used methods to determine heavy metals in environmental samples [1].

For solid samples such as sludges, soils and sediments, the solid form must be transformed to liquid phase. This process named digestion is required for the spectroscopic analysis. The principle is the releasing of metals from the solid matrix to the acid solution during the extraction process. Conventional acid leaching procedures and microwave assisted acid digestion systems are used to prepare the sample for further

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spectroscopic analysis. The conventional procedures are open systems in which the solid material is extracted on a heating source in the presence of acid and/or acid mixtures. In this procedure, different heating systems may be used such as sand-bath, heating plate and aluminum blocks [1]. Microwave assisted acid digestion procedures and pressure digestion bombs are closed systems providing higher temperature and pressure in closed vessels [4]. The critical parameters in these procedures are; the digestion temperature, applied programme, time, and the chemical power of the reagents used. For the extraction processes, a variety of acid mixtures have been used (HNO_3 , HNO_3 -HF, HNO_3 -HCl, etc.) as reagents. The choice of an individual acid or combination of acids depends on the nature of the matrix to be decomposed. Among the acids used for wet digestion, HCl (boiling point 110°C) is useful for salts of carbonates, phosphates, some oxides and some sulfides. HNO_3 (boiling point 122°C) makes an oxidizing attack on many samples not dissolved by HCl. Besides, HF is necessary for digestion of silica-based materials [5]. HF-based digestion methods tend to produce higher digest concentration of the metals. On the other hand, HF is toxic and may cause damage in the instruments [6]. Therefore, the use of HF should be kept at a minimum in the digestion procedures.

The need for the rapid and accurate determination of heavy metals in sediments and other solid matrixes (soils, sludges, etc.) has led to the development of various microwave procedures which provide the efficient dissolution of metals [7]. The procedures may be numerous depending on the choice of the reagent and specific heating programmes.

In most studies, high pressure powers are applied to the samples by using high technology digesters [1, 3, 8]. This paper aims to propose a rapid, practical, and efficient method for the determination of Cr, Cu, Pb and Zn in soil and sediment samples under lower pressure powers and short digestion times. Two different standard reference materials (SRMs) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA), Estuarine Sediment-1646a and San Joaquin Soil-2709 were used as the solid samples. EPA's Acid Digestion Procedure (EPA 3050B) was used as a conventional technique and three different microwave-assisted acid digestion procedures were modified and applied to the standard reference materials. The certified and obtained values were compared with each other to obtain the most appropriate procedure for each element.

2. MATERIALS AND METHODS

2.1. Standard Reference Materials

Depending on the different metal concentration levels, either the Estuarine Sediment-1646a or San Joaquin Soil-2709 obtained from NIST (National Institute of Standards and Technology) were used for the digestion procedures. Metal concentrations of San Joaquin Soil were greater than of the Estuarine Sediment (Cr and Cu concentrations were nearly three times greater where Pb and Zn values were doubly higher). Prior to the

analysis, the samples were dried at 110°C for two hours as indicated in their certificate.

2.2. Reagents

Among the concentrated acids, 65% (w/v) HNO_3 and 37% (w/v) HCl were provided by Riedel-de Haën where 40% (w/v) HF was obtained from Prolabo and 30% (w/v) H_2O_2 was obtained from Merck (Darmstadt, Germany). The calibration standard solutions for Cr, Cu, Pb and Zn were prepared by using Merck standard solutions with a purity of %99.8.

The solutions were prepared by using doubly de-ionized water. Before digestion, the sample flasks and digestion vessels were soaked into 10% HNO_3 for 24 h and then washed with de-ionized water.

2.3. Digestion Procedures

2.3.1 EPA Method 3050B

A procedure recommended by Environmental Protection Agency (EPA, Method 3050B) was used as the conventional acid extraction method. 1 g of sample was placed in 250 ml flask for digestion. The first step was to heat the sample to 95°C with 10 ml of 50% HNO_3 without boiling. After cooling the sample, it was refluxed with repeated additions of 65 % HNO_3 until no brown fumes were given off by the sample. Then the solution was allowed to evaporate until the volume was reduced to 5 ml. After cooling, 10 ml of 30% H_2O_2 was added slowly without allowing any losses. The mixture was refluxed with 10 ml of 37% HCl at 95°C for 15 minutes [9]. The digestate obtained was filtered through a 0.45 μm membrane paper, diluted to 100 ml with deionized water and stored at 4°C for analyses. The total extraction procedure lasted for 180-200 min (Table 1).

2.3.2 Microwave Acid Digestion

The Questron MicroPrep Q20 Microwave Digestion System with four digestion vessels was used for microwave assisted acid digestion procedures. Samples were placed in liners (TFM Teflon, softening point 250°C) which are mounted in ultem caps. The vessels support an operating pressure of 350 psi and a maximum temperature of 260°C and they are resistant to HF [10]. Rupture disks were placed in the Over Pressure Valve Stems in the vessels to become a pressure control device in the digester. The system allows the digestion of four samples at the same time.

Three different digestion programmes labeled as P1, P2 and P3 were tested with the SRMs. 0.1 g of sample was used for each digestion. Combinations of nitric acid (%65 HNO_3 - used for easily oxidizable material), hydrofluoric acid (%40 HF- used for extraction of inorganic matrixes), and hydrochloric acid (37% HCl) were added to each of the digestion vessels. For microwave-assisted digestion procedures, the total extraction time was set as 26 min. The highest power applied for all procedures was 600 watts, held for 1 min in P1 and P2, and 2 min for P3. 0.8 ml of HCl was added to the acid mixture for P2 and P3. The details of the heating programmes used are given in Table 1. The digestate obtained were then filtered through a 0.45 μm membrane filter, diluted to 20 ml for storage and further

analyses. For accurate results, all the extraction procedures were applied in triplicate.

2.4 Instrumentation

A Perkin Elmer Optima 4300 DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for the determination of metals. The ICP OES was calibrated daily using a standard solution. The analysis of the samples was performed only if the r2 of the calibration curve was greater than 0.99. A calibration check solution was prepared by another certified solution and the calibration curves were checked after the initial calibration for every 10 samples. In the case of more than ±10% deviation, the ICP OES was re-calibrated. Cr and Cu were detected at the wavelength of 267.716 and 327.393 nm, where Pb and Zn were determined at 220.353 and 206.200, respectively.

3. RESULTS AND DISCUSSION

For the extraction programmes used, Method 3050B consumed more time since the procedure includes repeated additions of reagents and volume reductions (The extraction lasted in approximately 180-200 min). However, all the microwave digestion procedures lasted in 26 min. The different results obtained from the three microwave procedures depend on the presence of HCl as a reagent and the extraction times applied in each step. The certified and obtained results for San Joaquin Soil and Estuarine Sediment are given in Table 2 and Table 3. In order to evaluate the analytical accuracy of the procedures, experimental values and the certified values of SRMs were compared and the percentage recovery of each metal was calculated as;

$$\% \text{ Recovery} = [\text{Mean value (measured concentration, mg/kg)} / \text{Certified value (mg/kg)}] * 100$$

It's indicated in their certificate that mixed acid digestion procedures were used for both of the SRMs for certification [11, 12].

Table 1. Steps of microwave heating programmes and acid digestion procedure

Programme	Sample weight (g)	Reactives and consumptions (ml)	Prog. step	Power (W)	Time (min)
P1 (26 min)	0.1	65% HNO ₃ (3 ml) 40 % HF (1 ml) (Total reactive volume :4ml)	1	200	8
			2	400	7
			3	600	1
			4	0	10
P2 (26 min)	0,1	65% HNO ₃ (3 ml) 40% HF (1 ml) 37% HCl (0.8 ml) (Total reactive volume :4.8 ml)	1	200	8
			2	400	7
			3	600	1
			4	0	10
P3 (26 min)	0,1	65% HNO ₃ (3 ml) 40% HF (1 ml) 37% HCl (0.8 ml) (Total reactive volume :4.8 ml)	1	200	8
			2	400	6
			3	600	2
			4	0	10
EPA Method 3050B (180-200 min)	1	50% HNO ₃ (10 ml) 65% HNO ₃ (5ml) 30% H ₂ O ₂ (10 ml) 37% HCl (10 ml) (Total reactive volume : 35-50 ml depending on HNO ₃ additions)	-	-	10
			-	-	30
			-	-	Until effervesce subsides 15

Table 2. Certified and Obtained Values for San Joaquin Soil – 2709 (n=3)

Metals	Certified Value (mg kg ⁻¹ ± sd)	P1 (mg kg ⁻¹ ± sd)	P2 (mg kg ⁻¹ ± sd)	P3 (mg kg ⁻¹ ± sd)	EPA 3050B (mg kg ⁻¹ ± sd)
Cr	130.0 ± 4	107.8 ± 5.8	109.6 ± 3.4	129.7 ± 5.4	113.9 ± 6.2
Cu	34.6 ± 0.7	26.8 ± 1.2	33.5 ± 1.3	33.6 ± 0.3	21.5 ± 2.0
Pb	18.9 ± 0.5	14.6 ± 1.4	19.3 ± 1.3	11.8 ± 1.6	6.8 ± 0.6
Zn	106.0 ± 3	83.5 ± 1.3	95.5 ± 5.2	71.9 ± 4.8	84.5 ± 3.8

Table 3. Certified and Obtained Values for Estuarine Sediment - 1646A (n=3)

Metals	Certified Value (mg kg ⁻¹ ±sd)	P1	P2	P3	EPA 3050B
		(mg kg ⁻¹ ±sd)	(mg kg ⁻¹ ±sd)	(mg kg ⁻¹ ±sd) ¹	(mg kg ⁻¹ ±sd)
Cr	40.9 ± 1.9	35.9 ± 2.5	37.1 ± 3.4	38.9 ± 3.3	34.8 ± 1.9
Cu	10.0 ± 0.3	5.1 ± 0.6	11.3 ± 1.4	11.1 ± 1.1	6.2 ± 0.3
Pb	11.7 ± 1.2	7.2 ± 0.5	13.1 ± 1.4	11.4 ± 0.4	4.5 ± 0.4
Zn	48.9 ± 1.6	41.7 ± 8.3	34.3 ± 4.7	47.1 ± 1.6	41.8 ± 1.2

3.1 San Joaquin Soil-2709

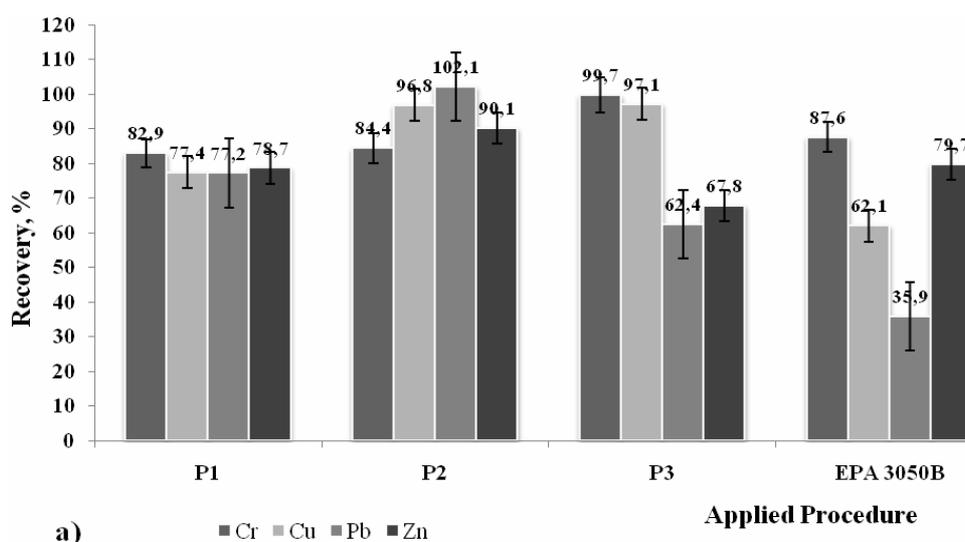
The results of metal analysis and certified values in San Joaquin Soil are presented in Table 2. This SRM contains higher heavy metals compared to the Estuarine Sediment. Figure 1 presents the comparison of recovery rates of the studied digestion procedures for the San Joaquin Soil-2709 and Estuarine Sediment-1646a. By using P1, the recoveries of Cr, Cu, Pb, Zn were 82.9, 77.4, 77.2 and 78.7%, respectively, while higher values than those of P1 were obtained with P2. The difference of P2 from P1 is the HCl addition into the HNO₃-HF mixture. Cr, Cu, Pb and Zn were extracted satisfactorily with this procedure with the recovery rates of 84.3, 96.8, 102.1, and 90.1%, respectively. Results of P3 showed varieties for each of the metals. Comparable recovery rates were obtained for Cr (99.8%) and Cu (97.1%) where Pb and Zn were poorly extracted with the ratios of 62.4% and 67.8%, respectively (Figure 1).

By using EPA's Acid Digestion Procedure, Pb was poorly recovered (36.0%) and the extraction efficiency of Cu was detected as 62.1%. Cr (87.6%) and Zn (79.7%) were extracted satisfactorily when compared to Pb and Zn.

3.2. Estuarine Sediment- 1646A

By using P1, poor recovery rates were obtained for Cu (51%) and Pb (61.5%) where Zn was recovered satisfactorily with 85.3% as well as Cr (87.9%). The difference of P2 from P1 is the HCl addition into the HNO₃-HF mixture. Recovery values for the Estuarine Sediment showed differences according to the metals. High recovery rates for P2 programme were obtained for Cu and Pb (113.2% and 112.0%, respectively) where Zn was poorly recovered with 70.1%. Cr was recovered satisfactorily with 90.6% in the sediment sample. In P3, 600 watts power was applied to the system for 2 min. Different than P2, this procedure showed consistent results for Estuarine Sediment. For all the metals studied, accurate recovery values were obtained (Cr; 95.1%, Cu; 111%, Pb; 97.4 %, Zn; 96.3 %) (Figure 1). This may be explained by the longer application of 600 watts power for the complex matrix of the sediment.

The use of EPA's Acid Digestion Procedure 3050B for Estuarine Sediment gave similar results when compared to San Joaquin Soil. Cr, Cu, Pb, and Zn were recovered with the ratios of 85.1%, 61.9%, 38.5%, and 85.5%, respectively.



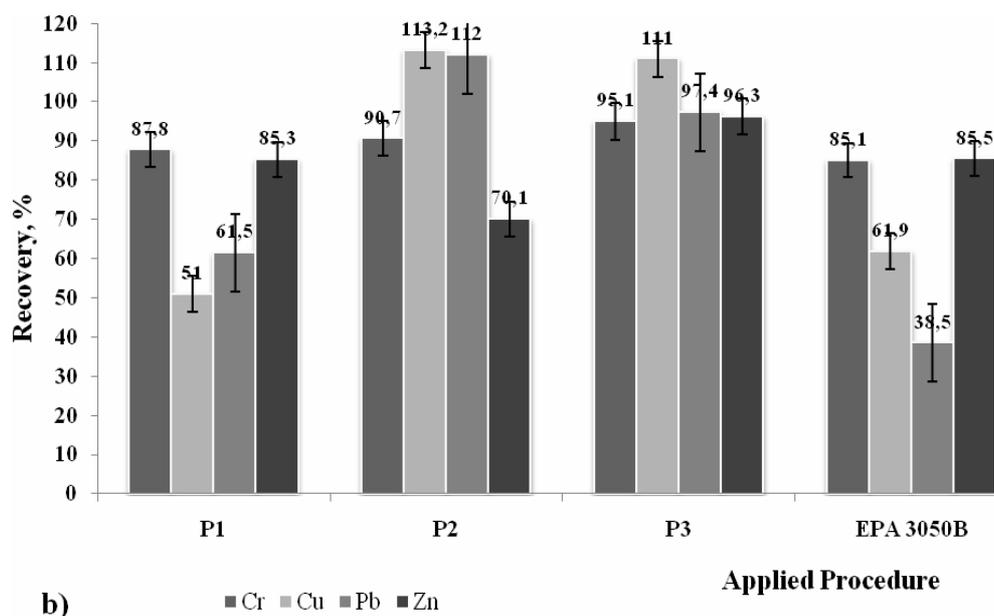


Figure 1. Comparison of recovery rates for the digestion procedures (a)San Joaquin Soil -2709; (b) Estuarine Sediment-1646A

3.3. Discussion

For the acid digestion procedures, the extraction time and the total reagent consumption are of great importance. In EPA Method 3050B, the samples were extracted for 180-200 min including evaporation and cooling. Depending on the repeated additions of HNO₃, total reactive consumption changed between 35-50 ml. Besides, all the microwave heating programmes had the total digestion time of 26 min which was sufficient to obtain clear fluid as digestate. Total reactive volume was 4 ml in P1 and 4.8 ml in P2 and P3. When compared with microwave procedures, EPA's method gave low recovery rates, especially for Pb and Cu. Although acid digestion procedure includes the use of strong acid mixture, poor recovery values of Pb and Cu may be explained by the deficiency of HF use, which means that HF is necessary to extract Pb and Cu in soil and sediment samples. On the other side, during the microwave heating programmes, the maximum power used was 600 watts, and this step was not allowed to work more than 2 min. P2 and P3 gave better results than P1, since they include the use of HCl in addition to HNO₃-HF mixture. HCl is a strong acid and used for the decomposition of organic substances in combination with HNO₃. When the results for the SRMs are examined individually, the Estuarine Sediment gave adequate results with P3. The recovery values for all the metals were over 95% except for Pb and Zn for San Joaquin Soil-2709. As mentioned before, the only difference between P3 and P2 is the length of time that the programme is held at 600 W (2 min for P3, 1 min for P2). Longer pressure power application of P3 resulted as better recovery rates in the complex matrix of sediment. P2 gave the most reliable results for San Joaquin Soil.

4. CONCLUSIONS

Acid digestion procedures are required for the quantification of heavy metals in the solid samples such as soils, sediments and sludges. Numerous studies have been developed to improve the most accurate methods for proper extraction of chosen elements. The advantages of short digestion time, less acid consumption and high extraction efficiencies in microwave digestion procedures make them preferable when compared with the conventional methods. In most studies, high pressure powers are applied to the samples by using high technology digesters. In the presented study, highest pressure power used was 600 watts and only in P3, it was applied for 2 min. For the microwave digestion procedures P2 and P3 (except for Pb and Zn for San Joaquin Soil-2709) gave satisfactory results for the determination of Cr, Cu, Pb and Zn. Different results showed that acid combinations used in the procedures directly influence the recovery values. Soil sample was properly extracted and recovered with P2 which involves the use of HNO₃, HCl, and HF for 26 min. The sediment sample gave the best results for P3. These digestion approaches are recommended for soil and sediment samples. By applying minor modifications to these procedures, they may be adapted to the digestion of other solid samples.

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