

# Application of Microwave–Assisted Digestion to Trace Heavy Metal Determination in Sea Sediment Sample

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## Abstract

The main goal of this study is to develop an efficient microwave digestion method for the determination of Pb, Cu, Cr, Co and Zn elements from a sea sediment sample. Microwave acid digestion techniques were investigated to obtain a simple, rapid and safe method for the determination of five trace elements in sediment. Sediment sample was air-dried, grinded, sieved ( $\leq 100$  mesh) and subjected to digestion. The digests were subsequently analyzed for metal content by atomic absorption spectrophotometry (AAS). Various combinations and volumes of hydrofluoric, nitric and hydrochloric acids were evaluated for the microwave acid digestion efficiency. Certified reference material (GSP-2, geological certified reference material) was used in the comparison of these digestion protocols. The microwave acid digestion with a mixture of 4 mL of 65% HNO<sub>3</sub>, 1 mL of 37% HCl, 4 mL of 40% HF produced the fastest, safest and accurate analytical results with a recovery of 75–92% and a precision better than 5% in most cases. Sea sediment sample whose sampling location was the deep sea discharge of the paper plant in Dalaman, Turkey, was analyzed.

**Key Words:** Sediment, Microwave digestion, Heavy metal determination, Atomic absorption spectrophotometry.

## INTRODUCTION

Trace elements, especially heavy metals, are considered to be one of the main sources of pollution in the environment, since they have a significant effect on its ecological quality. Human activities often mobilise and redistribute natural substances in the environment so much so that they can cause adverse effects [1]. Otherwise, high levels of heavy metals in sediments, sludges and soils, and through transfer processes, also in groundwater and plants, may have a negative effect on animals and human health [2]. The most

common methods used nowadays for the determination of heavy metals in environmental samples involve highly sensitive spectroscopic techniques, such as atomic absorption spectroscopy (FAAS, ETAAS) and inductively coupled plasma–optical emission and –mass spectrometry (ICP–OES and ICP–MS). The drawback of these techniques is that they first require the solid sample to be transformed into solution where the metal content is determined [3]. 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. There are different heating systems that can be used for digestion such as, sand-bath [4], heating plate [5,6], pressure digestion bombs [7,8] and aluminium blocks [9,10]. The introduction of microwaves, with both open and closed

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pressurised systems, has allowed a considerable reduction in the total time of analyses as well as in the risk of sample contamination [11–13]. Analytical chemists are continually exploring new techniques, and older techniques with new twists are receiving more attention. Hence, one important goal of this work is to increase the interest on this exciting and under-utilized area of chemistry for analytical purposes. More often the sample is analyzed as a liquid, hence a pre-treatment for the solid materials is required. Since the conventional digestion, based on conductive–convective heating, is the step most prone to errors, new methods for sample preparation have been developed. The use of microwaves (MW) as a heating source has become a standard practice. Many of digestion [14–19] and extraction [14,20–22] procedures for different samples have been developed. In recent years, the microwave-assisted leaching technique has become a simple, rapid and powerful sample preparation method for extraction of heavy metals from environmental samples such as soils and sediments. This technique needs low consumption of reagent and time. On the other hand digestion in sealed containers also reduces the risk of external contamination. These are all the advantages of microwave induced sample preparation method over the conventional hot-plate digestion method. The microwave oven heats the contents to a high temperature very rapidly and the closed vessel helps in preventing losses due to volatilization of elements. Microwave digestion also tends to yield more controlled and reproducible results than conventional methods [23,24]. Various kinds of acid mixtures have been used for microwave-assisted digestion procedures. Some methods use HNO<sub>3</sub>/HF [25]; others use HClO<sub>4</sub>/HNO<sub>3</sub> [26], HF/HNO<sub>3</sub>/HCl [27], HNO<sub>3</sub>/HCl and HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> [28]. In most cases, complete digestion of the sample is required to achieve reproducible and accurate results [28].

The object of this study was to develop an efficient

microwave acid digestion procedure in order to determine the concentration of selected heavy metals (lead, copper, chromium, cobalt and zinc) in a sea sediment sample by flame and electrothermal atomic absorption spectrometry (FAAS and ETAAS). The best sample preparation method by utilizing microwave assisted leaching was investigated to obtain a simple, rapid and safe method for the determination of named trace elements in sediment sample. The method was also verified by using certified reference material (CRM).

## EXPERIMENTAL

### Instrumentation

#### *Atomic Absorption Spectrometer*

The instrument used for the determination of metals in digests was a double–beam GBC Avanta Sigma 906 model atomic absorption spectrophotometer (AAS) equipped with graphite furnace and an auto sampler. For each element, hollow cathode lamps were used as radiation sources. The Pb(II), Cr(III), Co(II) measurements were carried out by ETAAS at 283.3 nm, 357.9 nm and 240.7 nm, respectively, while the Cu(II) and Zn(II) were determined by FAAS with air–acetylene flame at 324.7 nm and 231.9 nm, respectively.

#### *Microwave Digestion System*

The samples were digested in a MARS 5 microwave sample preparation system from CEM corp., USA equipped with teflon closed vessels. The power system used with a focused microwave apparatus provides continuous microwave emission at each power level. A pressure control system was used for the microwave digestion with maximum pressure of 200 psi was used.

#### *Reagents and Glassware*

All reagents were of analytical-reagent grade. Water was doubly distilled. Analytical standard metal ion

solutions were prepared daily by diluting standard acidic solutions (Reagecon) containing 1000 mg L<sup>-1</sup> metal ion for AAS. Where necessary, standards and samples were diluted with 0.14 M HNO<sub>3</sub>. GSP-2 (Granodiorite, Silver Plume, Colorado) geological certified reference material was used for validation of analytical results. All glassware and plastic material used was previously treated for 24 h in 2 N HNO<sub>3</sub> and then rinsed with double distilled water.

### Sampling and Pre-treatment of Samples

Sampling location was the deep sea discharge of a paper plant in Dalaman, Turkey. Sea sediment sample was taken into polyethylene bottles which had been pre-cleaned before. After that the sediment sample was air-dried. Then it was dried again in an oven at 50°C. The dry sediment sample was ground in a mortar. Then, the particles were passed through a sieve (100 mesh) and transferred to polyethylene bottles until analysis.

### Microwave Acid Digestion Procedure

Three procedures were followed for the microwave-assisted total digestion of samples. For the overall of procedures the sample intake was 0.5 g and operation pressure was fixed at 200 psi. 65% HNO<sub>3</sub>, 40% HF, 37% HCl and 4% H<sub>3</sub>BO<sub>3</sub> were the reagents used alone or in mixtures. After cooling, the final solution obtained in digestion procedures was filtered and diluted to 50 mL with doubly distilled water. The obtained digests were stored in polyethylene bottles at 4°C until trace metal analysis by AAS.

#### Procedure A

The digestion was carried out by utilizing 10 mL of 65% HNO<sub>3</sub> for 20 min at 150°C, 170°C, 190°C, 210°C.

#### Procedure B

The digestion was carried out by utilizing 8 mL of 37% HCl : 65% HNO<sub>3</sub> (3:1) mixture for 25 min at 210°C.

#### Procedure C

The digestion was carried out by utilizing the acid mixture (4 mL of 65% HNO<sub>3</sub>, 1 mL of 37% HCl, 4 mL of 40% HF) for 15 min at 210°C. After the program completion in 15 min, the vessels were removed from the microwave oven and were left to cool for 30 min. They were then opened and 25 mL H<sub>3</sub>BO<sub>3</sub> was added to the solution. The vessels were then sealed again and irradiated for another 15 min at 210°C. This second irradiation was done since it is recommended by the instrument manufacturer after the addition of boric acid for described procedure that uses HF [29].

## RESULTS AND DISCUSSION

### Validation

Three microwave digestion procedures, labeled A-C were compared to determine the capability of the methods to be used in sediment sample analysis, taking into account the information obtained when comparing the recovery. The certified reference material tested (GSP-2 geological certified reference material) was obtained from Granodiorite, Silver Plume, Colorado. Table 1 and 3 show the results of elements for the analysis of CRM together with the certified values. Three replicates were performed for the microwave acid digestion procedures. Table 2 and 4 show the recovery results obtained for the certified reference material using microwave acid digestion which yield a recovery of 39–94% for procedure A with varying temperature; 52–89, 59–90 and 75–92% for procedure A–C, respectively.

The recovery of each metal is calculated based on the mean value for CRMs :

$$\left[ \frac{\text{(measured concentration } (\mu\text{g.g}^{-1})\text{)} / \text{mean CRM certified value } (\mu\text{g.g}^{-1})}{\text{mean CRM certified value } (\mu\text{g.g}^{-1})} \right] \times 100$$

Table 1. Analysis of certified reference material by procedure A.

Element	Concentration ( $\mu\text{g g}^{-1}$ ), dry weight ( $n=3$ )				
	Certified value	150°C	170°C	190°C	210°C
Pb	42 ± 3	32.0 ± 1.7	32.1 ± 1.1	31.7 ± 2.6	31.9 ± 3.4
Cu	43 ± 4	30.2 ± 2.4	31.0 ± 1.9	30.6 ± 4.9	30.8 ± 3.2
Co	7.3 ± 0.8	2.85 ± 1	3.79 ± 1.4	4.38 ± 2.8	5.72 ± 1.1
Cr	20 ± 6	10.2 ± 1.9	13.7 ± 3.1	14.9 ± 2.3	16.8 ± 4.8
Zn	120 ± 10	105.8 ± 6	107.1 ± 4.4	109.9 ± 2.3	112.3 ± 5.7

Table 2. Recovery(%) values for the certified reference material obtained by procedure A.

Element	recovery (%) (150°C)	recovery (%) (170°C)	recovery (%) (190°C)	recovery (%) (210°C)
Pb	76	76	76	76
Cu	70	72	71	72
Co	39	52	60	78
Cr	51	69	75	84
Zn	88	89	92	94

As seen from Table 2, although the recovery values of Co, Cr and Zn elements increased by using procedure A with temperature variation, recovery values of Pb, Cu elements had no significant change. The recovery values for procedure A ranged from 52 to 89% are given in Table 4. Summarizing, one can state that microwave-assisted digestion procedure C yielded satisfactory recoveries. The obtained results were in good agreement with the certified values. The addition of HF can cause problems in instrumental analysis and sample preparation due to erosion of glassware. However, small volume of HF such as 4 mL, tested in this work, with additional treatment of boric acid solution for the removal of the excess of HF avoid glassware and hardware damage of AAS [30–32]. The microwave digestion procedure C seemed to be a more attractive procedure from the point of good accuracy.

Table 3. Analysis of certified reference material by procedure A, B and C.

Element	Certified value	Concentration ( $\mu\text{g g}^{-1}$ ), dry weight ( $n=3$ )		
		Procedure A	B	C
Pb	42 ± 3	32.1 ± 6	33.9 ± 4.2	35.8 ± 3.7
Cu	43 ± 4	31.0 ± 2.3	33.2 ± 4.5	35.3 ± 1.2
Co	7.3 ± 0.8	3.79 ± 1.5	4.32 ± 3.1	5.47 ± 2.4
Cr	20 ± 6	13.7 ± 5.7	14.2 ± 8	15.3 ± 3.6
Zn	120 ± 10	107.1 ± 2.8	108.4 ± 4.1	110.6 ± 5.3

Table 4. Recovery(%) values for the certified reference material obtained by procedure A, B and C.

Element	Recovery (%) for procedures.		
	A	B	C
Pb	76	81	85
Cu	72	77	82
Co	52	59	75
Cr	69	71	77
Zn	89	90	92

### Analysis of real-life sample

The developed method was applied for the analysis of sea sediment sample by AAS. The element concentrations determined in the sea sediment sample after utilization of microwave digestion procedure C are presented in Table 5.

Table 5. Analysis of sea sediment sample by procedure C (dry weight (n=3)).

Element Concentration ( $\mu\text{g g}^{-1}$ )	Procedure C
Pb	141.7 $\pm$ 2.2
Cu	150.2 $\pm$ 3.8
Co	75.5 $\pm$ 4.7
Cr	235.9 $\pm$ 4.2
Zn	57.1 $\pm$ 1.7

## CONCLUSION

In the analyses of the heavy metal content in environmental samples, the digestion of the solid sample is one of the more time-consuming steps. In the present work, three procedures dealing with microwave-assisted digestion have been proposed for trace heavy metal determination. Procedure C which is one of the presented procedures was the best of all according to the recovery values gained by digestion of CRM with this procedure. Then procedure C was applied to the sea sediment sample in order to determine Pb, Cu, Co, Cr and Zn concentration. The use of HF ensures a total digestion of the aluminosilicate matrix, and its use with microwave has shortened the time devoted to this step. The microwave digestion process selected presents considerable advantages, which include good precision and accuracy, reduced contamination, speed and safety. The disadvantage of the microwave digestion method is that it is more expensive and requires some experience.

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