

# MICROWAVE ASSISTED DIGESTION OF SOIL, SLUDGE AND SEDIMENT FOR DETERMINATION OF HEAVY METALS WITH ICP-OES AND FAAS

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## ABSTRACT

*The determination of total content of heavy metals (Cr, Cu, Mn, Ni, Pb and Zn) in soil, sludge and sediment was developed by microwave digestion technique combined with ICP-OES and FAAS. A complete digestion of soil, sludge and sediment was achieved by using an acid mixture of HF- H<sub>2</sub>O<sub>2</sub>- HNO<sub>3</sub> (2, 1, 4). The experimental studies were conducted using three standard reference materials (CRM 141R calcareous loam soil, CRM 144R sewage sludge from domestic origin and CRM IAEA 405 estuarine sediment). The recoveries for all elements in all samples were good (87-105%). The determination of heavy metal by ICP-OES was carried out with two calibration methods (calibration curve and standard addition) and the results were compared. In standard addition method the recoveries for some elements were improved. Also, the results of these two measurement techniques of ICP-OES and FAAS were compared. In determination by FAAS for some elements such as Pb in soil and sediment samples and Ni in sediment sample, the low recoveries were obtained.*

**Keywords:** Microwave digestion, Heavy metals, ICP-OES, Internal standard, standard addition

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## INTRODUCTION

Over the past two decades there has been an increase in public awareness of the hazards posed by contamination of the environment by toxic substances<sup>1</sup>. Many investigations have been carried out as a result of the fears over the health and ecological effects of heavy and other metals contamination of the terrestrial ecosystem<sup>2</sup>. Heavy metals are disposed in the environment, mainly through the effluents from industries such as tannery, metallurgy, dyes, explosives, ceramics, paints, textile<sup>3</sup>. The main man-made sources of metals in the environment are combustion of fossil fuels, mining and smelting operations, processing and manufacturing industries and waste disposal including dumping, release of domestic sewage and scrap metal handling. Farming and forestry, also, contribute to the contamination by metals due to the use of fertilisers and pesticides<sup>4</sup>.

Soils are complex systems with physical, chemical and biological characteristics that vary over time and space. Major components including silicon, aluminum (Al) and iron (Fe) along with oxygen, are responsible for much of the soil matrix. Other major components include but are not confined to manganese (Mn), magnesium (Mg), potassium (K), calcium (Ca) and titanium (Ti). These matrixes content a large number of elements are often described as trace elements when viewed as beneficials and heavy metals when present in amounts considered excessive or when known to be intrinsically hostile to living organisms at any level. The more significant ones number by common consent: cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), zinc (Zn), arsenic (As), chromium (Cr), cobalt (Co) and selenium (Se) that have comparable environmental impacts. They are included in a number of national regulations. All are physiologically active with significant effects on micro-organisms, higher plants and on animals including humans. All have known pathways that allow for movement to foodstuff and to water. All are toxic in excess and some have been implicated in human illness including carcinomas, hypertension and heart disease<sup>5</sup>.

The concentration of heavy metals available to terrestrial, aquatic and marine organisms (i.e. their bioavailability) is determined by the solubilisation and release of metals from rock forming minerals and

adsorption and precipitation reactions which occur in soils and sediments. The degree to which the metals are absorbed depends on the properties of the metals concerned i.e. valence, radius, degree of hydration and co-ordination with oxygen, physicochemical environment, nature of the adsorbent, other metals present and their concentrations and the presence of soluble ligands in the surrounding fluids<sup>6,7</sup>.

Accurate determination of potentially toxic trace metals in soils is important for cleaning up contaminated soils and monitoring land application of metal bearing nonhazardous materials<sup>8,9</sup>.

For all these reasons, analytical instruments and techniques have been developed over the past 20 years to determine the concentrations of metals in our ecosystem (atmosphere, water, soils and sediments). Most of the sample digestion methods for various environmental samples are largely limited to the conventional acid digestion procedures with different heating systems<sup>10-16</sup>. But most of these digestion procedures are somewhat limited by various primary factors including long dissolution times (hours to days), the potential loss of volatile elements, contamination of the sample by excessive amounts of reagents, high process blanks due to air born contaminants, etc.<sup>17</sup>

Digestion of solid samples for elemental analysis is now established as a routine sample preparation method<sup>18</sup>. Since the 1980s, microwave-assisted sample digestion techniques have become popular and are widely used<sup>8,19-24</sup>. The technique provides rapid, safe, and efficient digestion and is not susceptible to losses of volatile metals<sup>25</sup>. It has thus been adopted by the EPA (EPA Methods 3051 and 3051a) to extract metals from sludge, soil or sediment<sup>26-28</sup>. Low volume microwave digestion has been developed to allow the determination of analytes in small samples (0.1 g). In this way, the decrease of sensitivity because of dilution, and also, the loss of volatile analytes, is avoided<sup>18</sup>.

Wet digestion with oxidizing acids is the most common sample preparation procedure. The use of pure concentrated HNO<sub>3</sub> in a closed system under elevated temperatures and pressure is well known since 1860 from Carius<sup>29</sup>. Hydrogen peroxide was introduced by Classen and Bauer<sup>30</sup>. There are numerous publications giving useful information on the digestion (dissolution and/or decomposition) of soil, sludge and sediment<sup>31-54</sup>].

Microwave-assisted aqua regia digestion using a Teflon bomb is considered a rapid sample digestion method<sup>55-58</sup>. However, the aqua regia digestion failed to accurately quantify more than 20 elements in some sediments especially K and Al, which are part of some clay mineral structures<sup>59</sup>.

Nadkarni (1984) reported that employing of HF, and H<sub>3</sub>BO<sub>3</sub> provides satisfactory precision and accuracy for dissolving silicamatrixes<sup>60</sup>. The following reactions occur during digestion:  $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$  and  $\text{H}_3\text{BO}_3 + 3\text{HF} \rightarrow \text{HBF}_3\text{OH} + 2\text{H}_2\text{O}$ , and  $\text{HBF}_3\text{OH} + \text{HF} \rightarrow \text{HBF}_4 + \text{H}_2\text{O}$ <sup>61,62</sup>. Adding boric acid in the second stage of the digestion not only complexes the free fluoride ions in the solution, but also facilitates the dissolution of the precipitated fluorides<sup>61</sup>.

Inductively coupled plasma-optical emission spectrometry (ICP-OES) has been extensively used for multielemental analysis due to its low detection limits, large linear dynamic range, and high precision<sup>63-65</sup>. Compared to other sources of atomic excitation, ICP-OES shows the advantages of a multielemental determination with high analytical frequency and the versatility to be interfaced with other analytical techniques. The selectivity of ICP-OES in analytical spectrometry makes it suitable for elemental analysis in a variety of different matrices for simultaneous or sequential metal determination in a wide concentration range. The high signal-to-background ratio characteristic of the ICP-OES generates a low detection limit for this technique<sup>65</sup>.

Both the accuracy and precision of ICP measurements is dependent, in part, upon the calibration technique used. Matrix effects are arguably the subtlest danger to the ICP-OES analyst. Slight differences in the matrix can cause a considerable systematic error. The most common calibration technique options for ICP measurements are calibration curve and standard additions. In addition, the option of using internal standardization is available for the calibration curve technique and the ability of matrix matching may also be available. The role of the internal standard is to have behavior similar to the line of the analyte to be corrected. If signal variation results from the sample introduction system (samples of different viscosity, matrix constitution), all the elements will be corrected in the same way by a single internal standard. The standard additions method is used when the matrix is quite variable and/or when an internal standard that corrects for plasma related effects couldn't be found. This technique is also

useful in confirming the ability of an internal standard calibration curve technique to correct for both nebulizer and plasma related effects.

This work proposes a microwave-assisted acid digestion procedure for soil, sludge and sediment samples prior to element determination by ICP-OES and FAAS. The results of two measurement techniques of ICPOES and FAAS were compared. The comparison of two calibration methods of calibration curve and standard addition methods were performed.

## EXPERIMENTAL

### *Instrumentation*

For digestion of samples a microwave digestion system Berghof speed wave MWS-2 was used. Flame atomic absorption analyses were carried out by a ThermoElemental model solar M5 equipped with deuterium background correction. Hollow cathode lamps were used as a radiation source for the studies of all elements.

The emission measurements were done with a Vista-Pro CCD simultaneous ICP-OES.

### *Certified reference materials*

Certified soil and sludge were supplied by the Community Bureau of Reference sample (BCR)CRM 141R

“Calcareous Loam Soil”, CRM 144R “Domestic Sewage Sludge”. Certified sediment was IAEA 405 “estuarine sediment” from International Atomic Energy Agency.

### *Reagents and standards*

The reagent used, hydrogen peroxide (30% w/v) (Fluka), nitric acid (65%w/v) (Merck), hydrofluoric acid (40% w/v) (Merck) and boric acid were analytical grade. High-purity water was produced with a Milli-Q Millipore (Molsheim France) system. The  $\text{Cu}(\text{NO}_3)_2$ ,  $\text{Mn}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$ ,  $\text{Zn}(\text{NO}_3)_2$ ,  $\text{Cr}(\text{NO}_3)_3$ ,  $\text{pb}(\text{NO}_3)_2$  stock standard solutions, 1 g/l, were supplied by Merck (Darmstadt, Germany).

### *Microwave-Assisted Acid digestion procedure.*

200 mg of samples were accurately weighed, put in the microwave vessels and moisturized with a little of deionized water and then 2 ml of HF, 4 ml of  $\text{HNO}_3$  and 1 ml of  $\text{H}_2\text{O}_2$  were added the samples were left for one hour to react. Microwave heating conditions are given in table 1. 0.8 g boric acid transfer to the 50 ml Teflon tube and 20 ml of deionized water add to it and shake. After cooling the vessels, the digested solutions were quantitatively poured into the Teflon tubes and brought to volume with deionized water. For each set of the measurements, at least, one blank containing the same amount of acid as the samples was analysed. For each used material, three replicates were prepared.(Table 1).

### *Analyses*

Measurement of Cr, Ni, Mn, Co, Zn, Pb and Cu were carried out with ICP-OES. The two calibration methods of calibration curve and standard addition were used. For calibration curve methods, because the elements of interest span a different concentration range, five multielemental acid matched standards in the range 0.04-4 mg/l and one blank were used for calibration. All samples and standards were spiked with  $5\mu\text{g/g}$  Yttrium, which act as internal standard. The emission lines used are given in Table 2. The ICP-OES instrumental conditions are given in table 3.

Determinations of heavy metals by FAAS were performed too (table 2). For Cd, Ni, Cu, Pb and Zn determination an air acetylene flame was used, while Cr determination were performed in a nitrous oxide acetylene flame. At least three level calibrations were carried out for each metal.

## RESULTS AND DISCUSSIONS

### *Microwave acid digestion procedure*

The experimental data, obtained with microwave acid digestion procedure were compared with certified values. Tables 4, 5 and 6 show, the both, the experimental and certified values. The agreements between the experimental and certified values were good. Recoveries of all elements in all matrices were quantitative from 87-105%. Low recovery of Cr (87%) from soil and other materials has been attributed to the presence of insoluble Cr minerals such as chromspinel and chromites ( $\text{FeCr}_2\text{O}_4$ )<sup>66,67</sup>.

Medved et al. (1998) found that Cr is bound to insoluble minerals such as chromspinel and chromite in soils<sup>68</sup>. Low Cr recoveries in NIST SRMs 2709, 2710, and 2711 (75–89%) using microwave HNO<sub>3</sub>–HF digestion and in USGS standard rocks using microwave aqua regia + HF digestion have been reported<sup>60,61,69</sup>. A sequential extraction study on industrially contaminated soil indicated that both Cr and Ni were mainly associated with the residual fractions<sup>70</sup>. Low Cr recovery from river sediments AGAL-10 and AGAL-11 by both hotplate (36%) and microwave (43%) aqua regia digestions has been reported<sup>71</sup>. Low Cr recoveries (23–74%) from standard and sewage-sludge-amended soils have also been reported<sup>72</sup>.

#### ***Determination by ICP-OES***

The solutions obtained from digestion procedure of 141R, 144R and IAEA 405 were analysed by ICPOES. Two methods of calibration curve were performed. The calibration curve method with out internal standard provides the lower recoveries for all elements. This is because of the difference between the viscosity of samples and standards due to the solid content of samples that can change the nebulizer efficiency. Such differences in sample introduction efficiency represent an interference since an equal concentration of analyte in the standard and in the sample would not result in equivalent emission signals. For soil, sediment and sludge samples, the recoveries of all elements except of Mn with standard addition and calibration curve method, the both, were in good agreement.

#### ***Determination by FAAS***

The recoveries obtained by FAAS in comparison with ICP-OES for Ni and Pb in soil and sediment samples were slightly lowered. This is because probably of that the temperature of flame is lower than plasma and some types of molecules such as oxides and refractory carbides can not be dissociate into free atoms. For other elements in all samples the recoveries were in relatively good agreement with ICP-OES.

### **CONCLUSIONS**

Our results show in evidence that the digestion of soil, sludge and sediment by microwave in acid media is a good method that can be a viable replacement of open digestion methods. Contamination is minimized, sample preparation times are significantly shorter and the digestion efficiency is guaranteed. The results obtained with CRM 141R, CRM 144R and IAEA 405 are in excellent agreement with certified values. The recoveries obtained of three certified reference materials were good (87-105%). While the matrix matching of samples and standards was performed the using of an internal standard was necessary to reach the results with better accuracy. The relatively good agreement between the results obtained from two methods of calibration showed that the Yttrium can act as an internal standard to correct the both, nebulizer and plasma related effects. On the other hand, the amount of time and effort required for the technique of standard addition, compared to other correction techniques, has its limit use in ICP-OES.

**Table-1:** Microwave digestion program

<b>Step</b>	<b>Temperature (°o)</b>	<b>Pressure(W)</b>	<b>Time(min)</b>
1	100	600	7
2	200	600	18

**Table –2:** The absorption and emission lines used in FAAS and ICP- OES

element	ICP-OES wavelength (nm)	FAAS wavelength (nm)
Cr	267.716	357.9
Cu	324.754	324.8
Mn	257.610	279.5
Ni	231.604	232
Pb	220.353	217
Zn	213.857	213.9

**Table-3:** ICP-OES Instrumental Conditions

RF Power	1100 watts
Nebulizer pressure	200 KPa
Auxiliary Flow	1.5 L/min
Plasma Flow	15.0 L/min
Sample Pump Flow	1.5 mL/min
Plasma Viewing	Axial
Sample uptake delay	30 sec
Rinse	10 sec
Pump rate	15 rpm
Replicates	3
Wavelength of internal standard(Y)	242.219nm

**Table-4:**Determination of heavy metals in CRM 141R by micro-wave acid digestion procedure.

Element	Certified mg/kg	ICP-OES				FAAS			
		Calibration Curve With IS <sup>b</sup>		Calibration Curve without IS <sup>b</sup>		Standard Addition		Calibration Curve without IS <sup>b</sup>	
		Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)
Cr	195 ± 7	169 ± 1.5	87	164 ± 2.8	84	175 ± 2.5	89	174.3 ± 0.7	89
Mn	683 ± 16	642 ± 5.1	94	589 ± 2	86	661 ±	96	644 ± 2.3	94

						5.7			
Zn	283 ± 5	284 ± 2	100	261 ± 0.6	92	277 ± 0.6	98	265 ± 0.8	93
Ni	103 ± 3	98.2 ± 1	95	85.2 ± 1.5	82	98 ± 2.5	95	84.1 ± 1.5	81
Cu	46.4 ± 1.8	44.7 ± 0.3	96	41.2 ± 0.2	89	45.2 ± 0.1	97	44.8 ± 0.6	96
Pb	57.2 ± 1.2	51.4 ± 2	90	48.7 ± 2	85	52 ± 4.5	91	39.8 ± 0.6	69

<sup>a</sup>Recovery, <sup>b</sup>Internal standard**Table-5:** Determination of heavy metals in CRM 144R by micro-wave acid digestion procedure.

Element	Certified mg/kg	ICP-OES						FAAS	
		Calibration Curve				Standard Addition	Calibration Curve		
		With IS <sup>b</sup>		Without IS <sup>b</sup>			Without IS <sup>b</sup>		
		Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)
Cr	104 ± 3	94.6 ± 1	93	90.4 ± 2.3	90	98 ± 3.3	94	98.6 ± 0.8	95
Mn	208 ± 3	197 ± 0.2	95	190 ± 1.6	91	208 ± 2	100	199 ± 0.8	96
Zn	932 ± 23	910 ± 7	97	848 ± 9.2	91	897 ± 7.2	96	885 ± 3	95
Ni	47.7 ± 1.1	46.4 ± 1.5	97	42.3 ± 1.8	88	46.4 ± 0.1	97	43.3 ± 2.1	91
Cu	308 ± 7	292 ± 4.4	95	273 ± 3	89	292 ± 2	95	301 ± 1.6	98
Pb	106 ± 4	96.2 ± 1.8	91	91.4 ± 0.8	86	95 ± 2.6	89	96 ± 1.6	90

<sup>a</sup>Recovery, <sup>b</sup>Internal standard**Table-6:** Determination of heavy metals in CRM IAEA 405 by micro-wave acid digestion procedure.

Element	Certified mg/kg	ICP-OES						FAAS	
		Calibration Curve				Standard Addition	Calibration Curve		
		With IS <sup>b</sup>		Without IS <sup>b</sup>			Without IS <sup>b</sup>		
		Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)	Found mg/kg	R <sup>a</sup> (%)
Cr	84 ± 4	80.2 ± 0.5	95	77 ± 0.5	91	84.2 ± 1	100	81.7 ± 1.2	97

Mn	495 ± 11	479 ± 2.5	96	455 ± 7	92	510 ± 3.1	103	494 ± 3.2	100
Zn	279 ± 7	291 ± 1	104	275 ± 3	99	294 ± 2.4	105	275 ± 2.5	98
Ni	32.5 ± 1.4	33.9 ± 0.7	104	32.4 ± 0.1	100	33.8 ± 1.6	104	20.8 ± 1	64
Cu	47.7 ± 1.2	48.3 ± 0.3	101	47.6 ± 0.7	100	48.3 ± 1	101	47.6 ± 1.7	99
Pb	74.8 ± 2.2	76.6 ± 0.7	102	72.2 ± 2.2	96	76.5 ± 4	102	59.7 ± 3.7	80

<sup>a</sup>Recovery, <sup>b</sup>Internal standard

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