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A Simple and Accurate Method for Routine Analysis of Heavy Metals in Soil, Plant and Fertilizers

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ABSTRACT

With environmental issues relating to heavy metal contamination of natural resources becoming of increasing concern, there is an obvious need to have a method that can be used for routine analysis of a range of materials including soil, sediment, sewage sludge, plant, mineral and organic fertilizers, and other miscellaneous materials for heavy metals of concern. A single-step microwave digestion method was developed using aqua regia solution for digestion of finely ground samples for determining 15 heavy metals in soil, plant, and fertilizer materials using inductively coupled plasma-optical emission spectrometry (ICP-OES). Results on the recoveries of 15 heavy metals added via certified standard reference sample to soil, plant, or fertilizer samples showed that the results varied with the metal and the substrate; and with few exceptions, the results were satisfactory. The method is simple, rapid, and accurate, and seems ideal for the routine analyses of a range of materials. Using microwave-assisted digestion, an analyst can perform over 100 analyses in a working day.

Keywords: Heavy metal contamination, microwave-assisted digestion, natural resources, recovery of trace metals, single-step digestion method

INTRODUCTION

Contamination of natural resources especially soil, water, and food systems with heavy metals is becoming of increasing concern as potential toxicity hazard to human and animal health, and an overall environmental quality degradation (Bolan et al. 2013). Among the various contaminants, the accumulation of heavy metals in soils and water resources has received a lot of attention as a potential toxicity to humans through the food chain. Contamination of the environment also disrupts the safe delivery of ecosystem services to the community and wildlife (Tiller 1988).

A range of physical, chemical, and biological soil characteristics influence the retention and transport of heavy metals in the soil-water-plant systems. Among these soil texture, pH, organic matter, moisture regime, redox potential, and cation exchange capacity (CEC) are important (Adriano 2001; Arao et al. 2009; Ashworth and Alloway 2008; Bolan et al. 2013; Selim 2013; Smolders et al. 2009; Tiller 1988).

The sources of these trace metals in agricultural production systems are predominantly through addition to soil of a range of soil amendments including mineral and organic fertilizers used to supply major, secondary, and micronutrients. These amendments used add varying amounts of heavy metals to the soil depending on their rates of application and the nutrient source. These amounts of heavy metals added to the soil are in addition to the amounts of trace elements added via natural process of weathering of the parent material, termed natural

background concentration of these elements, on which soil has developed. In addition, the use of industrial and domestic waste water for irrigation in agriculture also adds varying amounts of heavy metals over time to the soil (Adriano 2001; Kumar and Chopra 2012; Sehgal et al. 2012).

Equally important, soil is also used as a general dumping ground for various wastes of diverse nature that add varying amounts of trace metals. Industrialization also adds its share of heavy metals through liquid and solid wastes disposal and through emissions to the terrestrial system, which eventually end up in the soil (Debeka and McKenzie 1995; Adriano 2001). In such situations, initially the soil acts as a sink to the accumulating trace elements that are added or that end up in it. However, when a soil's capacity to hold or retain the pollutants is exceeded, the soil begins to act as a source for these contaminants or pollutants such as heavy metals (Mortvedt 1996; Nogawa et al. 2004; Selim 2013).

Plants growing on the soils contaminated with heavy metals take up these elements in their biomass; and through food chain they find place in humans and animals (Bolan et al. 2013; Debeka and McKenzie 1995; Nogawa et al. 2004; Tiller 1988; Wright et al. 2010). In recent years, increasing cases of excessive food chain transfer of soil accumulated trace elements observed suggest that there is need to evaluate all fertilizers and soil amendments for their trace element especially for the toxic heavy metal contents. There is need to monitor and assess soil quality relative to toxic heavy metals concentrations considering the history of fertilization, especially the application of phosphorus fertilizers (Chaney 2012; Westfall et al. 2005).

For on-going research on the pollution of soils with heavy metals, a simple and accurate method was needed that can be used for the routine determination of heavy metals in a range of materials

including soil, sediment, plant and mineral, and organic carriers of various plant nutrients. The aim of this paper is to describe a rapid, simple, and accurate method that can be used for routine analysis of heavy metals in a range of materials.

MATERIALS AND METHODS

A modified version of the method described by Chen and Ma (2001) was adapted for the analyses of 15 heavy metals, which included arsenic (As), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), lead (Pb), mercury (Hg), molybdenum (Mo), nickel (Ni), platinum (Pt), zinc (Zn), tin (Sn), manganese (Mn), and boron (B).

The method used is based on microwave-assisted digestion of the finely ground samples (soil, plant, or fertilizer) with freshly prepared aqua regia solution consisting of 3: 1 (v/v) ratio of concentrated hydrochloric acid (HCl): nitric acid (HNO₃). After standardization of method in preliminary experiments, the following method was adopted and followed to study the recovery of 15 heavy metals added using certified reference material Plasma-Pure Standard solution samples (supplied by Tyledyne Leeman Laboratories, Hudson, NH, USA) to the soil, plant or fertilizer samples. The spiking of soil, plant, or fertilizer with heavy metals using the certified reference material was used to determine the efficacy of the digestion method used to recover these heavy metals.

Finely ground soil (2 g), plant (0.5 g), and fertilizer (0.5 g) (single superphosphate) samples were weighed into polytetrafluoroethylene (PTFE) Teflon-coated digestion vessels. Twelve ml of freshly prepared aqua regia was added to the samples. The samples were then digested at 0.83 x

106 Pa (120 psi) in a microwave oven (Marsxpress CEM microwave; CEM Corporation, Matthews, NC) for 15 minutes at 160°C. Following digestion of the samples, they were filtered through Whatman no. 42 filters (GE Healthcare, Little Chalfont, UK) into 100-ml volumetric flasks, and the contents diluted to 100 ml with distilled water. Blanks were included with each set of samples digested in triplicate. The heavy metal contents in the digests were determined using an inductively coupled plasma-optical emission spectrometry (ICP-OES) (Prodigy, Teledyne Leeman, Hudson, NH, USA) as described by Chen and Ma (2001).

The data were statistically analyzed and the results presented are the means of three independent analyses \pm standard deviation (SD).

RESULTS AND DISCUSSION

The recovery of the studied heavy metals was computed by analyzing the soil, plant or fertilizer (single superphosphate) sample without and with the addition of heavy metals from the standard certified solution sample.

The results on the efficacy of the digestion method based on the recoveries of the added 15 heavy metals to soil, plant, or fertilizer (single superphosphate) samples showed that the recovery varied with metal and the substrate (soil, plant, or fertilizer) used (Table 1). The recovery of the 15 heavy metals added to soil sample varied from 68 to 119%. The recovery of heavy metals added to plant sample ranged from 79 to 93%; and the recovery of trace metals added to the fertilizer sample (single superphosphate) varied from 88 to 111% (Table 1).

These results, especially those on the recovery of selected heavy metals are similar to those reported by Chen and Ma (2001). These authors reported that the recovery of the selected heavy metals from standard reference materials was generally satisfactory, except for As, Cd, and selenium (Se); and the average recovery of selected heavy metals, using microwave-assisted digestion with aqua regia solution was around 80%. The recovery of the selected heavy metals was 74% when the digestion with aqua regia was carried out using hot plate instead of microwave (Chen and Ma 2001).

In an earlier study, Chen and Ma (1998) reported that the microwave- assisted aqua regia method proved better alternative method for the hot- plate-based digestion method and the recoveries of most heavy metals and potassium (K), calcium (Ca) and magnesium (Mg) evaluated was satisfactory and ranged from 80 to 117%.

The results with few exceptions indicate that the results on the recovery of various trace metals applied to soil, plant, and fertilizer samples were acceptable, and the method can be used for routine analysis of trace metals in diverse range of samples.

Microwave-assisted method indeed seems efficient and less time consuming than the digestion using hot-plate (Binstock et al. 1991; Nieuwenhuize et al. 1991; Paudyn and Smith 1992; Chen and Ma 2001); and the microwave-based digestion has been widely used for microelement and trace metal analysis in a range of materials including soils.

The experience with the analysis of heavy metals in a range of materials using microwave-assisted digestion method along with the use of ICP-OES for determining the trace metals in the

digests is a rapid and accurate method suited for routine analysis. An analyst in an 8-hr working day can easily process > 100 samples for trace metal analyses.

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Table 1 Recovery of 15 heavy metals added to soil, plant and fertilizer (single superphosphate) samples following digestion in microwave and determined by ICP-OES. The metals were added using certified reference standard sample (Plasma-Pure standard solution obtained from Teledyne Laboratories, NH, USA). The results (mgkg^{-1}) presented are means \pm SD (standard deviation) of three replications

	Cd	Cr	Co	Cu	Pb	Mo	Ni	Pt
	Recovery from soil sample							
Amount in soil	0.00 \pm 0.00	23.89 \pm 0.06	7.19 \pm 0.01	12.27 \pm 0.02	6.03 \pm 0.02	0.00 \pm 0.00	14.35 \pm 0.02	0.27 \pm 0.00
Amount added	49.89 \pm 0.00	73.89 \pm 0.06	57.19 \pm 0.01	62.27 \pm 0.02	56.03 \pm 0.02	49.29 \pm 0.00	64.35 \pm 0.02	50.27 \pm 0.00
Determined	41.21 \pm 0.09	71.39 \pm 0.13	46.81 \pm 0.10	55.50 \pm 0.12	43.57 \pm 0.11	32.72 \pm 0.06	55.95 \pm 0.11	40.59 \pm 0.09
Recovery (%)	83	97	83	89	79	68	88	82
	Recovery from plant sample							
Amount in	6.73 \pm 0.00	9.68 \pm 0.00	9.38 \pm 0.00	17.01 \pm 0.00	11.97 \pm 0.00	9.09 \pm 0.00	13.61 \pm 0.00	9.08 \pm 0.00

plant	00	00	00	.00	.00	00	.00	00
Amount added	106.73± 0.00	109.68± 0.00	109.38± 0.00	117.01± 0.00	111.97± 0.00	109.09± 0.00	113.61± 0.00	109.08± 0.00
Determined	88.58±0 .00	91.46±0 .00	90.70±0 .00	100.85± 0.00	94.66±0 .00	93.05±0 .00	95.46±0 .00	93.67±0 .00
Recovery (%)	83	83	83	86	85	85	84	86
	Recovery from fertilizer sample							
Amount in fertilizer	8.67±0. 01	53.40±0 .01	10.10±0 .01	11.26±0 .00	11.84±0 .00	10.16±0 .00	24.49±0 .03	11.11±0 .01
Amount added	108.67± 0.01	153.40± 0.01	110.10± 0.01	111.26± 0.00	111.84± 0.00	110.16± 0.00	124.49± 0.03	111.11± 0.01
Determined	103.11± 0.07	145.44± 0.00	96.47±0 .03	105.65± 0.02	100.39± 0.00	99.68±0 .01	111.00± 0.00	103.34± 0.02

Recovery (%)	95	95	88	95	90	91	89	93
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Table 1

(Continued)

	Zn	Sn	Mn	B	As	Hg	Fe
	Recovery from soil sample						
Amount in soil	16.27±0.03	0.25±0.00	279.60±0.19	52.08±0.15	2.23±0.01	0.25±0.00	5483.38±9.45
Amount added	66.27±0.03	50.25±0.00	329.60±0.19	102.08±0.15	52.23±0.01	50.25±0.00	5533±9.45
Determined	59.92±0.13	40.37±0.08	324.34±0.59	115.68±0.23	42.48±0.11	40.08±0.09	6612±8.23
Recovery (%)	91	81	98	113	82	81	119

		Recovery from plant sample						
Amount in plant	50.14±0.01	9.17±0.00	112.50±0.00	15.43±0.01	7.66±0.01	9.53±0.00	415.30±0.04	
Amount added	150.14±0.01	109.17±0.00	212.50±0.00	115.43±0.01	107.66±0.01	109.53±0.00	515.30±0.04	
Determined	133.83±0.00	92.22±0.00	197.56±0.01	104.25±0.00	94.27±0.00	93.73±0.00	405.21±0.19	
Recovery (%)	89	84	93	90	88	86	79	
		Recovery from fertilizer sample						
Amount in fertilizer	110.05±0.00	7.51±0.00	286.95±0.01	38.20±0.00	12.32±0.00	10.26±0.02	5303.06±0.21	
Amount added	210.05±0.00	107.51±0.00	386.95±0.01	138.20±0.00	112.32±0.00	110.26±0.02	5403.06±0.21	
Determined	203.30±0.00	98.81±0.00	372.57±0.01	141.51±0.00	108.87±0.00	98.94±0.00	5981.63±0.21	

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	0.03	00	0.04	0.00	0.00	02	0.24
Recovery (%)	97	92	96	102	97	90	111