EFFICACY OF METHODS FOR HEAVY METAL EXTRACTION IN SOME SOILS IN NNEWI-NORTH, ANAMBRA STATE, SOUTHEASTERN NIGERIA.

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ABSTRACT

Industrial impact on selected heavy metals in some soils of Nnewi-North, Anambra State, Nigeria was studied. Five extraction methods namely, A, HNO_3 – HCl (1:3) with H_2O_2 prior to digestion, B, HNO_3 – H_2O_2 (3:1) C, H_2SO_4: HNO_3: HCl (1:3:1) D, H_2SO_4: HNO_3 (1:4) E, HNO_3 – $HClO_4$ (2:1) were compared by using five replicates samples of the different acid mixtures. The Approach of Precision and Student t-test were employed to determine the suitable acid mixture/method for extraction and the levels of seven heavy metals (Lead: Pb, Manganese: Mn, Zinc: Zn, Nickel: Ni, Chromium: Cr, Copper: Cu, and Cadmium: Cd) in top soil (15-20 cm), from Nnewi-North were determined using FAAS technique. The HNO_3-HCl-H_2O_2 method was used in the soil sample extraction with a precision of less than 10 % for five metals and t-calculated showed that for four metals, were not significantly different between AB (Zn, Cu, Cd and Ni) & AD (Cu, Pb, Mn and Ni) but only one metal, Ni showed that Method B was not different from Method D. Accuracy of the method was assessed by the determination of a reference material, CC-141, and the results showed agreement with certified values.

KEY WORDS: HEAVY METALS, CONTAMINATION, EXRACTION, ACID MIXTURES, NNEWI-NORTH, SOIL AND ENVIRONMENT

INTRODUCTION

Industrialization is essential for economic growth of any nation as it acts as a vehicle for development. Modern life style with increasing population and industrial growth has impacted negatively on the environment at a global scale (Asamudo, *et al.*, 2005). In order to sustain the basic requirements of increasing population, different types of industries have been set up in different regions of our country, Nigeria and these include pulp and paper, textile, cement, petrochemical, metal processing, food processing, fertilizer, sugar, pharmaceutical, distilleries among others. The fermentation industry is considered as one of the most polluting industries and has posed serious environmental problems throughout the world while chemical and metallurgical industries are the most important sources of heavy metals in soils (Ene, *et al*., 2009). Heavy metals are in various raw materials, such as fossil fuels and metal ores, as well as in industrial products.

Some trace metals are emitted entirely or partially from raw materials during the high-temperature production of industrial goods, combustion of fuels, and incineration of municipal and industrial wastes, entering the ambient air with exhaust gases (Pacyna, and Pacyna, 2011). Atmospheric emissions from industrial complexes are considered as the main source of the environmental pollution. These emissions travel along vast areas by the effect of the meteorological factors and become accumulated in soil, plant, and animal whether aquatic or terrestrial and may reach the food chain (Mohamed, 2006).

Cultivation of crops on polluted soil can adversely affect the health of plants and animals as well as man in the food chain. For instance, cadmium contaminated soil was known to have caused the itai-itai disease as a result of consumption of rice grown on contaminated soil in Japan in the 1950s (Singh and Kalamdhad, 2011). The determination of metals in soils is affected generally by the method of sample preparation and the analytical techniques employed. Utilization of single mineral acid and a combination of acids have been used for the digestion of samples prior to analysis of metals. Most analytical techniques require that the sample be in solution before analysis which makes the method of sample preparation very critical in metal determination. These techniques generally provide data on the elemental composition of particular matter, but differ in terms of detection limit and sensitivity (Berko, 2002). The use of simple and accurate methods for monitoring heavy metals in soil is of great value in environmental studies. For solid samples such as sludges, soils and sediments, the solid form must first be converted to liquid phase, this conversion process generally referred to as digestion is required to separate the metals from the soil for the spectroscopic analysis.

The common method for destroying organic matter and dissolving heavy metals are classified into two groups- wet digestions by acid mixtures and dry ashing, followed by acid dissolution of the ash prior to elemental analysis (Zeng-Yei, 2004). Most wet oxidation procedures require the use of a combination of acid and oxidant, of which the most commonly used are nitric (HNO_3), sulfuric (H_2SO_4), perchloric acids ($HClO_4$), hydrogen peroxide (H_2O_2), and hydrochloric acid (HCl) (Zeng-Yei, 2004). For the metals extraction from soil, a variety of acid mixtures have been used. The choice of an individual acid or combination of acids depends on the nature of the matrix to be decomposed. Gorsuch (1959) observed that the methods of digestion that involves a mixture of nitric, sulphuric or perchloric acids were satisfactory for digesting mineral elements in organic and biological materials. Baker and Amacher, (1982) recommended the use of $HF-HNO_3-H_2SO_4$ for the total analysis of Cd, Cu, Ni, and Zn in soils, but this was modified by Burau, (1982) by replacing H_2SO_4 with HCl. This is because Pb precipitates with H_2SO_4 in solution. The above methods have however been shown not to completely dissolve silicate, but they are sufficiently good to attack and dissolve heavy metals bound to soil. Sastre *et al.*, 2002 stated that nitric acid digestion was an optimum method for estimating heavy metal content in soil samples with high organic matter content. Hydrofluoric acid (HF)is commonly necessary for digestion of silica-based materials (Duyusen and Gorkem, 2011). However, HF-based digestion methods tend to produce higher digest concentration of the metals. On the other hand, use of HF in routine laboratories is not recommended, as it is highly corrosive and difficult to handle, and may cause damage in the instruments and to human, therefore the use of HF are always kept at a minimum or in most case excluded in the digestion procedures (Duyusen and Gorkem, 2011). Dry ashing may cause some elements to be lost by the volatilization or adsorption of elements on the walls of the furnace, such that As, Cr and Pb may be lost at ashing temperatures of 500–550 ^{O}C (Azcue and Mudroch, 1994). Numerous studies have been done to improve methods for proper extraction of desired metals.

However, no work has been carried out to statistically evaluate the most suitable acid digestion methods in order to access the impact of industries on soil samples in Nnewi-North. It was against this backdrop that this work was carried out. This study was aimed at assessing the efficacy of five acid digestion methods namely A, B, C, D and E which represented a combination of HNO_3 – HCl (1:3) with H_2O_2 prior to digestion, $HNO_3-H_2O_2$ (3:1), H_2SO_4: HNO_3: HCl (1:3:1), H_2SO_4: HNO_3 (1:4), HNO_3-HClO_4 (2:1) respectively, hence, recommended the most appropriate acid mixture for determining seven selected heavy metals Ni, Zn, Cu, Mn, Cd, Pb, and Cr. The analysis of heavy metals was conducted using the Flame Atomic Absorption Spectrometry (AAS) situated in Sheda Science and Technology Complex, Abuja.

MATERIALS AND METHOD

Study Area

Nnewi is the second largest city in Anambra state, southeastern Nigeria (Figure 1). Nnewi-North Local Government Area is commonly referred to as Nnewi central, and comprises four autonomous quarters: Otolo, Uruagu, Umudim, and Nnewichi (NCCIMA, 2015). Its geographical coordinates are $6^{0}1'0''$ North and 6^{0} 55'0" East. The city is located east of the Niger River, and about 22 kilometers south east of Onitsha in Anambra state, Nigeria (Erosion, 2009).

Nnewi is home to many major indigenous manufacturing industries. Nnewi is part of eastern Nigeria's industrial axis and acts as sophisticated networks expanded to include an international dimension through trading relations with exporters from Asia (NCCIMA, 2015). In fact, Nnewi is usually referred to as the Japan of Nigeria because of its high industrialization and has about thirty giant manufacturing plants and over a hundred cottage industries (Rose *et al.*, 2005). By 1940, Nnewi residents were at the center of an international trading network that dominated the supply of motor parts in Nigeria. The town subsequently became a center for commerce and industry, and is known to have one of the largest automotive parts markets in Africa (Onwutalobi, 2015).

Sample Collection and Preservation

Soil samples were collected from four areas in Nnewi-North Local Government Area. The four areas include Otolo, Uruagu, Umudim, and Nnewichi (Figure 2). Control soil samples were collected from Ebonato. Triplicate samples (15-20 cm depth), from each study site and control site were collected ten meters apart in a straight form using a stainless steel knife and pooled into polythene bags labelled with site locations. The soil samples were collected twice in rainy and dry seasons. In the laboratory, the soil samples were mixed thoroughly to obtain a composite sample for each site. The composite samples were air-dried for seventy-two hours at room temperature, ground in a glass mortar with pestle and sieved through 2.0 mm sieve and further pulverized to a fine powder and passed through 0.5 mm sieve for the total metal content determination (Amune and Kakulu, 2012). This ensured that the analyte is not lost and good results were achieved. A description of the sampling sites is listed in Table 1.

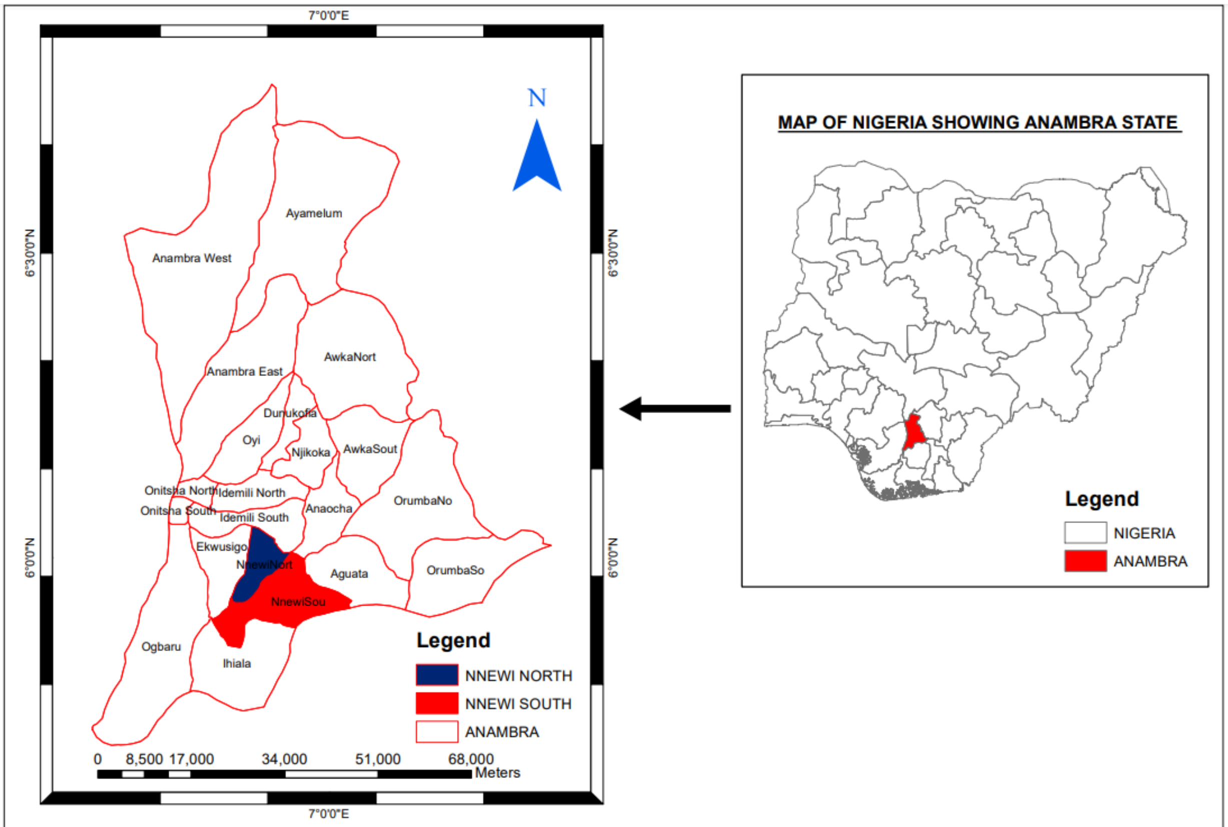

FIGURE 1: MAP OF ANAMBRA SHOWING NNEWI-NORTH

Selection of Methods of Sample Preparation for Metal Determination in Soil Sample

All reagents and acids used were of high purity and analytical grade supplied by BDH laboratory supplies England. Stock standard solutions of the elements were obtained from standard inorganic ventures, USA. Serial dilutions were made with de-ionized water in order to prepare working solution. The Precision for the each of the digestion methods A, B, C, D, and E were determined by using five replicates samples to analyze for the Pb, Ni, Cu, Zn, Mn, Cd, and Cr.

Method A: HNO_3 – HCl (1:3) with H_2O_2 prior to digestion

Five grams (5.0g) of soil sample was digested with 10ml of concentrated (35%) hydrogen peroxide for 10–15 minutes to destroy any organic matter. After cooling, 15ml mixture of aqua regia was added and boiled gently using a conical beaker on hot plate in a fume chamber for about 40mins (EPA-ROC, 1994). After digestion, the digest was filtered into 50ml volumetric flask and diluted to volume with distilled water.

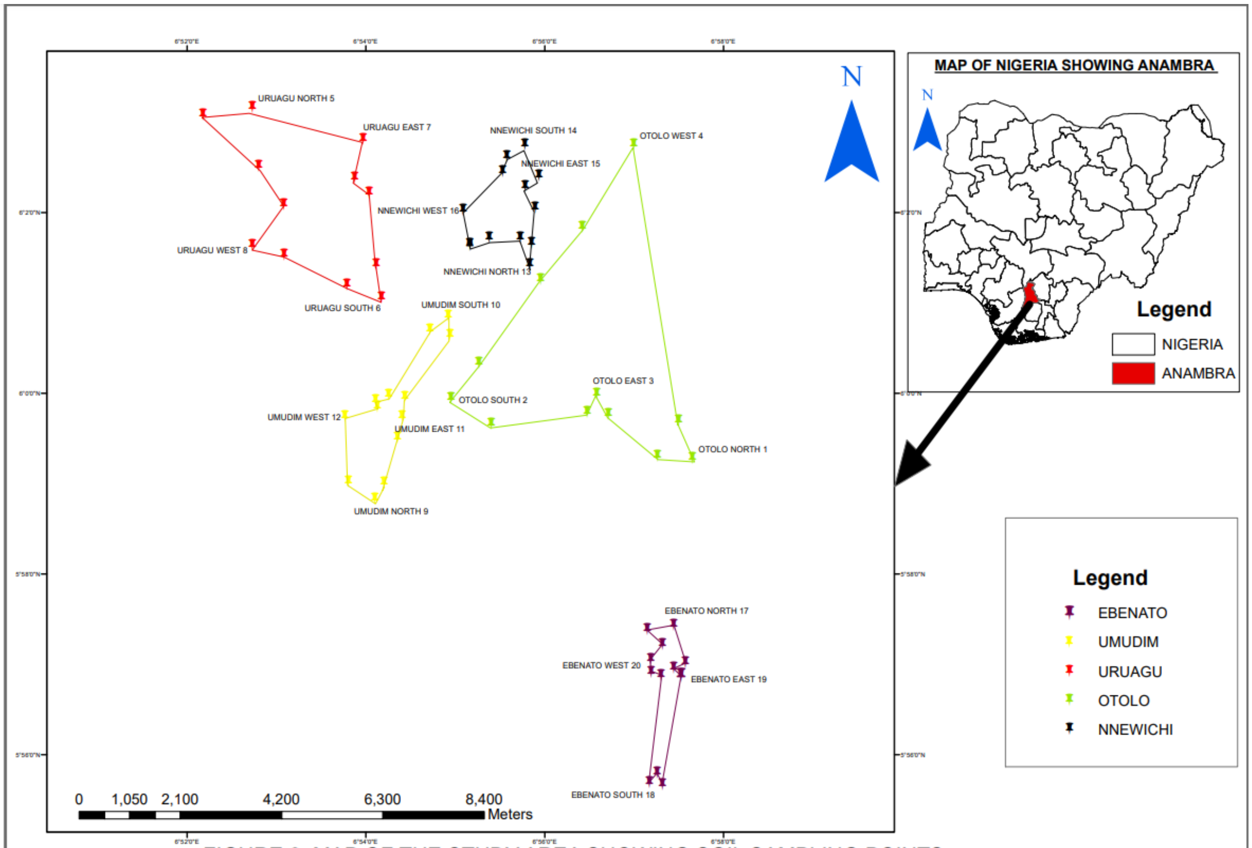

FIGURE 2: MAP OF THE STUDY AREA SHOWING SOIL SAMPLING POINTS

Table 1: The sample sites and coordinates

S/N	Areas	Code	Sample site Address	The Coordinates
1	Otolo	OTN	Otolo North	05^{o}59.282^{l}N/06^{o}57.656^{l}E
2	Otolo	OTS	Otolo South	06^{o}00.342^{l}N/06^{o}55.264^{l}E
3	Otolo	OTE	Otolo East	05^{o}59.768^{l}N/06^{o}56.716^{l}E
4	Otolo	OTW	Otolo West	06^{o}01.258^{l}N/06^{o}55.958^{l}E
5	Uruagu	URN	Uruagu North	06^{o}02.512^{l}N/06^{o}52.800^{l}E
6	Uruagu	URS	Uruagu South	06^{o}01.059^{l}N/06^{o}54.175^{l}E
7	Uruagu	URE	Uruagu East	06^{o}02.225^{l}N/06^{o}54.038^{l}E
8	Uruagu	URW	Uruagu West	06^{o}01.575^{l}N/06^{o}56.032^{l}E
9	Umudim	UMN	Umudim North	05^{o}59.009^{l}N/06^{o}54.209^{l}E
10	Umudim	UMS	Umudim South	06^{o}00.860^{l}N/06^{o}54.927^{l}E
11	Umudim	UME	Umudim East	05^{o}59.662^{l}N/06^{o}53.915^{l}E
12	Umudim	UMW	Umudim West	05^{o}59.928^{l}N/06^{o}54.594^{l}E
13	Nnewichi	NNN	Nnewichi North	06^{o}01.647lN/06^{o}55.738^{l}E
14	Nnewichi	NNS	Nnewichi South	06^{o}02.462^{l}N/06^{o}55.530^{l}E
15	Nnewichi	NNE	Nnewichi East	06^{o}01.654^{l}N/06^{o}55.165^{l}E
16	Nnewichi	NNW	Nnewichi West	06^{o}02.210^{l}N/06^{o}55.823^{l}E
17	Ebenato	EBN	Ebenato North	05^{o}57.440^{l}N/06^{o}57.446^{l}E
18	Ebenato	EBS	Ebenato South	05^{o}55.675^{l}N/06^{o}57.318^{l}E
19	Ebenato	EBE	Ebenato East	05^{o}56.962^{l}N/06^{o}57.446^{l}E
20	Ebenato	EBW	Ebenato West	05^{o}56.886^{l}N/06^{o}57.305^{l}E

Method B: HNO_3 – H_2O_2 (3:1)

Five grams (5.0g) of soil sample was slurred with 5ml of water to minimize sample splash and facilitate rapid reaction with the acid. 15ml of concentrated HNO_3 was added to the slurry and digested for about 40minutes using a conical beaker on a hot plate and after cooling, 5ml of 35% H_2O_2 was added drop-wise to the extraction mixture and heating was continued for 20 minutes (Anderson, 1975). After digestion, the digest was filtered into 50ml volumetric flask and diluted to volume with distilled water.

Method C: H_2SO_4: HNO_3: HCl (1:3:1)

H_2SO_4: HNO_3: HCl (1:3:1) mixture with slight modification was performed, following the procedure described by (Wasim *et al*., 2010). 5.0g of soil sample was digested with 25ml H_2SO_4: HNO_3: HCl (1:3:1) mixture using a conical beaker on a hot plate for about 40minutes. After digestion, the digest was filtered into 50ml volumetric flask and diluted to volume with distilled water.

Method D: H_2SO_4: HNO_3 (1:4)

5.0g of soil sample was digested with 25ml H_2SO_4: HNO_3 (1:4) mixture using a conical beaker on a hot plate for about 40minutes (Twyman, 2005). After digestion, the digest was filtered into 50ml volumetric flask and diluted to volume with distilled water.

Method E: HNO_3 – $HClO_4$ (2:1)

HNO_3 – $HClO_4$ (2:1) was performed with slight modification following the procedure recommended by (AOAC, 1990). 5.0g of soil sample was digested with 25ml HNO_3 – $HClO_4$ (2:1) mixture using a conical beaker on a hot plate for about 40minutes. After digestion, the digest was filtered into 50ml volumetric flask and diluted to volume with distilled water.

Recovery Studies on the method

The soil samples were spiked with known standards of Pb, Ni, Cu, Zn, Mn, Cd, and Cr and digested according to method of (EPA-ROC, 1994). The spiked samples were re-analyzed in order to calculate percentage recovery.

$$\% \text{ Recovery} = \frac{\text{Conc. of metal in spiked samples} - \text{Conc. of metal in the sample}}{\text{Conc. of metal added in spike}}$$

Quality Assurance and Method Validation

Validation of the method presented in this study was performed by analyzing three (3) replicates of certified reference materials, soil samples CC-141, obtained from European Commission, Joint Research Centre(JRC) Belgium. The reference material was digested using the method of (EPA-ROC, 1994) and was done as reference for quality control and assurance of the method used in this research.

Instrumentation

The digests were all analyzed for Pb, Ni, Cu, Zn, Mn, Cd, and Cr using the Flame Atomic Absorption Spectrophotometer, manufactured by Thermo-Scientific Spectrometer model ICE-3000 V1.30, situated in Sheda Science and Technology Complex, Abuja.

RESULTS AND DISCUSSION

Precision

Table 2 shows the precision obtained when five methods were utilized in the preparation of the soil samples for metal determination. Based on the fact that a precision of about 10% is said to be good for instrumental methods, three methods viz; A, B, & D were selected to be good because these had a precision of less than 10% for five metals, compared to C and E with four metals.

Students t-test

Based on this, the results obtained with the three methods were further subjected to t-test in order to know if the results were not significantly different from one another (Table 3). Based on Tcal being lower in value than Ttab the results obtained for method A were compared with Method B and D. The t-calculated showed that for four metals, were not significantly different between AB (Zn, Cu, Cd and Ni) & AD (Cu, Pb, Mn and Ni) but only one metal, Ni showed that Method B was not different from Method D.

Recovery studies

With this, method A was further subjected to recovery studies and these results are summarized in Table 4. The % recoveries are 93, 97, 87, 87, 96, 97 and 97 for Ni, Zn, Cu, Mn, Cd, Pb, and Cr respectively.

Analysis of reference material

With these good recoveries, the method A was used to analyze the CRM and the result is summarized in Table 5. The results of the experimental values of the replicate analysis of these reference materials were good. The results showed good agreement with certified values indicating that the sample preparation method adopted for this work is reliable and accurate.

Table: 2 Precision (%) for the Digestion Methods (RSD)

Metal/Method	A	B	C	D	E
Zn	3	12	2	4	4
Cu	9	3	10	9	4
Pb	5	6	3	4	2
Mn	2	3	8	3	3
Cd	5	12	3	20	32
Ni	11	7	12	9	21
Cr	9	9	3	1	7

Table 3 Students t-test for A, B and D for all the Metals

Metal		PAIRED METHODS		
		AB	AD	BD
Zn	t_{Cal}	7.9118**	64.5219*	49.1651*
	t_{Tab}	8.610	6.869	6.869
	Df	4	5	5
Cu	t_{Cal}	1.1659**	0.0000**	14.7475*
	t_{Tab}	5.408	5.959	5.408
	Df	7	6	7
Pb	t_{Cal}	68.2828*	2.1358**	78.7912*
	t_{Tab}	8.61	6.869	6.869
	Df	4	5	5
Mn	t_{Cal}	14.750*	0.333**	14.417*
	t_{Tab}	5.959	6.869	6.869
	Df	6	5	5
Cd	t_{Cal}	2.3565**	13.1878*	14.1015*
	t_{Tab}	6.869	6.869	8.61
	Df	5	5	4
Ni	t_{Cal}	5.8302**	1.9616**	8.3261**
	t_{Tab}	6.869	6.869	8.61
	Df	5	5	4
Cr	t_{Cal}	82.5840*	218.9233*	43.5955*
	t_{Tab}	5.408	5.408	5.959
	Df	7	7	6

Df- degree of freedom, **-accept, *-reject

Table 4 Result of Recovery Studies Obtained (μg/g)

Metal	Amount added (μg)	Amount Detected (μg)	Amount-in sample (μg)	Amount Recovered (μg)	Recovery (%)
Ni	2.00	4.20	2.30	1.90	
	2.00	4.10	2.30	1.80	93
	2.00	4.20	2.30	1.90	
Zn	10.00	30.00	21.00	9.00	
	10.00	31.00	21.00	10.00	97
	10.00	30.00	20.00	10.00	
Cu	5.00	15.00	11.00	4.00	
	5.00	15.00	11.00	4.00	87
	5.00	15.00	10.00	5.00	
Mn	5.00	54.00	50.00	4.00	
	5.00	55.00	50.00	5.00	87
	5.00	54.00	50.00	4.00	
Cd	2.00	3.20	1.30	1.90	
	2.00	3.20	1.30	1.90	96
	2.00	3.30	1.30	2.00	
Pb	10.00	75.00	65.00	10.00	
	10.00	75.00	65.00	10.00	97
	10.00	80.00	71.00	9.00	
Cr	10.00	110.00	100.00	10.00	
	10.00	101.00	100.00	9.00	97
	10.00	105.00	95.00	10.00	

Table 5 Result of the Analysis of the Certified Reference Material (ERM –CC 141) based on Aqua Regia Extractable Content

METAL	CERTIFIED VALUE(μg/g)	EXPERIMENTAL VALUE ±sd(μg/g)
Zn	50.00	47.50±2.16
Pb	32.20	32.50±3.53
Ni	21.90	21.80±2.82
Cu	12.40	12.15±0.69
Cd	0.25	0.29±0.14

CONCLUSION

In this study, the reproducibility of the measurements showed similar results and when subjected to precision test proved methods A, B and D to be good. The t-test analysis further showed method A to be the best extraction method for the analysis. However, there is no digestion method which was widely efficient in the extraction of all metals. Simplicity and adaptability as a routine procedure have led to the widespread use of the *aqua regia* method for the determination of total amounts of Cd, Cr, Cu, Ni, Pb, and Zn in contaminated soils and sediments. The *aqua regia* method with hydrogen peroxide can destroy any organic matter, metal oxides, but recommended for Ni, Zn, Cd, Pb and Cr in this present study with higher recoveries from soil samples.

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