

Analytical Method for Comparison of Suitable Wet Digestion Methods for Heavy Metal Analysis in Soil around a Cement Industry

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Abstract: - The approach of determination of precision and use of statistical analysis was applied in order to determine the suitable acid mixture for digestion of soil sample for heavy metal analysis in this work. Four different acid mixtures (HNO_3 (60%v/v), $\text{HNO}_3:\text{H}_2\text{SO}_4$ (2:9), HNO_3/HCl (1:3), $\text{HNO}_3/\text{HCl}/\text{H}_2\text{SO}_4$ (5:1:1), were compared over nine selected heavy metals (Pb, Cr, Cd, Ni, Zn, Fe, Mn, Co and Cu), and soil near a cement factory were analyzed. The precision for each of the metal in each of the acid mixture, the recovery and analysis of variance were applied to determine the most suitable acid mixture for digestion. From the results it was deduced that the t-calculated for 6 metals (Cd (0.577), Co (1.165), Mn (0.380), Cu (0.545), Ni (1.449) and Zn (1.424) (Cd, Co, Mn, Ni, Cu and Zn) were not significantly different for methods $\text{HCl}:\text{HNO}_3$ (3:1) and $\text{HNO}_3:\text{HCl}:\text{H}_2\text{SO}_4$ (5:1:1), except for Fe, Cr and Pb with significant difference. The heavy metal precision results, shows that method $\text{HNO}_3:\text{HCl}:\text{H}_2\text{SO}_4$ (5:1:1), had 7 metals with higher precisions which includes Fe and Cr, while $\text{HCl}:\text{HNO}_3$ (3:1) had 5 metals with higher precision but does not include Fe and Cr. The statistical analysis revealed that method $\text{HNO}_3:\text{HCl}:\text{H}_2\text{SO}_4$ (5:1:1) was the most efficient digestion method for the soil heavy metal analysis as it had given a significant high recovery ($p < 0.05$) for most of the metals under review. Accuracy of the acid mixture selected ($\text{HNO}_3:\text{HCl}:\text{H}_2\text{SO}_4$ (5:1:1)) was evaluated by the analysis of experimental reference material (ERM CC-141) loam soil obtained from the European Commission, Joint Research Centre (JRC), Belgium. The ERM analysis presented good recoveries for most of the metals ranging from 86.4 to 111.0%. The determined concentrations were in good agreement with the certified values from the ERM CC-141.

I INTRODUCTION

Metal pollution of the soil including agricultural soils arising from industrial activities, vehicular emissions, and waste disposal sites are well documented (Schuhmacher *et al.*, 2004). 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 (Sastre *et al.*, 2002).

Heavy metals can be regarded as a group of inorganic chemical, and those most commonly found at contaminated sites are Lead, Chromium, Arsenic, Zinc, Cadmium, Copper, Mercury, and Nickel (Sofani, 2014). Soils are the major sink for heavy metals released into the environment by aforementioned anthropogenic activities and unlike organic

contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation, and their total concentration in soils persists for a long time after their introduction. Changes in their chemical forms (speciation) and bioavailability are however, possible. The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants (Wuana and Okieimen, 2011). Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phyto-toxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems (Zhang *et al.*, 2009). 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 (Friberg *et al.*, 1986). The cement industry forms part of the industries that are well known to be problematic in environmental pollution. Exposure to cement dust for a short period may not cause serious problem, however prolonged exposure can cause serious irreversible damage to plants and animals (Heather, 2003). Besides gaseous and particulate pollutants there are also enhanced levels of toxic heavy metals in the environment of a cement factory likely lead, nickel, zinc, Cadmium, copper posing very potential hazard for all living organisms (Yahaya *et al.*, 2012).

Most cement factories have been noted as potential sources of metals such as Hg, Zn, Pb, Cr, and Cd and so on (Addo *et al.*, 2012B). It has been established that dust containing elevated amounts of trace metals emanating from the vicinity of cement factories may adversely affect humans, plants, and soil composition within the vicinity (McBride, 1989). Typical raw cement is made up of the following trace metals aside from the main and core raw materials 25 mg/kg of Cr, 21 mg/kg of Cu, 20 mg/kg of Pb, and 53 mg/kg of Zn. Further to this elemental composition, it was also reported that about 0.07 kg of dust is generated into the atmosphere when 1 kg of cement is manufactured (Sadhana *et al.*, 2014). Most cement factories

have been noted as potential sources of heavy metals such as Hg, Zn, Pb, Cr, and Cd (Addo *et al.*, 2012B). 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 process is to release the metals from the solid matrix to the acid solution during the digestion process.

The common method for destroying organic matter and dissolving heavy metals are classified into two groups-wet digestion by acid mixtures and dry ashing, followed by acid dissolution of the ash prior to elemental analysis (Zeng-Yei Hseu, 2004). Various methods have been presented for digesting plant tissue and soil samples for metal analysis. 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 °C (Azcue and Mudroch, 1994). Most wet oxidation procedures require the use of a combination of acid and oxidant, of which the most commonly used are nitric (HNO₃), sulfuric (H₂SO₄), perchloric acids (HClO₄), hydrogen peroxide, and hydrochloric acid (HCl) (Zeng-Yei Hseu, 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. Hydrofloric acid (HF) is commonly necessary for digestion of silica-based materials (Duyusen and Görkem, 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 Görkem, 2011).

This study was aimed at the application of statistical assessment of the digestion of four acid digestion methods namely A, B, C and D which represented a combination of nitric-hydrochloric acid (1:3), nitric acid, Sulfuric acid-Nitric acid (2:9), Nitric Acid - Sulfuric acid-Hydrochloric Acid (5:1:1) respectively, over nine selected heavy metals (Pb, Cr, Cd, Ni, Zn, Fe, Mn, Co and Cu) and analysis done in order to determine the precision and recovery efficiency. Eight soil samples around a cement factory in Obajana in Kogi State were collected and mixed together and digested with the above mentioned methods. The digestion processes were conducted using the conventional open vessel heating system as it provided the advantage of low equipment cost (Güler and Arzu 2006). The analysis of heavy metals was conducted using the atomic absorption spectrometry (AAS) situated in Sheda Science and Technology Complex, Abuja.

II. METHOD

2.1 Soil Sample

Soil sample were collected at about 1 km apart in 8 different points in Obajana, Kogi State of Nigeria the homeland of the Dangote Cement Industry. A total of 8 different soil sampling points in Obajana, were collected in June 2017. The soil samples were collected from topsoil at the depths of 0–10 cm (ASTM Guide D6044) using soil auger and at about 1 km apart. The coordinates of each of the soil sample (Labeled Obj S1- S8) collected were recorded with the Handy GPS Version 30.1, as shown in Table 1. The Google-map plot for each of the points were also shown in Fig. 1. The soil samples were pretreated by drying, sieving and homogenized. This soil sample was used to perform the optimization of the acid digestion methods.

| Sample | Northing | Easting | Latitude | Longitude |
|--------|----------|---------|---------------|----------------|
| OBJ S1 | 877893 | 216718 | N7° 56' 2.8" | E 6° 25' 50.1" |
| OBJ S2 | 878690 | 217226 | N7° 56' 28.8" | E 6° 26' 6.6" |
| OBJ S3 | 879154 | 217375 | N7° 56' 44.0" | E 6° 26' 11.3" |
| OBJ S4 | 878279 | 217660 | N7° 56' 15.6" | E 6° 26' 20.8" |
| OBJ S5 | 876999 | 218211 | N7° 55' 34.0" | E 6° 26' 39.0" |
| OBJ S6 | 876686 | 219122 | N7° 55' 24.0" | E 6° 27' 8.8" |
| OBJ S7 | 877031 | 220122 | N7° 55' 35.5" | E 6° 27' 41.4" |
| OBJ S8 | 876701 | 221276 | N7° 55' 24.9" | E 6° 28' 19.1" |
| | | | | |



Figure 1. Geo-Map showing the Coordinate points for Obajana soil samples

2.2 Chemicals and sample preparation

All chemicals and reagents used in this study were of analytical and trace metal grades. Trace metal grades 65 % HNO_3 , 37 % HCl , and 98 % H_2SO_4 were obtained from Chemistry Laboratory in the University of Abuja. Stock standard solutions for each metal cadmium (Cd), lead (Pb), nickel (Ni), zinc (Zn), and iron (Fe) with a concentration of 1000 ppm were prepared. Deionized water was used throughout the study. The proficiency of the selected acid medium was determined by analysis of an experimental reference material (ERM CC-141) obtained from Belgium using the Lindsay and Norvell, (1978) method. Reagents blanks were also analyzed to know the contribution of reagents to the metal levels in the reference sample. The heavy metal concentrations were determined by the Atomic Absorption Spectrophotometer, Manufactured by Thermo-Scientific Spectrometer model ICE-3000 V1.30. Due care was taken to avoid metal contamination in the process of sampling, extracting and analysis. Before analysis, the devices were rinsed with acidified water (10% HNO_3) and washed to remove dissolve metals. Also, all equipment and containers were soaked in 10% HNO_3 for 24 h then rinsed thoroughly in distilled water before use. Moreover, quality control was assured by performing duplicate analyses on all samples and by using reagent blanks and standards. All glassware were soaked in 5 % (v/v) HNO_3 overnight then rinsed with deionized water and dried using lab dryer FDD-720 prior to use.

2.3 Methods of digestion

Soil samples were accurately weighed (1.0 g each) and placed in a 250-mL Erlenmeyer flask. The samples were subjected to four different acid digestion methods, as will be explained, to identify the most appropriate digestion method to determine the contents of Pb, Cr, Cd, Ni, Zn, Fe, Mn, Co and Cu in the soil sample by AAS.

2.3.1 Method A (nitric-hydrochloric acid digestion 1:3)

To 1.0g of the soil, 10 mL of freshly prepared acid mixture of HNO_3 : HCl (1:3) was added, then, the mixture was boiled over a hot plate (95 °C) for 4–5 h until the sample had completely dissolved or until soil sample had turned white, adding the acid mixtures to avoid dryness (Ang and Lee 2005).

2.3.2 Method B (nitric acid digestion)

To the 1.0 g of the sample, 30 mL of 65 % HNO_3 was added, and then the mixture was boiled gently over a hot plate (90 °C) for 1–2 h or until a clear solution was obtained. Later, 2.5 mL of 65 % HNO_3 was added, followed by further heating until all the brown sample has turned white or colourless (Zheljzakov and Nielson 1996).

2.3.3 Method C (Sulphuric acid : Nitric acid (2:9))

To 1.0g of the soil in a 250 cm^3 conical flask, 20 cm^3 of freshly prepared mixture of sulfuric acid-nitric acid (2:9) as added, and then the mixture was boiled gently over a hot plate for 3 h at 110°C, the inner walls of the beakers were washed with 2 cm^3 of deionized water to prevent the loss of the sample during the digestion. After evaporating to near dryness, 2 cm^3 of 1% nitric acid was added. Sahrawat *et al* (2002).

2.3.4 Method D (Nitric Acid: Sulphuric acid: Hydrochloric Acid (5:1:1))

To 1.0g of the soil in a 250 cm^3 conical flask, 20 cm^3 of the mixture of 5:1:1, Nitric acid, hydrochloric acid and sulfuric acid was added. The mixture was allowed to stand for 30 min at room temperature and then placed on a hot plate in a fume cupboard; heating was continued for 2 hrs while distilled water was added at interval to avoid dryness. The interior walls of the conical flask were washed down with a little distilled water and the conical flask was swirled during the

digestion to keep the wall clean and prevent the loss of the sample. After cooling, 2 cm³ of 1% HNO₃ was added to the sample. The solution was filtered with Whatman No. 42 filter paper. It was then transferred quantitatively to a 50 cm³ volumetric flask and made up to mark by adding distilled water. (Lindsay and Norvell, 1978).

During the digestion procedures in each of the method, the inner walls of the beakers were washed with 2 ml of deionized water to prevent the loss of the sample, and at the last part of the digestion processes, the samples were filtered with Whatman 42 (2.5-µm particle retention) filter paper. Then, a sufficient amount of deionized water was added to make the final volume up to 50 cm³. Blanks for each of the method were prepared to see the contribution of reagents to metal levels.

2.4 Spiking and Recovery of Studies

1.0 g each of sample was weighed into four different conical flasks. Into the first flask (1) no standard was added, to flasks 2, 3, and 4 different concentrations of metal standard were added. In the first series 20 cm³ of HNO₃:HCl (1:3) mixture was added and the mixture was heated on a hot plate at about 110 °C for 3 hrs to near dryness, into this was further added 20cm³ of 2% nitric acid and heated and allowed to cool. This was filtered into a 50 cm³ volumetric flask and diluted to volume with distilled water. The same procedure above was also repeated for the HNO₃:HCl:H₂SO₄ (5:1:1) acid medium. The concentrations of the five heavy metals in the samples were determined to know the amount of the metals recovered by each method.

2.5 Quality Assurance and Method Validation

The method of Lindsay and Norvell, (1978) was used in the analysis of the reference sample (ERM CC-141) digested as described in section 2.3.4. Reagents blanks were also analysed to know the contribution of reagents to the metal levels in the reference sample. The heavy metal concentrations were determined by the Atomic Absorption Spectrophotometer described in section.

2.6 Determination of Heavy metal content

The heavy metals in the soil digests, were determined using the flame Atomic Absorption Spectrophotometer, manufactured by Thermo-Scientific Spectrometer model ICE-3000 V1.30, situated in Sheda Science and Technology Complex, Abuja.

2.7 Analysis of the standard reference material

The accuracy of the optimized method was verified by the analysis of an experimental reference material (ERM CC-141) loam soil obtained from the European Commission, Joint Research Centre (JRC), Directorate F-Health, Consumers and Reference Materials, Retieseweg 111 street, B-2440 Geel, Belgium using the Lindsay and Norvell, (1978) method the Atomic Absorption Spectrophotometer, Manufactured by Thermo-Scientific Spectrometer model ICE-3000 V1.30.

2.8 Statistical analysis

Results were expressed as the mean of triplicates ± standard deviation (SD). The data were analyzed by one-way analysis of variance (ANOVA) followed by Dunnett’s post hoc test for multiple comparisons using SPSS.

III RESULTS AND DISCUSSION

3.1.1 Precision for each heavy metal in the mixtures

Table 3 summarizes the precision of each method of sample preparations for each of the heavy metals. The nitric acid-hydrochloric acid (1:3) mixture and the nitric acid-hydrochloric acid –sulfuric acid (5:1:1) gave a precision of less than 10% for eight metals while the nitric acid (60% %) and the HNO₃/H₂SO₄ (2:9) methods only gave a precision of less than 10% for 5 metals.

As a result of the precision results for most metals exhibited by the HNO₃/HCl (1:3) mixture and the HNO₃/HCl/H₂SO₄ (5:1:1) mixtures, the concentration of metals in the sample were subjected to the student t-test at a probability of 0.05. Table 4.2 summarizes the t-calculated for each metal with the exception of Pb, Fe and Cr with t-values of 2.161, 5.519 and 2.570 respectively higher than the tabulated t-values, all the six metals (Ni, Zn, Cd, Cu, Co, and Mn) had t-values lower than the t-tabulated indicating that the concentrations of the metals obtained were not significantly different.

Table 2 Precision for each metal in the methods

| Metal/Method | Methods | | | |
|--------------|-------------------------------|-------------------------------|---|---|
| | HCl:HNO ₃ (3:1) | HNO ₃ (60% v/v) | HNO ₃ :H ₂ SO ₄ (2:9) | HNO ₃ :HCl:H ₂ SO ₄ (5:1:1) |
| Ni | 8 | 10 | 9 | 7 |
| Zn | 7 | 6 | 6 | 8 |
| Cd | 9 | 7 | 8 | 9 |
| Fe | 9 | 12 | 11 | 4 |
| Cu | 6 | 13 | 7 | 10 |
| Co | 10 | 4 | 10 | 8 |
| Pb | 8 | 8 | 10 | 8 |
| Cr | 8 | 8 | 8 | 6 |
| Mn | 6 | 8 | 6 | 5 |

3.1.2 Student t-Test of the Methods

Results in table 3 shows the t-calculated for the Student t-test for methods A and D for each of the metals for a two tail, Degree of Freedom =8, and P =0.05.

| Table 3 t-test Results for comparison of method A (HCl:HNO ₃ (3:1)), and method D (HNO ₃ :HCl:H ₂ SO ₄ (5:1:1)) | | | | | | | | | |
|---|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| t- TABLE = 1.860 (from Stat. T-table) | | | | | | | | | |
| t-CALCULATED FOR MTHEODS (HCl:HNO ₃ (3:1)), and HNO ₃ :HCl:H ₂ SO ₄ (5:1:1) FOR EACH METAL | | | | | | | | | |
| | Ni | Cd | Fe | Cu | Co | Pb | Cr | Mn | Zn |
| A/D | 1.449 | 0.577 | 5.519 | 0.545 | 1.165 | 2.161 | 2.529 | 0.380 | 1.424 |
| A: Nitric acid/Hydrochloric acid (1:3) method D: Nitric Acid/Hydrochloric acid/Sulfuric acid (5:1:1) method | | | | | | | | | |

The student t-test result shows the different t-Calculated for each pair of the Methods. The t-Tabulated = 1.860 at degree of freedom = 8 and at P = 0.05 (confident level) from Statistical Tables.

From the results of the Student-t test for A and D (Table 3) It can be deduced that the t-calculated for 6 metals (Cd, Co, Cu, Mn, Ni and Zn) was less than the t-tabulated hence the results are not significantly different for methods A and D, except for Fe, Cr and Pb with significant difference as the t-calculated for these metals were higher than the t-tabulated.

However from Table 2, method D has 7 metals with higher precisions which includes Fe and Cr, while A has 5 metals with high precisions but does not include Fe and Cr as seen with D.

3.1.3 Recovery Studies for the methods

The results of the recovery studies carried out on the two methods under investigations are summarized in Table 4 a and 4b

Table 4a Results for Recovery and Accuracy Analysis for Method (D) HNO₃:HCl:H₂SO₄ (5:1:1).

| Method HNO ₃ :HCl:H ₂ SO ₄ (5:1:1) | | mg/kg | | |
|---|--------------------|--------------|------------------|-------------|
| Element | Sample + std added | Amount Found | Amount Recovered | % Recovered |
| Pb | 0 | 8.15 | - | — |
| | 20 | 27.81 | 19.66 | 98.00 |
| | 40 | 45.52 | 37.37 | 93.43 |
| | 60 | 71.00 | 62.83 | 104.75 |
| Cd | 0 | 0.17 | - | -- |
| | 0.2 | 0.38 | 0.21 | 105.00 |
| | 0.4 | 0.55 | 0.38 | 95.00 |
| | 0.6 | 0.76 | 0.59 | 98.33 |
| Cr | 0 | 6.54 | - | — |
| | 2 | 8.54 | 2.0 | 100.00 |
| | 4 | 10.92 | 4.38 | 109.50 |
| | 6 | 13.19 | 6.65 | 110.83 |
| Cu | 0 | 76.40 | - | — |
| | 20 | 93.44 | 17.04 | 85.20 |
| | 40 | 114.37 | 37.97 | 94.92 |
| | 60 | 138.86 | 62.46 | 104.09 |
| Ni | 0 | 23.48 | - | — |
| | 10 | 34.39 | 10.91 | 109.07 |
| | 20 | 42.92 | 19.44 | 97.18 |
| | 30 | 54.04 | 30.56 | 101.86 |

Table 4b Showing The Results for Recovery and Accuracy Analysis for Method A (HCl:HNO₃ (3:1)).

| Method HCl:HNO ₃ (3:1) | Sample + std added | mg/kg | | |
|-----------------------------------|--------------------|--------------|------------------|-------------|
| Element | | Amount Found | Amount Recovered | % Recovered |
| Pb | 0 | 8.56 | - | — |
| | 20 | 28.04 | 19.48 | 97.40 |
| | 40 | 46.02 | 37.46 | 93.64 |
| | 60 | 75.30 | 66.74 | 111.23 |
| Cd | 0 | 0.17 | - | -- |
| | 0.2 | 0.38 | 0.21 | 105.00 |
| | 0.4 | 0.55 | 0.38 | 95.00 |
| | 0.6 | 0.76 | 0.59 | 97.78 |
| Cr | 0 | 6.90 | - | — |
| | 2 | 8.73 | 1.83 | 91.33 |
| | 4 | 11.52 | 4.62 | 115.42 |
| | 6 | 14.76 | 7.86 | 131.00 |
| Cu | 0 | 76.51 | | — |
| | 20 | 91.80 | 15.29 | 76.47 |
| | 40 | 98.40 | 21.89 | 54.72 |
| | 60 | 128.14 | 51.63 | 86.06 |
| Ni | 0 | 23.77 | | — |
| | 10 | 32.26 | 8.49 | 84.90 |
| | 20 | 43.99 | 20.22 | 101.13 |
| | 30 | 40.73 | 16.96 | 56.53 |

As seen in the Table 4a for method HNO₃:HCl:H₂SO₄ (5:1:1) the recoveries ranged from 93.43% to 104.75% for Pb, from 95.00% to 105.00% for Cd, from 99.67% to 110.72% for Cr, from 85.20% to 104.09% for Cu, and from 97.18% to 108.27% for Ni. The precision represented by relative standard deviation ranged from 2.62% to 9.36% hence the method falls within the acceptable limit of 10% precision.

From Table 4b for method HCl:HNO₃ (3:1), the recoveries ranged from 93.64% to 111.23% for Pb, from 95.00% to 105.00% for Cd, from 91.33% to 131.00% for Cr, from 54.72% to 86.06% for Cu, and from 56.53% to 101.13% for

Ni. And the precision represented by relative standard deviation for method A for the metals under review ranged from 6.56% to 13.58%.

From the results (3.1.1 to 3.1.3) analysis, Method D (HNO₃:HCl:H₂SO₄ (5:1:1)) was selected in preference to the other methods under review in this studies.

3.1.4 Quality Assurance

Analysis of the Certified Reference Material (ERM-CC-141) with Method D.

Table 5 Results for the analysis of the Certified Reference Material (ERM-CC-141)

| METAL | Certified Result | This Result | % Recovery |
|-------|------------------|---------------|------------|
| Cd | 0.25 | 0.22 ± 0.03 | 88.0% |
| Cr | 31 | 28.36 ± 2.20 | 91.5% |
| Cu | 12.4 | 10.71 ± 1.16 | 86.4% |
| Mn | 387 | 391.27 ± 2.98 | 101.1% |
| Ni | 21.9 | 24.31 ± 0.99 | 111.0% |
| Pb | 32.2 | 29.30 ± 1.91 | 90.9% |
| Zn | 50 | 46.27 ± 2.21 | 92.5% |

As shown in the Table 5 the concentrations of the heavy metals selected for analysis in the Certified Reference material are 0.25mg/kg, 31mg/kg, 12.4mg/kg, 387mg/kg, 21.9mg/kg, 32.2mg/kg, and 50mg/kg for Cd, Cr, Cu, Mn, Ni, Pb, and Zn respectively and the method: Nitric Acid/Hydrochloric acid/Sulfuric acid (5:1:1) yielded 0.22±0.03mg/kg, 28.36±2.2mg/kg, 10.71±1.16mg/kg, 391.27mg/kg, 24.31±0.99, 29.30±1.91, and 46.27±2.21mg/kg for Cd, Cr, Cu, Mn, Ni, Pb, and Zn respectively, which presented good recoveries for most of the metals ranging from 86.4 to 111.0 %. The determined concentrations were in good agreement with the certified values and within the specification limit of AOAC (American Organization of Analytical Chemistry) guidelines which verifies the accuracy of the methods.

IV. CONCLUSIONS

Sample preparation is a crucial step in spectroscopic elemental analyses as it can considerably affect the accuracy of results. Significant differences between the digesting capacities of different methods were identified. The digestion capacity using a mixture of Nitric Acid/Hydrochloric acid/Sulfuric acid (5:1:1) method was the most efficient method in terms of the recovery of most of the metals under review in soil samples.

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