Determination of Heavy Metals (Ag$^+$, Cd^{2+} and Pb^{2+}) Using FAAS and ISE in Soil Samples of Selected Eastern Hararghe Area

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Abstract— Soils are composed of mineral constituents, organic matter (humus), living organisms, air, and water, and it regulates the natural cycles of these components. Heavy metal is the metallic chemical element that has a relatively high density and it is toxic and poisonous at low concentrations. This work designed to determine and analyses the distribution of heavy metals present in the soil samples obtained from newly closed landfill at Haramaya, Awaday and Harar areas. The amount of heavy metals (Cd^{+2}, Pb^{+2}, Ag$^+$) present in the soil sample was determined using Atomic Absorption Spectroscopy (AAS) and ion selective electrode. In the study the level of Pb^{2+} determined in various province of eastern Hararghe, was above the acceptable values of WHO guideline (< 0.01 ppm). However, the concentration of Cd^{2+} and Ag$^+$ were within permissible values of WHO guideline (<3 and 0.05-2 ppm respectively). The method developed using ISE further validated its precision by relating the results obtained using AAS. The average percent of recovery for the ISEs when compared to AAS was 76.7%, which is largely due to differences in the fundamental response characteristics of the two methods, as ISEs only detect the free metal, whereas AAS detects total concentration.

Keywords—Soil, Heavy Metal, Ion Selective Electrode, Environmental Contamination, and Atomic Absorption Spectroscopy

I. INTRODUCTION

Soil is biologically active, and organic material found on the immediate earth surface that serves as a natural medium for plants growth and other developmental activities [1].Soil is a variable mixture of minerals, organic matter and water capable of supporting plant life on the earth's surface. It is the product of the weathering action of physical and chemical process on the rocks, which largely produce clay minerals. The soil fraction of typical productive soil is approximately 5% organic matter, 25% water, 45% minerals and 25% air. Topsoil layer contain largest amount of heavy metals. Protecting and enhancing the ability of the Earth's soils to provide clean water in sufficient quantities for humanity, ecosystems and agriculture will be a key element in delivering the SDGs [2]. Soils are key for storing and transmitting water to plants, the atmosphere, groundwater, lakes and rivers. The contaminant concentration in soil mainly depends on the adsorption properties of soil matter. The solubility of heavy metal ions in soil was mainly influence by many factors such as pH, conductivity, moisture content. Soil pollution by heavy metals, such as cadmium, lead, and silver, etc. is a problem of concern.

Many heavy metals are toxic to the living beings and tend to accumulate in plants, soils, and animals, causing chronic adverse effects on human health [3]. Even though there is some metals that are good to the soil which is may come from dumping waste, (such as nitrate that can act as fertilizer to the soil), but most of the soil will accepted more type of dangerous heavy metals in the soil that will lead to the negative effects. Heavy metals (Ag, Pb, and Cd) have been proved to be toxic to both human and environmental health [4]. There are different sources of heavy metals in urban soils [5] their loads in and around human settlements are a global problem. Heavy metals enter the soils by different pathways, including: 1) aerial deposition (industries, vehicles and volcanoes), 2) paints, 3) pesticide and fertilizer application, 4) waste utilization, 5) disposal of degraded sediments, and 6) river and irrigation waters [6]. Heavy metals pass through the air and food into the human organism, where they are usually not degraded, and hence they accumulate and may cause cancer, neuropathy and other diseases [7]. High levels of heavy metals in the sediments and soils may pass to the aquatic environment, groundwater, and plants through the transfer processes and reach to the animals and humans [8]. Therefore, establishing a rapid and cheap analytical method for the determination of metals in soil has an interest for a wide range of to enlighten the society since their life directly associated with agriculture [9]. Analytical techniques, atomic absorption spectroscopy and ion

selective electrode have been applied for the determination of some heavy metal in soil sample [10].

Although atomic absorption spectroscopy (AAS) have good sensitivity, well controlled experimental conditions, and narrow working concentration ranges. However, they have several disadvantages, such as the use of an expensive apparatus, complicated operation, high operation and maintenance costs.

For this experiment, after we pulverized and sieved the sample, we extracted the sample using Acid Digestion Method, and then all metals concentration in the sample was determined by using Atomic Absorption Spectroscopy (AAS) and ion selective electrode (ISE). Sample digestion is often a necessary step before determining "total" element mass concentrations in soil sample. A safe dissolution method that provides an analytical recovery of at least approximately 90% of elements was required. Open beakers heated on hot plates, digestion tubes in a block digester, and digestion bombs placed in microwave ovens are the most commonly used equipment to digest solid sample matrices.

Atomic Absorption Spectrometry (AAS) is a technique for measuring quantities of chemical elements present in environmental samples by measuring the absorbed radiation by the chemical element of interest. Although, atomic absorption spectroscopy is a power full and an accurate method, it is destructive when large amount of sample is used.

 Ion-selective electrodes (ISEs) are very sensitive and inexpensive analytical tools that can be applied to the determination of heavy metals that were until recently thought to be inappropriate for many environmental applications due to relatively high limits of detection. The ion selective electrode (ISE) is simple and cheap, and can directly measure the free metal ion concentration in solution. Because of their advantages in terms of low cost, easy fabrication, simplicity, sensitivity, and fast response time, potentiometric sensors based on ion selective electrodes have attracted much attention in electro-analytical chemistry and have been successfully used to determine trace levels of mercury. However, its detection limit is high, and other metal ions in solution interferes measurement. ISEs are used to measure the concentration of metal in digested field   samples, and the results are compared with a reference method (AAS). The average percent of recovery for the ISEs when compared to AAS is 65% which is to a large extent due to differences in the fundamental response characteristics of the two methods, as ISEs only detect the free metal, whereas AAS detects total concentration. A good correlation between the two methods is observed which suggests that ISEs can be used for in-situ direct measurements.

II.   RELATED WORK

The finding of this study was aimed to increase the farmer's productivity by analyzing the heavy metal status

of the soils of selected area and to compare the accuracy of the AAS and ISE. Then paves way for the concerned body to work in collaboration with the community to improve the quality of soils in Haramaya, Awaday and Harar to make suitable for agricultural purposes.

III.   METHODOLOGY

Experimental Methodology
Chemicals and reagents
Analytical grades of cadmium nitrate, silver nitrate, nitric acid, lead nitrate, hydrochloric acid, ammonium chloride, sodium chloride, potassium chloride, sodium nitrate, ammonia, Buffer solution (pH 7 and 4), deionized and distilled water were used.

Instruments
Atomic absorption spectroscopy(210 VGP, Buck scientific USA),Ion selective electrode(Jenway Ltd, UK), beakers(100ml,50ml,25ml),volumetric flasks, pipette, measuring cylinders, hot plate, glass rod, electrodes, fume hood, Deionizer (ELGA, UK), pH meter (JENWAY, Model 3310, UK), conductivity meter (JENWAY, Model 4330, UK), and oven were used.

Standard Solution Preparation
Lead stock solution and standards
Lead stock solution (1000 mg/l) was prepared by dissolving 0.799 g of lead (II) nitrate in 500 ml of distilled water and then made up to 1 liter of solution using distilled water. Through serial dilutions, standard working solutions of lead of 0.1, 0.5, 1,5,10 ppm were made which are used to generate a calibration curve for lead.

Cadmium stock solution and standards
Cd stock solution (1000 mg/l) was prepared by dissolving 0.275 g of Cd nitrate salt in 500 ml of distilled water and made up to 1 liter of solution using distilled water. Cd standard solution (10 mg/l) was made by diluting 10 ml of the stock solution to 100 ml of solution with deionized water. The calibration graph was made by using solutions with the following concentrations; 0.1, 0.5, 1, 5, and 10 mg/l of Cd.

Silver stock solution and standards
Silver stock solution (1000ppm) was prepared by dissolving 0.782 g of silver nitrate in 500ml of de-ionized water and 5ml of nitric acid and dilute to 100ml using deionized water through serial dilution standard working of silver would be made. The calibration graphs were made by using with concentration 0.1, 0.5, 1, 5, 10ppm of silver.

Soil Sample Digestion Procedures
Two grams of each of our soil samples were added into Separate, labeled, clean, and dry 100 mL beakers. The beakers were Put on acid gloves, and throughout the rest of the sample digestion procedure. In a hood, 5 mL water, and 5 mL concentrated HNO_3 were added respectively each slurry was mixed. With the bare glass end of a different stirring rod and cover each beaker with a non-ribbed watch

glass, placed concave up. The top of the beaker was sealed with the watch glass, to reduce gas loss. To avoid sample loss and a risk of cross-contamination, stirring rods was left in the pouring spouts of the beakers. All of the samples were heated together on one hotplate until they are refluxing (that is, until vapor is Condensing on the bottom of the watch glass and dripping back down into the beaker), and keep them at reflux for 10 min, stirring a few times: the hotplate's heat setting was started at 10, but was kept watch and reduce it to 1 at the first sign of boiling. The samples were removed from the hotplate and allowed to cool until they can be safely handled. Another 5 mL of concentrated HNO_3 was added to each beaker, the watch glasses, and refluxes were replaced for another 10 minutes. The materials were rinsed into the beaker, if it is condensed on the bottom of the watch glass by using small amount of water. 5 mL of concentrated HCl was added again once the samples were gained cool enough to handle and then 10mL of water was added. The watch glass cover was replaced and refluxed for 15 minutes, stirred occasionally. The mixture was heated up slowly. Each solution was filtered through qualitative filter paper into a 50 mL volumetric flask. After the solution was cooled to room temperature, it was diluted to the mark and then commence obsessive-compulsive behavior (i.e. invert each of three flasks at least 13 times to mix).

Calibration and measurements
Calibration of ion selective electrode
Ion selective electrode was calibrated by preparing three different concentrations. In order to quantify the elements in the soil samples, external calibration curves were built on three different concentrations. Standard solutions were prepared by diluting a multi element solution of Cd, Pb, and Ag at 1000 mg/mL the concentration ranges for the elements are between 0.01–100 mg/ml.

(a) Adding Ionic strength Adjustment Buffer (ISAB)
Ionic Strength Adjustment Buffer was normally added to samples and standards in order to ensure that all measured solutions have the same Ionic Strength and avoid errors due to differences between the measured activity and the actual concentration. Indeed, many ISE manufacturers advocate always adding ISAB to samples and standards, irrespective of whether the samples have high ionic strength or not, because this can help to stabilize the liquid junction potential of the reference electrode and hence reduce errors in measurement, and reduce the time taken to reach a stable reading but this may not be necessary if the reference electrode has an "equi-transferrent" filling solution (i.e. both ions have the same, or nearly the same, mobility e.g. Lithium Acetate, or Potassium Nitrate). Nevertheless, it must be noted that most electrode systems was given faster stabilization with ISAB when measuring low concentration samples in the non-linear range.

(b) Cleaning electrodes and minimizing hysteresis between samples
The electrode tips were rinsed by spraying with a jet of de-ionized water and gently dabbed dry with a low-lint laboratory tissue between measurements. For the most precise results, it may help to minimize hysteresis effects if the electrodes are soaked in de ionized water for 20 or 30 seconds after rinsing, before every measurement, so that each new reading is approached from the same direction, (i.e. always from low concentration to high as recommended for calibration measurements, to also minimize cross contamination) rather than just being dependent on the last sample measured.

Calibration of atomic absorption spectroscopy
Atomic absorption spectroscopy was calibrated by preparing five standard 100ml solution of known concentration of Pb, Cd, and Ag. Then, atomic absorption spectroscopy was calibrated by stock solution of each metal.

(a) Setting up the instrument: Set up the spectrophotometer according to the operating instructions. In this experiment, the measurements were made with the long axis of the flame both parallel and perpendicular to the light path. After measurement was finished with one flame position, the burner was turned head 90 degrees. Then continue on to make the rest of the measurements in the other flame position (on the separate MRT).

(b) Measuring the absorption intensity: Auto zero the instrument with deionized water, and measure the absorption intensity of all the standards and water samples. Dilute the unknown samples if the absorption   intensity is too high (i.e., beyond the range of the calibration curve).

IV.   RESULTS AND DISCUSSION

Physical parameters
Several physical parameter tests in this study has been done on moisture content, soil electrical conductivity (SEC), and soil pH because, a physicochemical study of soil is based on moisture content, soil electrical conductivity (SEC), and soil pH to get intended concentration amount of heavy metals in soil samples.

Moisture content determination

Table1. Moisture content of soil samples collected around Harar town

No	Sampling area	Initial mass	Mass after heating	Moistures
1	Haramaya(1)	50.0033	48.5688	1.4345
	Haramaya(2)	50.0093	47.8021	2.2072
	Haramaya(3)	50.0067	47.7229	2.2838
2	Awadey(1)	50.0115	46.7421	3.2694
	Awadey(2)	50.0387	45.6229	4.4158
	Awadey(3)	50.0251	46.7484	3.2767
3	Harar (1)	50.0016	47.6140	2.3876
	Harar(2)	50.0412	46.2677	3.7735
	Harar(3)	50.0591	46.9200	3.1391

Moisture of the soil is the difference between mass after heating and before heating. It depends on soil texture, structure, and soil type as shown in table 1. Sandy soil can

hold less water than saturated heavy silt clay. Sand has large particles, which take up a lot of physical space. In addition, as sand particles do not bind water, a lot of water will drain out of the sand due to gravity before field capacity is reached. For these two reasons, sand has much lower water content than a clay soil does. According to the above table 1, Haramaya location (1) soil sample more sandy and has least moisture content (1.4345). On the other hand, Awadey location (2) soil sample is less sandy and possess clay nature in turn has maximum moisture content (4.4158).

Soil pH and electrical conductivity (EC) measurements
The following table 2 shows, the pH and electrical conductivity value of soil samples collected from Harar area.

Table 2. PH and electrical conductivity of soil samples collected around Harar town

No	Samples area	P^H	Electrical conductivity(mean $\pm$ SD)
1	Haramaya(1)	2.54±0.01	189.43±0.5081
	Haramaya(2)	2.643±0.093	80.37±0.56471
	Haramaya(3)	2.723±0.064	69.933±0.4932
2	Awadey(1)	5.06±0.01	189.48±1.83870
	Awadey(2)	5.023±0.012	101.06±1.8528
	Awadey(3)	5.006±0.006	29.07±0.90702
3	Harar(1)	3.01±0.01	147.26±1.2636
	Harar(2)	3.043±0.015	61.26±0.32145
	Harar(3)	3.043±0.021	132.03±1.9905

PH- of soils indicates basicity or acidity of soil samples. As it is listed in Table 2, the pH value of soil samples collected from Eastern Hararghe were in the range of 2.54±0.01_5.06±0.01.

The PH of <4.6 are extremely acidic, between 4.6-5.5 are strongly acidic, 5.6-6.5 are moderately acidic and 6.6-6.9 are slightly acidic. The sample collected from Haramaya and Harar were extremely acidic, because their PH were <4.6.But, the soil samples collected from Awadey is strongly acidic, because its PH was between 4.62_5.5. In general, the soils collected from Awadey, Harar and Haramaya were not better for the development of common plants.

EC- Conductivity is an indicator of salinity. Salinity often originates from the earth's crust, although the additions of fertilizers and organic matter may also contribute salts. Soil EC is a measurement that correlates to soil properties affecting crop productivity, including soil texture, cation exchange capacity, drainage conditions, organic matter level and subsoil characteristics. With field verification, soil EC can be related to specific soil properties that affect crop yield, such as topsoil depth and water-holding capacity. Excessively high salinity can affect plants by the high Specific toxicity of a particular ion (such as Sodium). A high EC reduces the uptake of water and so the cell stretching of the growing point is inhibited. This is the real salt effect. A higher EC causes a higher risk for a too salty

substrate and so root dying. Therefore, this study reveals that the Awadey soil sample location 1, (189.48±1.83870) and Haramaya soil sample 1, (189.43±0.5081) have high electrical conductivity. Whereas, Awadey soil sample 3, (29.07±0.90702), Harar2, (61.26±0.32145), Haramaya3, (69.933±0.4932) and Haramaya 2, (80.37±0.56471) have low electrical conductivity. Therefore, Awadey soil sample location 1, (189.48±1.83870) and Haramaya soil sample 1, (189.43±0.5081) were not good for plant growth. On the other hand, Awadey soil sample 3, (29.07±0.90702), was good for plant growth.

Determination of heavy metals concentration in soil samples by ISE
Starting from a standard solution of 1000 ppm of Pb (NO3)$_2$, Cd (NO3)$_2$, and AgNo$_3$, a successive solution in the concentration range from 0.01 to 10 ppm were prepared for lead nitrate, cadmium nitrate and silver nitrate. As shown in figure 1, the calibration curve was constructed by plotting potential, E (mV) against log concentration of Cd^{2+}, Pb^{2+} and Ag^+ in ppm using Origin 7 software. The potential values were determined by direct inserting the corresponding electrode in each soil samples at room temperature. As can be seen from figure 1, the slope factor (RT /nF) of the calibration curve of Cd^{2+}, Ag^+ and Pb^{2+} were obtained at 27.61659,61.09013mVdec-1 and 25.5914 mVdec-1, respectively. Furthermore, the values of the slope factor correspond to the expected values by Nernst for a divalent ion and monovalent. In each case, nine soil samples were taken to read and the potential values presented in Table 3.
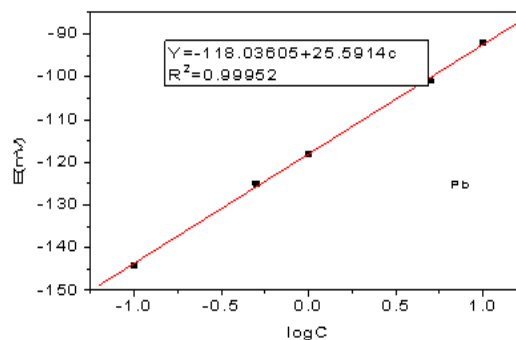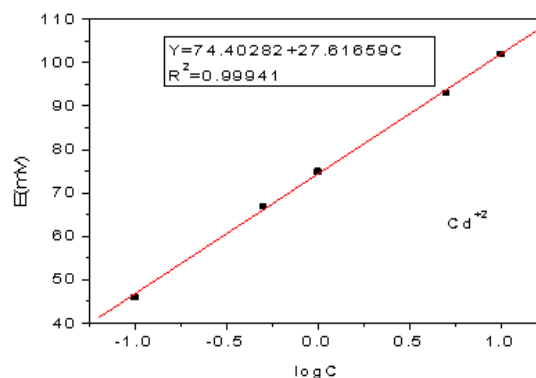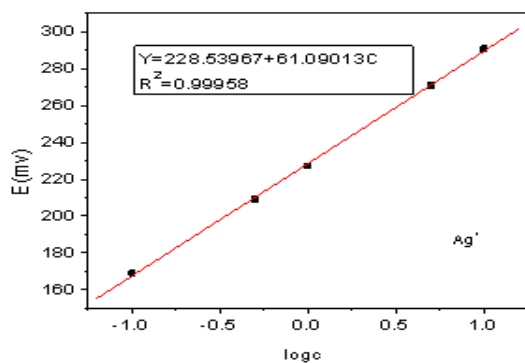
Figure 1. A calibration curve plotted potential against logarithmic concentration of Cd^{2+} ,Pb^{2+} and Ag^+ solutions

Nine soil samples collected from three sample sites and the levels of the ions present in each soil samples have shown in Table-3. The results were calculated by taking the mean value of triplicate samples (i.e. mean ± SD) from each sample sites. The concentrations of the ions present in each soil samples were calculated according to equation below.

$$C = 10^{\left(\frac{E-E_0}{slope}\right)} \tag{1}$$

Where E is Potential of unknown soil, EO is Constant (intercept), C=Concentration of unknown soil samples

Table 3. The concentration in ppm of various soil samples collected from Harar, Haramaya and Awadey obtained using ISE.

Sample no	Cd^{2+}	Pb^{2+}	Ag^+
Awadey 1	0.052±0.00152	0.1543±0.045	0.114±0.0017
Awadey 2	0.013±0.00152	0.152±0.040	0.118±0.0017
Awadey 3	0.043±0.002	0.165±0.041	0.215±0.003
Haramaya1	0.046±0.0015	0.096±0.003	0.223±0.006
Haramaya2	0.063±0.00152	0.0763±0.003	0.187±0.006
Haramaya3	0.0743±0.00208	0.0760±0.0025	0.3953±0.004
Harar1	0.176±0.0497	0.0873±0.002	0.0337±0.024
Harar2	0.0463±0.002	0.083±0.00208	0.0483±0.010
Harar3	0.079±0.003	0.097±0.0032	0. 233±0.015

The maximum allowed concentration of cadmium in soil sample established by WHO is <3 ppm. The level of Cd^{2+} ion in the present study was in the range of 0.013-0.176 ppm, being highest at site Harar location (1) (0.176±0.0497 ppm) and lowest at site Awadey location (2) (0.013±0.00152ppm). Therefore, the comparison of Cd^{2+} content of present values with that of the WHO reveals that it is less than the permissible limits. It was also observed that the concentration of Pb^{2+} ions was higher than the maximum permissible limits by WHO (< 0.01 ppm). The

value ranged between 0.0760±0.0025ppm at Haramaya location (3) site to 0.165±0.041ppm at Awadey location (3) site. The possible source of a significant Pb^{2+} concentration was found in all soil samples may be caused by lead contaminate of water runoff during summer season. Similarly the concentration of Ag^+ ion was within the range of 0.0337±0.024 - 0.3953±0.004ppm with the highest concentration at Haramaya (3) followed by lowest concentration at Harar location (1) respectively. It was also observed that the concentration of Ag^+ ions lower than the maximum permissible limits by WHO (0.05-2 ppm).

Determination of metal ions concentration in soil samples by AAS

Starting from a standard solution of 1000 ppm of Pb ($NO_3)_2$, 1000 ppm of Cd ($NO_3)_2$, and $AgNo_3$, a successive solution in the concentration range from 0.01 to 10 ppm were prepared for lead nitrate, cadmium nitrate and silver nitrate. As shown in figure 2, the calibration curve was constructed by plotting absorbance against concentration of $Cd^{2+,}$ Pb^{2+} and Ag^+ in ppm using Origin 7 software. The absorbance values were determined by direct inserting the corresponding sample injector in each soil samples at room temperature. As can be seen from figure 2, the slope factor (RT /nF) of the calibration curve of Cd_2+,$Ag+$ and Pb_2+ were obtained at 0.05911,0.00306 and 0.041, respectively. In each case, nine soil samples were taken to read and the absorbance values presented in Figure 2 below.
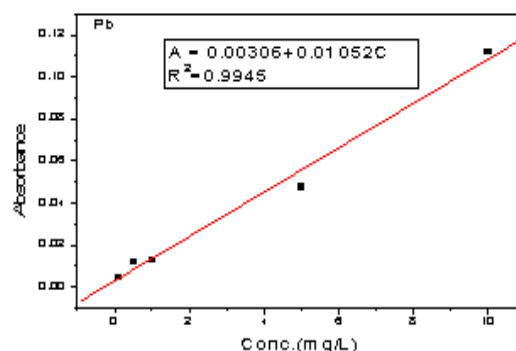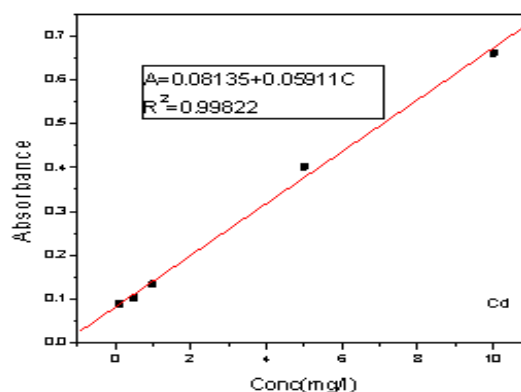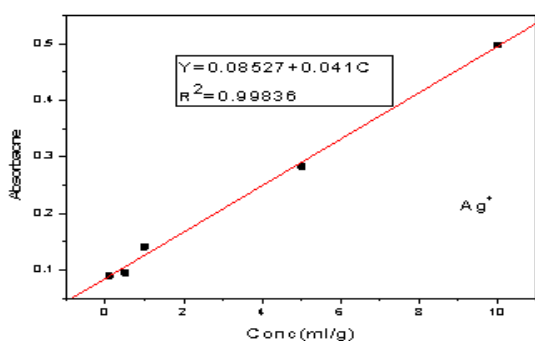
Figure 2: A calibration curve plotted potential absorbance vs. concentration of Ag^+, Cd^{2+} and Pb^{2+} solutions using atomic absorption spectroscopy

The fact that toxic metals are present in high concentrations in soil samples is of particular importance in relation to environmental contamination, fertilizers, pesticides, industrial processing containers and natural sources. A total of nine soil samples collected from three sample sites and the levels of the ions present in each soil samples have shown in Figure 2. The results were calculated by taking the mean value of triplicate samples (i.e. mean ± SD) from each sample sites. The concentrations of the ions present in each soil samples were calculated according to equation below.

$$Y = A + BX \qquad (2)$$

Where, Y=Absorbance of sample
A=Intercept from graph of standard
B=slope from graph of standard
X=Concentration of unknown soil sample

Table 4. The concentration in ppm of various soil samples collected from Harar, Haramaya and Awadey obtained using AAS

Sample area	Cd^{2+}	Pb^{2+}	Ag^+
Awaday 1	0.046±0.003	0.299±0.00607	0.1549±0.00218
Awaday 2	0.018±0.00115	0.271±0.008113	0.1337±0.0031
Awaday 3	0.036±0.001	0.149±0.001307	0.2802±0.0160
Haramaya1	0.0627±0.0012	0.0887±0.00413	0.249±0.0015
Haramaya2	0.083±0.0052	0.0675±0.00321	0.154±0.00361
Haramaya3	0.088±0.00152	0.073±0.004293	0.3533±0.0023
Harar1	0.140±0.00180	0.0809±0.004141	0.0367±0.00041
Harar2	0.045±0.005	0.0601±0.00357	0.0587±0.00068
Harar3	0.062±0.004	0.0858±0.00130	0.240±0.0042

The level of Cd^{2+} in the present study was in the range of 0.018-0.140ppm, being highest at site Harar (1) (0.140±0.00180ppm) and lowest at site Awadey (2) (0.018±0.00115 ppm).Therefore, the comparison of Cd^{2+} content of present values with that of the WHO reveals that it is much less than the permissible limits. It was also observed that the concentration of Pb^{2+} ions higher than the maximum permissible limits by WHO (< 0.01 ppm). The

value ranged between0.299ppm at Awadey (1) site to0.0601ppm Harar (2) site. The possible source of a significant Pb^{2+} concentration was found in all soil samples maybe caused by the presence of some concentration of $Pb+_2$ in soil. Similarly the concentration of Ag^+ ion was within the range of 0.0367-0.3533ppm with the highest concentration at Haramaya (3) followed by lowest concentration at Harar (1) respectively. It was also observed that the concentration of Ag^+ ions lower than the maximum permissible limits by WHO (0.05-2 ppm).

Recovery Tests
Recovery tests may reveal a significant bias in the method used and may prompt a correction factor to be applied to the analytical results.
The recovery was calculated with:

$$Recovery(\%) = \frac{\overline{X_s} - \overline{X}}{X_{add}} \times 100\% \qquad (3)$$

Where $\overline{x}s$ = mean result of spiked samples, $\overline{x}$ = mean result of unspiked samples, $\overline{x}add$= amount of added analyte. If a blank (sample) is used for spiking then the mean result of the unspiked sample will generally be close to zero. The mean results of 0.2 ml of spiked samples for (Ag^+, Pb^{+2}, $Cd2^+$) using ISE method was 0.162±0.0506 with mean result for un-spiked sample of 0.01mg/L. The calculated value for the recovery of the method was 76.7%. Similarly, the mean results of 0.2 ml of spiked samples for (Ag^+,Pb^{+2},Cd^{2+}) using AAS method was 0.1265±0.0601 taking the mean result for un-spiked sample of 0.01mg/L shows 58.2% recovery of the method.

V. CONCLUSION AND FUTURE SCOPE

The results demonstrated in this work show that ISEs could be successfully utilized for soil analysis. It was shown that the detection limit of the electrodes is comparable with the detection limit of AAS, a routinely used instrumental technique in environmental analysis. Sample digestion with diluted nitric acid resulted in concentrations of Pb^{2+}, Cd^{2+} and Ag^+ that were measurable with both ISEs and AAS, with good correlation between the two methods. This digestion can then be applied for in situ soil digestion significantly simplifying sample preparation. Furthermore, a good correlation between results obtained with ISEs and AAS implies the possibility of application of the former technique in soil analysis. Inexpensive construction, good detection limits and a simple experimental setup make ISEs an excellent prospect for in situ environmental analysis. The average percent of recovery for the ISEs when compared to AAS was 76.7%, which is to a large extent due to differences in the fundamental response characteristics of the two methods, as ISEs only detect the free metal, whereas AAS detects total concentration.

In this study, the level of Pb^{2+} determined in various province of eastern Hararghe, was above the acceptable values of WHO guideline (< 0.01 ppm). However, the

concentration of Cd^{2+} and Ag^+ present in all soil samples collected from Awadey, Harar, and Haramaya were within permissible values of WHO guideline(<3 and 0.05-2 ppm respectively).According to the values of moisture content, pH and Conductivity parameters the soil sample collected from Awadey area can only be used for agricultural purpose. Therefore, the concerned body in collaboration with the community should work to improve the quality of soils in eastern Hararghe province to make suitable for agricultural purposes.

ACKNOWLEDGMENT

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