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*Original Research Article*

# Efficiencies of Acid Digestion/Leaching Techniques in the Determination of Iron Concentrations in Soils from Challawa Industrial Estate Kano, Nigeria

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**Abstract**

**For most analytical techniques, it is necessary to destroy the collected material by wet oxidation. Wet oxidation (Digestion) procedures require only simple apparatus and are not subject to significant losses of elements by volatilization or adsorption onto container surfaces. Rigorous digestion procedures are required to solubilize the metals in the soil sample. Soil leaching technique also extracts metals and other soluble constituents from the soil by dissolving them in a liquid phase. The results for the efficiencies of two digestion methods were then compared to soil leaching technique. Solutions obtained by these methods were analyzed for Iron concentrations using Atomic Absorption Spectrophotometer. The Iron concentrations were (1165 to 2542) µgg-$^{1}$ for soil digestion using Conc. HCl and $HNO_3$, tri acid digestion using Conc. Hf, $HClO_4$ & $HNO_3$ gives Iron concentrations of (1305 to 2700) µgg-$^{1}$ while Iron concentration of (102 to 336) µgg-$^{1}$ is for soil leaching technique using Conc. HCl, suggesting that tri Acid digestion technique gives higher Iron concentrations in the soil samples analyzed than soil leaching technique.**

**Keywords:** Digestion, Leaching, Atomic Absorption Spectrophotometer, Iron, Soil, Acid

## INTRODUCTION

Soil varies in their chemical makeup; this variation is due to the chemical composition of the parent material and to the climate, plants and animals life under which the soil developed (Miller, 1985).

The chemical makeup of soil can be released into solution and then be analyzed. It is therefore always necessary to bring solid samples into solution prior to analysis. This could be achieved by digestion or leaching of the samples.

For solid samples such as sludge, soils and sediments, the solid form must be transformed to liquid phase. This process named digestion is required for the spectroscopic analysis. The principle is the releasing of metals from the solid matrix to the acid solution during the extraction process (Duyusen and Gorkem, 2011).

Leaching is the process by which inorganic or organic substances are released from the solid phase into the liquid phase under the influence of mineral dissolution. This separation process is called liquid – solid leaching or simply leaching. Because in leaching the solute is being extracted from the solid, is also called extraction (Christie, 2004).

The process of sample decomposition, the first step of all analyses, consists of the destruction of some or all of the original minerals as part or prior to the dissolution of the constituent of interest. Carbonate minerals are decomposed either in the cold or on digestion at an elevated temperature, with dilute hydrochloric acid.

Concentrated nitric acid serves to decompose not only carbonate minerals, but also any sulphides minerals present. Hydrofluoric acid has long been used for the decomposition of silicate rocks, usually in combination with nitric acid, perchloric acid or sulphuric acid (Scott and Thomas, 1977) in platinum crucible.

Langmyhr and Sveen (1965) recommended hydrofluoric acid but at a temperature of up to 250° C. Most authors have, however, preferred to use hydrofluoric acid in the presence of some other mineral acid. This serves to moderate the initial reaction between hydrofluoric acid and finely powdered silicate material. For this reason it is recommended that all powdered rock material should be moistened with water prior to adding hydrofluoric acid, failure to do this can result in overheating and subsequent loss of material by spitting.

The critical parameters in the digestion procedures are; the digestion temperature, applied programme, time, and the chemical power of the acids used. For the extraction processes, a variety of acid mixtures have been used (HCl, $HNO_3$, $HNO_3$-HF, $HNO_3$-HCl, HCl-HF, etc.) as reactives. The choice of an individual acid or combination of acids depends on the nature of the matrix to be decomposed. Among the acids used for wet digestion, HCl (boiling point $110^0$C) is useful for salts of carbonates, phosphates, some oxides and some sulfides. $HNO_3$ (boiling point $122^0$C) makes an oxidizing attack on many samples not dissolved by HCl. Besides, HF is necessary for digestion of silica-based materials (Dean, 2003). HF-based digestion methods tend to produce higher digest concentration of the metals. On the other hand, HF is toxic and may cause damage in the instruments (Cook et al., 1997). Therefore, the use of HF should be kept at a minimum in the digestion procedures. HCl is a strong acid and used for the decomposition of organic substances in combination with $HNO_3$ in ratio 1:3 is called Aqua regia.

The need for the rapid and accurate determination of heavy metals in sediments and other solid matrixes (soils, sludges, etc.) has led to the development of various digestion procedures which provide the efficient dissolution of metals (Lo and Sakamoto, 2005). The procedures may be numerous depending on the choice of the reagents and specific heating programmes. Different digestion methods were used which include the mixture of hydrochloric acid (HCl), nitric acid ($HNO_3$), perchloric acid ($HClO_4$) and hydrofluoric acid (HF).

Since many decades sequential extraction of soils to determine metals has been a very well established technique and numerous multi-step extraction schemes have been developed. Just recently such investigations have been applied to other materials such as sewage sludge and anaerobic sludge (Markus O. 2014).

The aim of this research work is therefore to determine the efficiencies of various digestion techniques in determination of iron and its various concentrations in soil samples in Challawa industrial estate Kano.

## MATERIALS AND METHODS

### Study Area

The study area is the dump site of tanneries in Challawa industrial estate in Kumbotso local government area of Kano state. Kumbotso local government area lies between latitudes 11º50´S to 12ºN and longitude 8º24´W to 8º40´ E. It falls within the Kano settlement zone bordering the south and west by Madobi, Northwest by Rimingado, North by Gwale and East by Tarauni local government areas respectively. The sampling zone covers an area of 30,072$m^2$.

### Sample Source

Soil samples were collected from Challawa industrial estate, and Challawa town of Kano State.

### Sampling Procedure

Three soil samples were collected at each sampling point, and at an interval of 10m away from each sampling point. Also soil was sampled as a control from Challawa town.

### Sample Treatment

Soil samples obtained were air dried and crushed to pass through 2mm sieve (Dikko and Ibrahim, 1999).

### Digestion of soil samples and determination of iron concentrations

Dried soil sample (0.2g) was accurately weighted into a Pyrex digestion flask. Few drops of de-ionized water were added to dampen the sample, 6$cm^3$ of concentration HCl acid and 1$cm^3$ of Nitric acid were added, and the mixture was heated on a hot plate. After cooling, 5$cm^3$ of Nitric acid and 1$cm^3$ concentrated HCl acids were added. The mixture was heated on a sand-bath at a temperature of 200-230° C and the acids evaporated to dryness. A quantity 6$cm^3$ 1$moldm^{-3}$ hydrochloric acid was added after cooling and the resulting solution was boiled for 10 minutes. It was filtered, made up to mark with de-ionized water in a 25$cm^3$ volumetric flask. The sample solutions were analyzed using atomic absorption spectrophotometer (Jimoh and Imam, 2011). The procedure was repeated

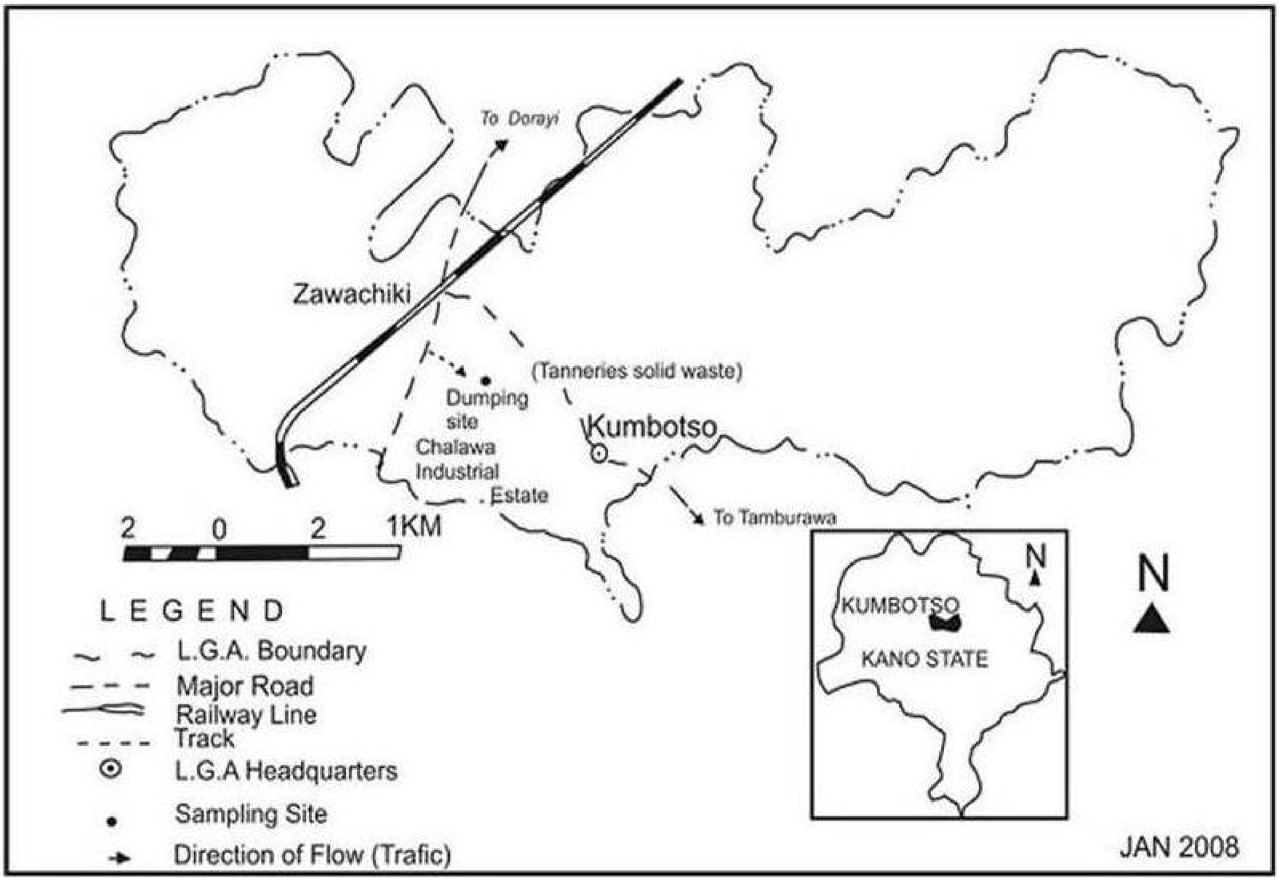


**Figure 1.** Kumbotso L. G. A. Showing the sampling sites

**Source:** Ministry of environment Kano, 2008"

**Table 1.** Concentration of Iron (µgg-[1]) in Soil Samples analyzed using Different Extraction Methods

| S/no | Sample Code | Leaching (HCl) | Digestion (HCl and $HNO_3$) | Digestion (HF, $HClO_4$ & $HNO_3$) |
|---|---|---|---|---|
| 1 | A (90m away from H) | 102.56±2.90 | 1507.50±68.34 | 1713.36 ±106.21 |
| 2 | B (80m away from H) | 169.36±9.26 | 1767.50±121.87 | 1789.90±84.32 |
| 3 | C (Control) | 137.47±7.92 | 1595.00±62.10 | 1680.00±71.20 |
| 4 | D (70m away from H) | 188.65±31.34 | 1810.00±249.53 | 2011.62±134.30 |
| 5 | E (60m away from H) | 156.18±31.34 | 1165.00±249.53 | 1305.19±96.00 |
| 6 | F (50m away from H) | 108.43±31.34 | 1725.00±249.53 | 1976.36±212.00 |
| 7 | G (40m away from H) | 121.13±31.34 | 1634.50±249.53 | 1921.00±184.21 |
| 8 | H (First sampling point) | 328.62±3.18 | 2415.00±208.71 | 2680.26±205.00 |
| 9 | I (10m away from H) | 336.21±3.18 | 2542.50±208.71 | 2700.19±178.00 |
| 10 | J (20m away from H) | 330.87±3.18 | 2050.00±208.71 | 2280.46±148.12 |
| 11 | K (30m away from H) | 207.35±10.51 | 2197.50±163.45 | 2321.12±132.03 |

for each and every soil sample to be analyzed.

## Digestion of soil samples and determination of iron concentrations

Dried soil sample (0.2g) was accurately weighted into Platinum crucible and a mixture of $HNO_3$: $HClO_4$: HF in the ratio of 3:1:3 was added. The mixture was heated on a hot plate for three hours at 80ºC, the digest was filtered and made up to 100cm$^3$ marks with deionized water and the resulting solution analyzed using Atomic Absorption Spectrophotometer V1200 with air acetylene flame (Nwajei and Gagophein, 2000).

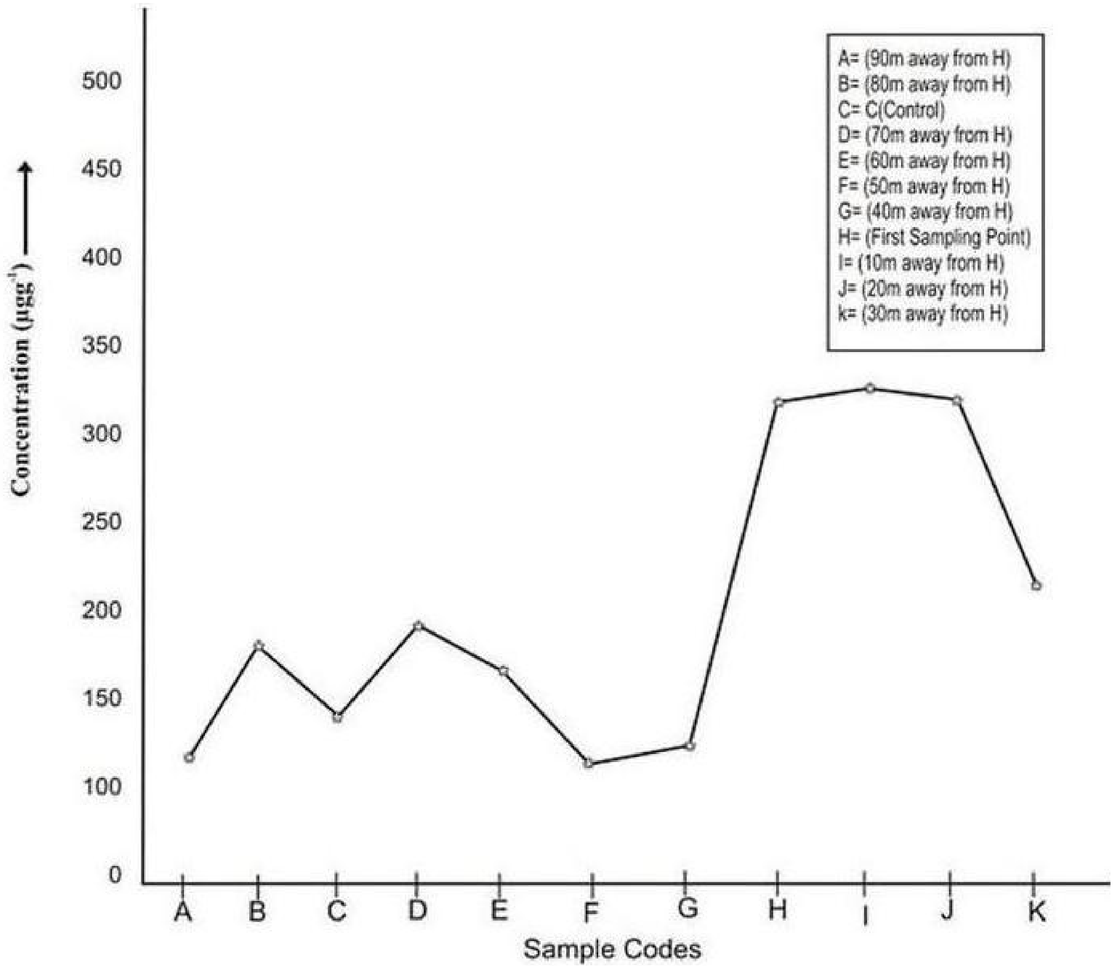


**Figure 2.** Distribution of iron in various soil samples using leaching (HCl)

**Leaching of soil samples and determination of iron concentrations**

Dried soil sample (2g) was weighed and transferred into a round bottom flask; 10cm$^3$ analar concentrated HCl acid was added. The flask was placed on a sand-bath and refluxed for several hours until the sand turned white. The mixture was transferred into a beaker and evaporated to dryness. It was then rinsed with de-ionized water and leached with 25cm$^3$ of 1moldm$^{-3}$ hydrochloric acid. The content was centrifuged for 6 minutes in a centrifuging machine to obtain 25cm$^3$ sample solutions which was analyzed using Atomic Absorption Spectrophotometer V1200 with Air Acetylene flame (Jimoh and Imam, 2011).

The procedure was repeated for each and every soil sample to be analyzed. (Figure 1)

**RESULTS**

All values are mean values of triplicate determinations.

Table 1 above presents the mean concentration of iron in soil samples analyzed by leaching and digestion techniques. The results show differences in Iron concentration at various sampling points using different methods employed.

The distribution pattern of iron for various samples analyzed using HCl and $HNO_3$ as shown in Figure 3 reveals high concentration of iron in the soil. Soil 10m away from the first sampling point has the highest concentration of 2542µgg$^{-1}$ and the lowest is soil 60m away with concentration of 1165 µgg$^{-1}$. The results of the soil samples analyzed using HF, $HClO_4$ and $HNO_3$ as shown in Figure 4 reveals the highest Iron concentrations from 1305 µgg$^{-1}$ at a distance of 60m away from first sampling point to 2700 µgg$^{-1}$ at 10m away. These concentrations are higher than those obtained in determination of iron in the same soil samples using concentrated HCl in a reflux condenser (Leaching) with highest concentration of 336µgg$^{-1}$ at a distance of 10m away from the first sampling point as shown in Figure 2.

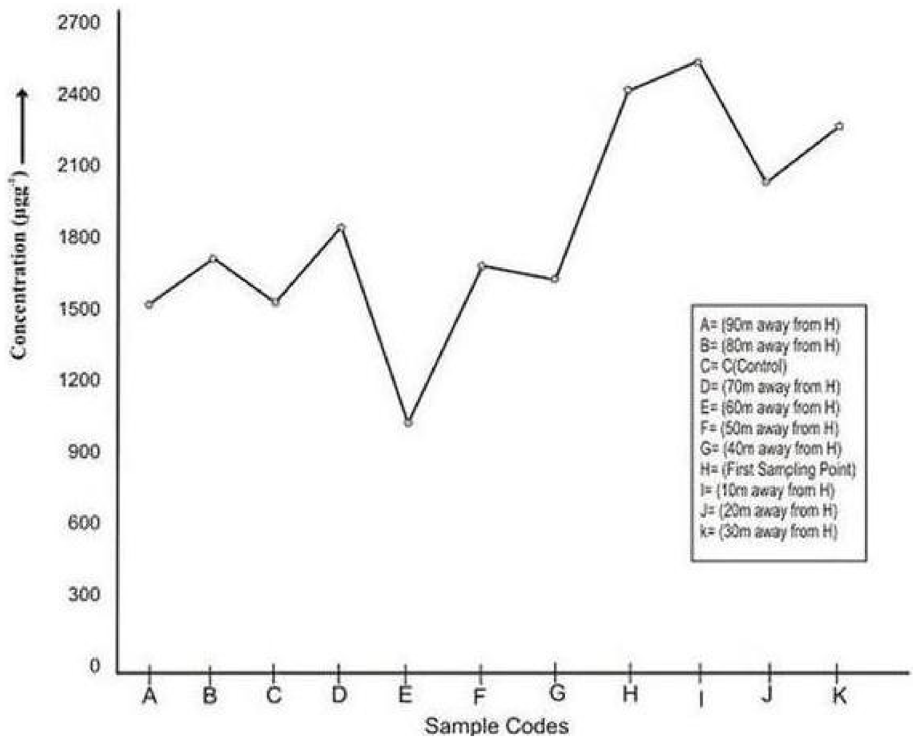


**Figure 3.** Distribution of iron in various soil samples using digestion (HCl and $HNO_3$)

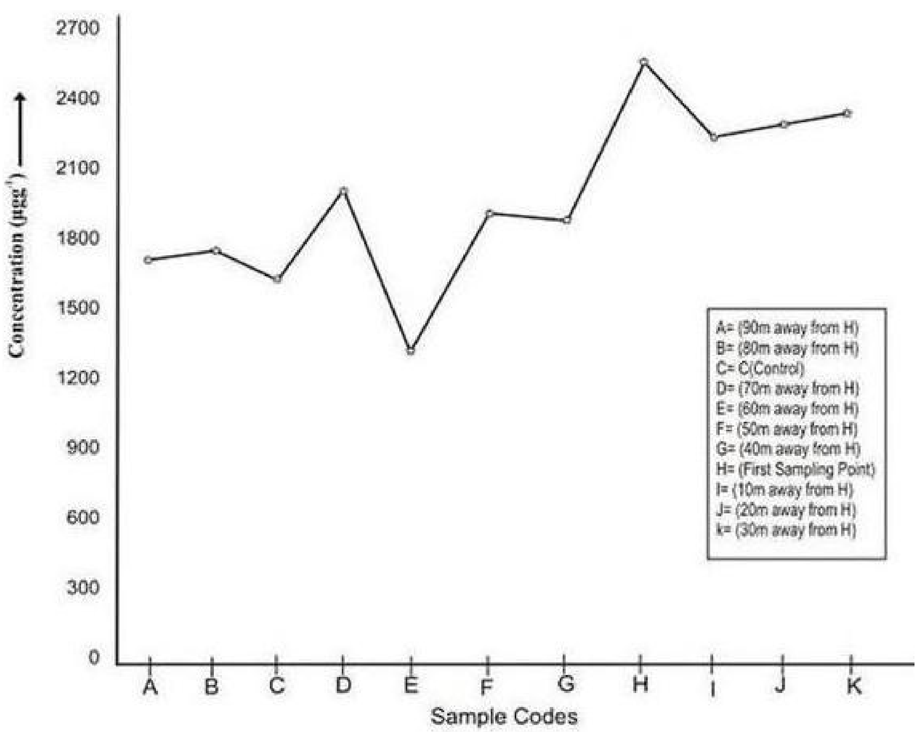


**Figure 4.** Distribution of iron in various soil using digestion (Hf, $HCLO_4$ and $HNO_3$)

## DISCUSSION

Many methods of analysis including flame emission and atomic absorption spectrophotometry generally require the sample to be in the form of solution. The processes of decomposition vary considerably from extraction with water, organic solvents or mineral acids to the more elaborate techniques of sintering or fusion. Few of these techniques will decompose completely all type of soil or rock material. Many of the decomposition procedures serve to dissolve the major part of the constituent minerals but leave a fraction as a residue that can be separated from solution by filtration. Whether or not this residue will require separate decomposition will depend upon the amount of residue and more particularly whether it can be expected to contain the elements of interest. Iron is the metal of interest in this research due to its natural abundance in soil as Iron Silicate (Yaroshevsky, 2006).

Before choosing a wet oxidative procedure from among a number of alternatives, (Skogerboe, 1974) it is well to recognize the functions of the various acids. Both acid digestion and alkali fusion have long been used to break down silicates. Fusion is essential if silica is to be determined. Soil contains Silicate and silicate matrices dissolution requires hydrofluoric acid. Since this acid will also dissolve chemical glassware, it should be used with care, and non glass container should be employed. It is important to keep the total salt content as low as possible, for this reason, acid decomposition is commonly used. When silicate matter is to be analyzed and when silicon is not of interest, a mixture of hydrofluoric and other mineral acids can be employed in an open dish.

The fusion of minerals with anhydrous sodium carbonate brings them into forms which are completely soluble in hydrochloric acid. To ensure complete dissolution a large excess of sodium carbonate must be used. For most minerals the weight used must be at least four times that of the sample (Washington, 1930). Hydrofluoric acid attacks silicates in soil to give silicon tetra fluoride which is volatile when heated in the presence of strong acids. Organic matter is decomposed with perchloric acid.

A mixture of hydrofluoric acid and perchloric acid thus provides a satisfactory method for the decomposition of soils. Soils containing large amounts of organic matter must be pre-heated with nitric acid- perchloric acid mixture first to remove most of the organic matter and to avoid explosive conditions during the subsequent removal of silicon tetra fluoride. Nitric acid solutions are effective in attacking ores of metals such as cobalt, copper, manganese, nickel and lead. Carbonates and sulphides are decomposed by concentrated nitric acid, and boiling nitric acid has been recommended for leaching sulphides of elements such as lead and zinc from a silicate matrix.

Although perchloric acid is a little less effective than sulphuric acid in the removal of the residual fluorine (Langmyhr, 1967; Hillebrand *et al*., 1953), the evaporation, crystallization, and dissolution of residue usually proceed more smoothly when perchloric acid is used. Where the solution contains sulphuric acid, some sparingly soluble sulphates, such as barium sulphates may also remain (Hoops, 1964). A further advantage of perchloric acid is the smaller likelihood of interferences when flame spectrometric methods of analysis are used. Elements that can be taken into solution following hydrofluoric acid attack include the alkali and alkaline earth metals, iron, aluminum, manganese, titanium, and most of the transition elements that commonly occur in trace amounts in silicate rocks.

Three digestion extraction techniques have been tested. The results of the comparison are shown in table 1. From the results it could be inferred that mixture of nitric and hydrochloric acids digestion is a better technique than soil leaching technique. However, both methods left a residue after digestion. A series of samples were then analyzed using a three acids (perchloric, nitric and hydrofluoric) mixture digestion and the result gives the highest concentrations of iron and therefore the most effective. The samples were analyzed in triplicate to test the reproducibility of the method.

The observed iron concentrations in the soil samples analyzed might be due to the natural background concentration of iron in the environment. Though considering the industrial activity in the area, wastes containing Iron must have been introduced to the soil which is unevenly distributed in the area at various distances. It has been confirmed that natural soils contain significant concentration of iron (Aluko *et al.,* 2003; Dara, 1993 and Eddy, 2004). Eddy *et al. (2004),* suggested that the pollution of environment by iron cannot be conclusively link to waste material alone but other natural sources of iron must be taken into consideration.

Some communities have iron water pipes, iron can be leached from pipes especially if the water is acidic. Iron pipes are also subject to rusting, allowing iron oxide flakes to be added to the water.

Iron toxicity is quite prevalent and variety of sources can contribute to wide range of diseases from heart failure to thyroid and liver diseases .Inhalation of Iron fumes causes Pneumonia and Siderosis, a dust which imparts a red discoloration of the lungs (Butler, 1970) .Toxic effects begins to occur at doses above 10-20mg/kg of elemental iron. Ingestion of more than 50mg/kg of elemental iron are associated with severe toxicity.

Also the high concentration of Iron obtained in the digestion methods is due to total dissolution of the Iron silicate in the soil by the acids employed. It is known that concentrated hydro fluoric acid dissolves silicate easily forming Silicon tetra fluoride(Duyusen and Gorkem, 2011), while soil leaching technique using concentrated hydrochloric acid dissolve the soluble constituents in the soil leaving high concentration of Iron un dissolved.

From these results it is clear that tri-acid mixture digestion method is the most efficient and reliable technique for analyzing the soil samples. From the results of the soil leaching technique it shows that, it is the least efficient extraction technique, because of its in ability to dissolve the high proportion of the fraction. Only the soluble constituents were removed leaving high concentration of iron as silicate in the soil.

Research was carried out to see if organic acids can be used to leach lithium and Cobalt from spent batteries with some success. Experiments performed with varying temperatures and concentrations of Malic acids show the optimal conditions are 2.0M organic acid at a temperature of 90ºC (Jing et al., 2010a).

The same analysis with Citric acid showed similar results with an optimal temperature and concentration of 90ºC and 1.5M Citric acid (Jing et al., 2010b).

## CONCLUSION

Acid digestion procedures are required for the quantification of metals in the solid samples such as soils, sediments and sludges. Numerous studies have been developed to improve the most accurate and efficient methods for proper extraction of chosen elements. The advantages of high extraction efficiencies in the results of the digestion procedures make one digestion procedure preferable over others. Also short digestion time and less acid consumption are factors to consider in the choice of digestion procedure. The results showed that acid combinations used in the procedures directly influence the efficiency of the digestion process. The soil samples treated with the tri acid mixture (HF, $HClO_4$ and $HNO_3$) gave the best result, followed by mixture of HCl and $HNO_3$, and lastly soil leaching using Conc. HCl acid.

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