

Evaluation of the Effectiveness of Different Acid Digestion on Sediments

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Abstract: The efficiency of four different acids mixtures were evaluated in the determination of total concentration of Pb, Zn, Cu, Cd, Cr and Fe in sediments samples. The acids combination employed included nitric- perchloric acid (NP), aqua regia (NH), sulphuric- hydrogen peroxide (SP) and nitric acid. Sediment samples were taken from five different Lagos lagoon locations; mid lagoon (ML), University of Lagos (UL), Oworonsoki (OW), Ikoyi (IK) and Oko-baba (OB). Validation of the method was performed by using certified reference material IAEA-158 from the International Atomic Energy Agency analytical quality control services, Vienna, Austria. Using Principal component Analysis (PCA), the results revealed that SP acid mixture was efficient for the recovery of Pb, Cd and Cr while NP and NH gave good results and to some extent nitric acid for the extraction of Zn, Fe and Cu; these procedures were recommended for the qualitative determination of Zn, Cu and Fe in sediment. When employing the NP method, the perchloric acid should be added at the later stage of digestion to avoid explosion.

I. Introduction

As a growing global population, there has been need to produce food, water and shelter and this has caused focus on the ocean to help sustain some of our basic needs. The contamination of the seafloor by chemical inputs (pollution) affects and threatens the benthic environment. These pollutants are consumed up by bottom dwelling organisms and transferred up the food chain, adversely affecting organism's activity, growth, metabolism and reproduction [1], killing some organisms in the process and reducing food availability in the ocean. The formation of seawater and seafloor with relation between chemical compounds (inorganics and organics), how chemical inputs (pollution) affects it and how the chemistry of the ocean affects or is affected by biological geographical and physical factors has been of great concern over decades. However, the water body, sediments and aquatic life (bio indicators) have been used as monitors to evaluate the level of pollution in the marine environment [2].

Heavy metals have been a source of pollution to the environment over the last century. This is due to fast growing economy and industrialization. Sources of these pollutants range from residential wastes, industrial effluent/wastes, agricultural tools waste, mechanic village scraps and more recently electronic waste. The receiving systems are soil, underground water, rivers/streams, lagoons and sea, which finally settle down or accumulate in the ocean. Scientists over time have assessed the level of heavy metals in the environment as well as investigated the level at which it could be detrimental to life [1,3,4,5,6,7,8].

Heavy metal quantitative determinations have been done majorly through two different methods; wet digestion and dry ashing followed by acid dissolution [9]. Wet digestion involves destruction of the organic matter and dissolution of heavy metals. Hossner [10] reported that the advantages of the dissolution of heavy metals in sediments and soils using concentrated inorganic acids are low cost and low salt matrix in the final solution for the determination of total heavy metal content. Acids used for wet digestion include nitric acid, sulphuric acid, hydrochloric acid, perchloric acid, hydrogen peroxide [11]. These acids have been used either alone or in ratios. Hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO₃), perchloric acid (HClO₄), and sulphuric acid (H₂SO₄) have been used singly and extensively to optimize extraction from the organic matrix [12,13].

Gorsuch [14] discovered 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. However, perchloric acid is potentially hazardous during the digestion of biological materials and can cause the loss of potassium and boron [15]. Baker and Amacher [16] recommended use of HF-HNO₃-HClO₄-H₂SO₄ for the total

analysis of Cd, Cu, Ni, and Zn in soils, but this was modified by Bureau [12] 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. It was reported by Stephen P. et al. [17] that using aqua regia and block digesters, digestion is faster, more economical and can be very simply modified to suit different types of soil. Aqua regia (ratio 3:1 or 4:1 v/v) has been said to extract effectively trace metals in sediments [18]. Sastre et al. [19] stated that nitric acid digestion was an optimum method for estimating heavy metal content in soil samples with high organic matter content, being superior to microwave-assisted and aqua regia digestions. important compost constituents [20]. Heavy metals in the silicate mineral require digestion with hydrofluoric acid (HF) and strong acids. However, the use of HF in routine laboratories is not recommended, as it is highly corrosive and difficult to handle.

Numerous studies have succeeded in improving methods for proper extraction of chosen elements. The objectives of our study are twofold. First, we aim to evaluate and recommend the most appropriate acids mixture for the dissolution of marine sediments in determination of specific heavy metals content. This has resulted in suggesting simple, rapid, reliable and accurate method for the preparation of large numbers of marine sediment samples. Second, we determine the total concentration of the heavy metals obtained from acid digestion mixtures, to know the level of pollution of Lagos Lagoon. We hence discuss the extent of heavy metal pollution around the highly populated locations of Lagos Lagoon. The overall objective of the study is to evaluate and recommend the most appropriate digestion method for determining Pb, Zn, Cu, Cd, Cr and Fe in sediments from various sites putting into consideration the above advantages.

II. Materials and Methods

2.1 Study Area

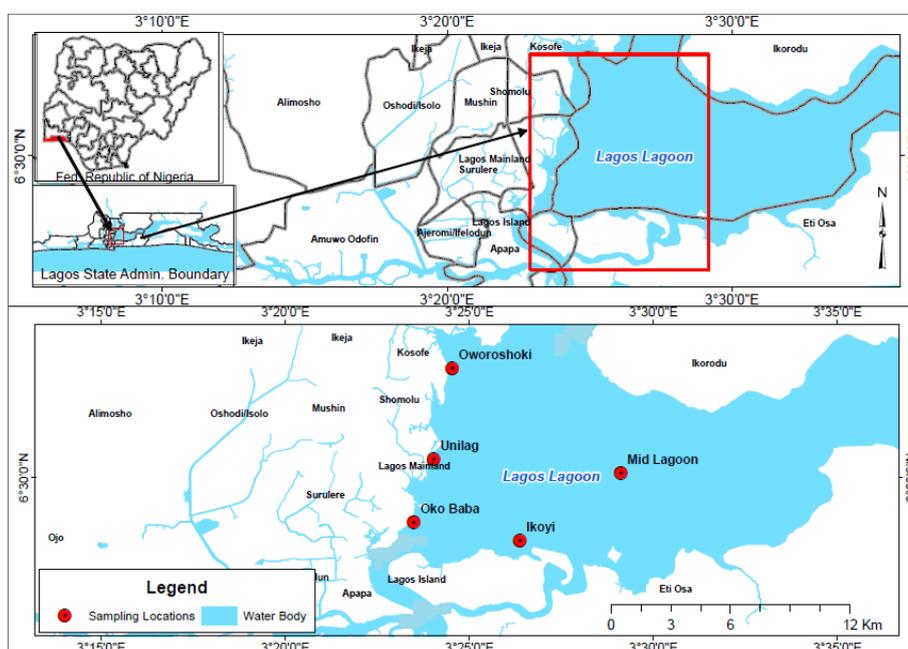


Figure 1: Map of the study area.

Fig. 1 above shows the sampling stations on Lagos Lagoon while Table 1 below recorded the coordinates and approximate depth for each sampling station respectively. Lagos Lagoon has estimated area of 150.56 km². Lagos Lagoon receives a number of important large rivers, namely: Yewa, Ogun, Osun and Ona [21]. The brackish water lagoon surrounds the Lagos Island and empties at Lagos harbour into the Atlantic Ocean. Lagos is located on the western side of Nigeria and has in size 3,577 sq. km with a maritime shoreline of about 180 km as its southern border. The Lagos Lagoon is generally shallow in most parts with the exception of some dredged parts (depth >10 m), notably in the Lagos harbour. Lagos Lagoon ecosystem serves as a source of affordable protein in term of sea foods and means of transportation for the local populates living around it. It has been reported that the discharge of urban and industrial wastes into the Lagos Lagoon have resulted in a significant depletion of its coastal terrain and negative impact on the brackish water [22,23].

Sediment samples were taken from five different Lagos lagoon locations; mid lagoon (ML), University of Lagos (UL), Oworonsoki (OW), Ikoyi (IK) and Oko-baba (OB). Sediments were collected via grab sampler, placed in nylon bags and freeze dried. The sediment samples vary from clayey, sandy and loamy textures. The

sediment samples were decomposed using four different acids and subsequently boiled on a hot plate of about 100°C.

Table 1: The study stations, their coordinates and approximate depth

LOCATION	COORDINATES	APPROXIMATE DEPTH (m)
OWORONSOKI	N 06°32.961'' E 003°24.532''	0.40
OKO BABA	N 06°28.800'' E 003°23.468''	1.25
UNILAG	N06°30'479'' E003°24'024''	1.50
MID LAGOON	N 06°30.770'' E 003°28.212''	4.20
IKOYI	N0628.209 E00323.872	2.40

2.2 Reagents

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 double-distilled water in order to prepare working solution.

2.2.1 Nitric acid digestion method (N)

One gram each of sample was placed in a 250ml conical flask and 10ml HNO₃ was added, the sample was heated for about 45mins. 10ml of HNO₃ was then added and heated at a constant temperature of about 120°C until a clear solution was obtained and the volume was reduced by evaporation to about 5mls. The flask was cooled at room temperature and the mixture was filtered through a 0.45-µ Millipore membrane filter paper transferred quantitatively to a 50ml volumetric flask by adding de-ionized and double-distilled water.

2.2.2 Aqua-regia digestion method (NH)

This method was partly modified from that of ISO 11466 [24]. 1.0 g each of sample was treated with 15 ml HCl and 5 ml HNO₃ (ratio 3:1). The sample was then heated on a hot plate with the temperature gradually increased until decomposition was complete and volume reduced by evaporation to about 5ml. The samples were filtered, washed with de-ionized and double-distilled water, transferred quantitatively to a 50 ml volumetric flask.

2.2.3 Sulphuric acid- Hydrogen peroxide digestion method (SP)

Jones and Case [25]'s approach was adopted. 1g each of sediment sample was weighed into a conical flask. 7ml of concentrated H₂SO₄ was added. The mixture was allowed to stand for 45mins at room temperature. 7ml of 30% H₂O₂ was added to the sample and heated on a hot plate for about 45mins. The mixture was allowed to cool at room temperature and 2ml H₂O₂ was added and the mixture further heated gradually. The mixture was removed when the solution was clear and volume was about 5ml. Following cooling, the mixture was filtered through a 0.45-µ Millipore membrane filter paper transferred quantitatively to a 50ml volumetric flask by adding de-ionized and double-distilled water.

2.2.4 Nitric-perchloric acid digestion method (NP)

One gram each of sample was weighed into a conical flask and 10ml concentrated HNO₃ was added. The mixture was boiled at a constant temperature for about 45mins. After cooling, 5ml of 70% HClO₄ was added and the mixture further boiled to release white fumes. After cooling 20ml distilled water was added and heated until a clear solution was obtained [26]. At room temperature, the mixture was filtered through a 0.45-µ Millipore membrane filter paper transferred quantitatively to a 50ml volumetric flask by adding de-ionized and double-distilled water.

2.3 Quality control

Validation of the method presented in this study was performed by standard reference material from the International Atomic Energy Agency (IAEA-158), analytical quality control services; Vienna, Austria was digested using the four different digestion methods. This was done as a reference for quality control and assurance of the different methods; nitric acid method (SN), aqua regia method (SNH), nitric-perchloric acid method (SNP) and sulphuric acid- hydrogen peroxide method (SSP).

2.4 Instrumentation

An Agilent Atomic Absorption Spectrometer model 240A was used for the determination of all the elements after successive dissolution, decomposition and made up to the 50ml mark in a volumetric flask. Simultaneous background corrections were made using a deuterium lamp.

III. Results and Discussion

Fig. 2 shows percentage recoveries of heavy metals in standard reference material IAEA-158 by four digestion methods described above. The standard deviation of replicated standard samples was less than 2%. The concentrations of heavy metals are expressed as milligram/Kilogram (mg/Kg) of dried sediment. The recoveries of Pb, Zn, Cd, Cu, Cr and Fe ranged from 74-104% for Pb, 88-99% for Zn, 87-123% for Cd, 78-90% for Cu, 95-108% for Cr and 65-108% for Fe. The recovery of Zn and Cu were similar as they are said to have similar behaviours in soil [27] with the lowest percentage recovery of 78-99%. The best recoveries were found in Cd which ranged from 87-123% for the digestion methods. The measured values were within 1% of accepted values.

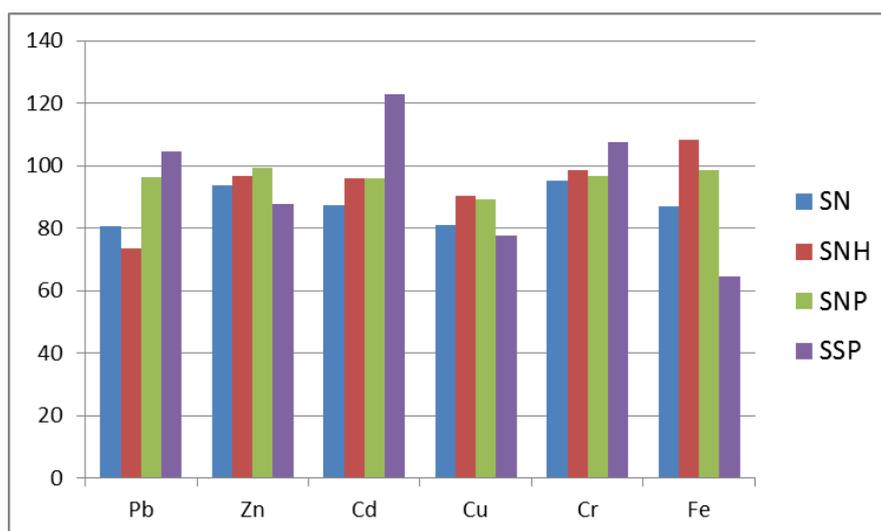


Figure 2: Percentage (%) recovery analysis of heavy metals content in standard reference material

The mean values and standard deviations of the total content of heavy metals in sediment determined by the different digestion methods are shown in Table 2. The data showed levels of heavy metals in sediment at different points of the Lagos lagoon; Mid-lagoon (ML), Unilag (UL), Oworonsoki (OW), Ikoyi (IK) and Oko-Baba (OB).

For Pb, it was observed that the SP acid mixture gave the highest extraction for the entire sampled sites. Although H_2SO_4 has been said to reduce the sensitivity of metal detection since it precipitates metals [12,28,29], the reverse was the case for this study. Simpson et al. [30] reported that in anthropogenically metal contaminated sulphide enriched estuarine sediments, Pb and Zn contaminants might not occur as metal sulphides but metal powder oxides. Stum and Brauner [31] also explained that in oxygenated seawater, Pb occurred predominantly as carbonates of inorganic species. The relative affinity of soil for various heavy metals was said to increase in order $Ni < Zn < Cd < Cu < Cr < Pb$ [27]. This emphasises the effectiveness of the strongest oxidizing acid mixture SP used in this study for the extraction of Pb. NP extraction was the next preferred acid mixture, although the values were lower compared to that of SP acid mixture, its values were higher than that of nitric acid and NH. This shows that for effective release of Pb, the use of a strong oxidizing acid mixture must be employed.

In this study, all sediments decomposed with acid mixture sulphuric acid and hydrogen peroxide (SP) gave good extraction of Cd concentration. Earlier investigation supports the efficiency of SP acid mixture in the determination of Cd, which reveals that Cd bond to acid volatile sulphur can be liberated rapidly as a result of aeration of sediment and elevated oxygen [32,33]. Due to the high oxidizing quality of hydrogen peroxide, Cd is oxidized to soluble $CdSO_4$ during aerobic extraction [34]. Based on this result, aqua regia (NH) predominantly gave a lower extraction in the determination of Cd followed by nitric acid (N) extraction. Zeng et al. [28], presented similar results in the digestion methods for total heavy metals in sediment and soil, which revealed that the total mean Cd content of sediments digested by NH method was lower compared to other acid mixture digestion.

From the plot below (Fig. 3) nitric acid, NH and NP acid mixtures were good for the extraction of Zn. Although all the acid mixtures showed high extraction of Zn concentration from the sampled sites, however, it cannot be clearly determined the method that best determines Zn. Thalita [35] showed that EPA 3050 and EPA 3051A presented the highest recovery of Pb and Zn for most residues. Also Nemati et al. [36] reported that microwave assisted EPA 3015A is most recommended for determination of Zn. Adsorption density of heavy metals is said to increase in order of Pb<Cu<Zn which shows that adsorption behaviour of Cu and Zn is very much similar in terms of maximum adsorption capacity [27]. Morillo et al. [37] reported that Zn metal has the greatest mobility. Large amount of these element are present in the acid soluble fraction.

Table 2: Heavy metal content (mg/kg) in sediment samples by four digestion methods

	Pb	Zn	Cd	Cu	Cr	Fe
MLN	14.035±0.001	104.845±0.0010	3.55±0.0004	22.25±0.0001	7.95±0.0002	1182.5±0.0006
MLNH	2.86±0.0001	39.125±0.0006	2.6±0.0007	38.75±0.0001	7.5±0.0004	1443±0.0009
MLNP	21.87±0.0004	33.66±0.0004	4.3±0.0023	28.5±0.0001	12.35±0.0001	1465.5±0.0004
MLSP	67.535±0.0058	30.38±0.0009	9.1±0.0004	10±0.0001	26.05±0.0001	2601±0.0006
ULN	32.005±0.0005	130.07±0.0014	3.75±0.0003	17.95±0.0002	53.35±0.0001	39010±0.0030
ULNH	30.24±0.0005	140.935±0.0007	4.5±0.0004	19.25±0.0001	62.4±0.0004	40458.5±0.0029
ULNP	46.035±0.0003	148.07±0.0002	5.55±0.0007	21.55±0.0001	68.35±0.0004	41564±0.0024
ULSP	67.94±0.0004	70.43±0.0002	8.45±0.0004	10.15±0.0001	59±0.0002	10091±0.0006
OWN	19.85±0.0006	63.815±0.0005	5.65±0.0005	6.7±0.0001	34.8±0.0003	26047±0.0023
OWNH	19.125±0.0003	113.69±0.0013	4.55±0.0004	13.65±0.0001	48.85±0.0004	36478±0.0019
OWNP	35.435±0.0007	110.455±0.0008	7.05±0.0002	13.35±0.0001	57.2±0.0001	38036±0.0029
OWSP	94.625±0.0002	75.825±0.0008	11.3±0.0006	9.4±0.0001	96.15±0.0002	34510.5±0.0008
IKN	14.83±0.0003	36.135±0.0003	5.25±0.0002	2.2±0.0001	37.4±0.0001	13997±0.0016
IKNH	6.55±0.0013	35.635±0.0003	2.85±0.0037	2.35±0.0001	42.5±0.0001	17091.5±0.0016
IKNP	11.145±0.0022	25.485±0.0002	4.8±0.0001	1.45±0.0001	36.55±0.0003	12555±0.0031
IKSP	79.81±0.0005	30.695±0.0002	9.1±0.0003	2.95±0.0001	57.45±0.0004	10831.5±0.0014
OBN	16.27±0.0005	34.84±0.0007	6±0.0003	1.6±0.0001	39.7±0.0003	19797±0.0018
OBNH	11.255±0.0005	51.78±0.0009	4.05±0.0003	2.15±0.0001	47.35±0.0001	25276.5±0.0017
OBNP	19.525±0.0007	37.33±0.0001	5.75±0.0001	1.7±0.0001	49.95±0.0002	23578±0.0005
OBSP	93.21±0.0003	39.74±0.0003	5.6±0.0015	2.55±0.0001	56.5±0.0003	24297±0.0011

It was observed that the NH acid mixture showed good extraction of Cu for the entire sampled sites. Tayab [27] reported that aqua regia gave higher results because of the solubility of Cl⁻ and NO₃⁻ species. Zeng [38] presented results which correlate to those obtained as he verified that NP and SP acid mixtures were more efficient in the recovery of Cu. Sco [39] explained further that Cu can be leached to achieve 80% recovery using H₂SO₄ which can further be improved to <90% by the addition H₂O₂.

Very high levels of Fe concentration were recorded in all the samples site. Metals are said to be mainly bond in silicate such as feldspar and Fe-Mn micas by replacing Ca²⁺, Fe²⁺ and other cations in the structure [40,41]. This process liberates Fe ions which can easily be extracted. Nitric acid (N) more often showed the least extraction of Fe. WAS [42] reported that Fe may not be fully recovered from some matrix type (example-grains) using nitric acid. Investigation on digestion of organic matrix with nitric acid found that the digestion did not oxidise the organic matrix completely [43,44]. NP has been used for the determination of heavy metals in sediments [37,41]. Higher Fe content was reported by Thalita et al. [35] using nitric- perchloric acid mixture and EPA 3050 (HCl + HNO₃ + H₂O₂). However, to overcome safety issues associated with the use of perchloric acid and lack of recovery of Fe and Al using nitric acid, WAS [42] stated that the use of aqua regia is preferred for total recovery of Fe in plants, however when soil is a part of the sample matrix (contaminant), this method does not recover all the Fe. From the result given, NH predominantly gave a better result for the extraction of Fe in sediments from all the sampled sites.

Due to the relative stable nature of Cr in sediment [27], the use of SP acid mixture was predominantly the most effective for extraction of Cr followed by the NP acid mixture. This confirms results from Thalita et al. [35] work where higher contents of Cr and Fe were recovered when nitric-perchloric acid and EPA 3050 were used in the opening of organic matrices. From the result shown, nitric acid showed the lowest extraction for Cr for most of the sampled sites. WAS [42] stated that nitric acid cannot be used for total recovery of Cr from plant matrix. Schlieckman et al. [45] reported that the use of chloric acid in combination with HF and HNO₃ in the digestion of dust sample at different temperatures lead to loss of Cr through the formation of chromyl chloride at higher temperature.

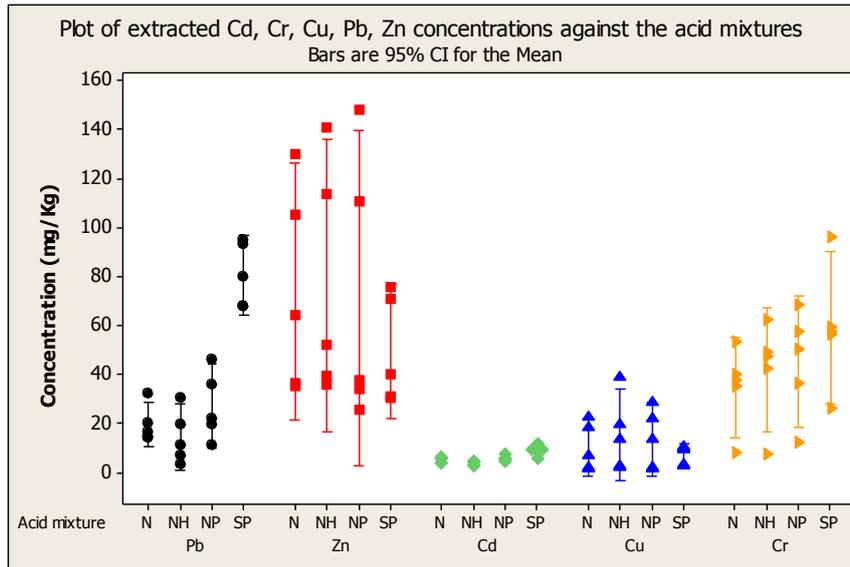


Figure 3: Plot of Pb, Zn, Cd, Cu, Cr extracted concentrations against acid mixtures

Table 3 below shows past works on the efficiency of different acid mixtures for determination of metal concentrations in organic samples using standard reference samples. Abreu et al. [46] showed that NH gave the best recoveries for all metals when compared with the use of NP and N. It was clearly shown that nitric acid containing mixtures gave good results for the recovery of Cu with preference to NH which gave higher percentage recoveries. Fe recovery was seen to follow the same trend with NH being the preferred method followed by NP and N. Sulphuric acid containing mixtures gave good results for recoveries of Cr and Cd, alternatively, NH was shown to also give good percentage recoveries. For the recoveries of Zn and Pb, there were variations in results shown below which ranged from NH to NP with optimal results of recovery.

Table 3: Comparison of acid mixtures for recovery of heavy metals in standard materials
 NH-Aqua regia, N-Nitric acid, NP- Nitric-Perchloric acid, SP- Sulphuric-Hydrogen peroxide, NS-Nitric-Sulphuric acid

	Abreu et al.[46]	Oyeyiola et al.[47]	Badran et al.[48]	Present Study
Cd	NH>NP=N	NH>NS>NP>N	N>NS>NP	SP>NP=NH>N
Cr	NH>NP=N	NS>NH>N>NP	N>NS>NP	SP>NH>NP>N
Cu	NH>NP=N	NH>NS>NP>N	NP>N>NS	NH>NP>N>SP
Pb	NH>NP=N	NP>NH>NS=N	NP>N>NS	SP>NP>N>NH
Zn	NH>NP=N	NH>NS>NP>N	NP>NS>N	NP>NH>N>SP
Fe	NH>NP=N	-	NP>N=NS	NH>NP>N>SP

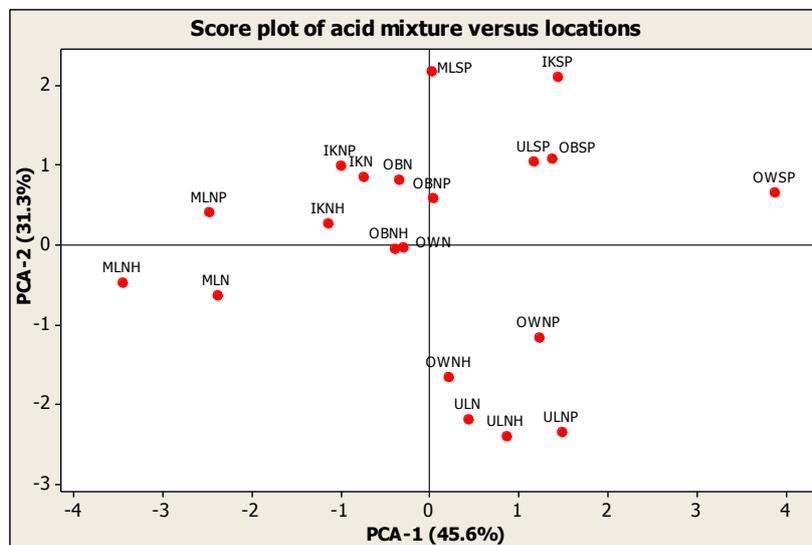


Figure 4: Score Plot of Acid Mixtures versus Locations

The purpose of Principal Component Analysis (PCA) is to reduce a number of observed variables into a relatively smaller number of components. In this present study, PCA was used with the aim of analyzing the extraction efficiency of acid mixtures within the sediments sampled at different locations on Lagos Lagoon. The score plot of the first two components allows for the characterization of the sampling areas according to acid mixtures concentrations. The three principal components (PCs) explained 77.0% of the total variance with the values for PC1, and PC2 of 45.6% and 31.3% respectively. SP acid mixtures exhibited high extraction efficiency of the metals in all the stations, Oko-Baba, Unilag, Mid-lagoon, Ikoyi and Oworonsoki (Fig. 3) and were well differentiated by the higher scores on the first component in the positive part. Sediment samples from Ikoyi and Oko-Baba were separated from other stations in the positive part of the second component suggesting relative good extraction efficiency of acid mixtures NH, NP and N for the regions. Oworonsoki and Unilag sediment samples decomposed by acid mixtures NH, NP and N were clearly separated from other stations in the negative part of the first component suggesting poor/low decomposition (extraction) of metals from sediment of these regions. PC-3 (16.3%) represented NH and N acid mixture in the negative part and NP in the positive part due to geochemical characteristics of sediment from Mid-Lagoon.

The variation of the effectiveness of the different acid mixture used at the different sites could be explained using the soil texture. McLean and Bledsof [49] reported that sandy soil did not retain metal effectively, this correlates with the result given where a less oxidizing reagent NH was gave good results for clayed soil of Mid-lagoon and Oworonsoki which stronger oxidizing mixtures of NP and SP gave better results for clay-loamy soils of Unilag, Ikoyi and Oko-baba.

IV. Recommendation

The SP acid mixture gave the greatest extraction for Pb, Cd and Cr. H_2O_2 and H_2SO_4 are powerful oxidizers and dehydrating agent. The combination of these two have been said to be the most powerful oxidizing reagent for organic matter in sediment [50] (Polley and Miller, 1955). It was shown that the dissolution of Pb, Cd and Cr using NH acid mixture and nitric acid method were mostly lower compared to the SP and NP acid mixture. This was also shown by Stoeppler et al. [43] who found that digestion of organic matrix using nitric acid did not completely digest the organic matrix and also Monika [51] who stated that aqua regia digestion does not obtain the true content of species. NP and NH gave good results and to some extent nitric acid for the extraction of Zn, Fe and Cu. This is in agreement with Griepink [52] work who reported that addition of strong oxidants $HClO_3$ and $HClO_4$ to HNO_3 increases the power of oxidation.

The recoveries of Zn, Cu and Fe in the standard reference material IAEA-158 which ranged from 19-54% were highest using NP for Zn extraction; NH for Fe and Cu extraction. This indicates that these acid digestion mixtures were not efficient for the extraction of Zn, Cu and Fe. Studies have shown that HF has been used for extraction of heavy metals in sediments and soil because it bonds with silicate to form SiF_4 enabling total digestion [28,29,53,54], however Atgin et al. [55] pointed out that HF can result in damage of the FAAS apparatus. According to Garcia et al. [54], microwave digestion with HF can decrease the recovery of some chemical element due to the formation of calcium fluoro-aluminates or precipitate calcium. Also the PTFE material used in HF digestion is expensive and when used repeatedly, the seemingly stable inert vessel may gradually increase its surface area (cracks) into which part of the digest diffuses losses and memory effect [52].

V. Conclusion

The choice of extractants should depend on the aim of the study, type of contaminants, properties of the extractants and experimental conditions. Unfortunately, there was no digestion method which was widely efficient in the extraction of all the metals. This is due to the differing characteristic of each metal in sediment. The advantages of safety, short digestion time, less acid consumption, and high extraction efficiencies should be put into consideration in heavy metal determination. For every metal a possible optimal digestion technique has been recommended. Most of the sediment samples analysed showed that SP acid mixture was efficient for the determination of Pb, Cd and Cr. NP, NH and also nitric acid mixture are recommended for the qualitative determination of Zn, Cu and Fe. However perchloric acid may cause severe explosion if used with large amount of oxidizable matter. It is recommended to use this acid to complete digestion by adding in later stage of digestion.

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