

Comparison of Three Methods of Digestion for Trace Metal Analysis in Surface Dust Collected from an E-waste Recycling Site

Ehi-Eromosele C.O.^{1,*}, Adaramodu A.A.², Anake W.U.¹, Ajanaku C.O.¹, Edobor-Osoh, A.¹

¹Department of Chemistry, Covenant University, P.M.B. 1023 Ota, Nigeria

²Department of Chemistry, University of Lagos, Nigeria

cyril_720@yahoo.com

Abstract: The recycling of e-waste materials potentially contaminates the environment with heavy metals. Analysing the exact contents of heavy metal in e-waste products is germane for the routine monitoring, risk assessment and regulation of the environment. Therefore, the efficiency of three methods of digestion was evaluated for Cd, Fe, Pb, Cr and Zn by AAS in surface dust from an e-waste recycling site and to recommend the most efficient digestion method. The digestion methods were aqua regia, dry ashing followed by aqua regia and nitric acid digestion followed by extraction with HCl. Analysis of variance, Student's t-test and F-test were performed separately for the indoor, outdoor and control dust samples analytical result. Analytical results indicated that the nitric acid digestion followed by extraction with HCl was the most efficient in recovering Pb and Fe based on recovery efficiency. Aqua regia was found to be an alternative method for recovering Pb and Fe based on cost and time effectiveness. Aqua regia was the most efficient in recovering Zn while aqua regia and nitric acid digestion followed by extraction with HCl were satisfactory for the recovery of Cd. Dry ashing followed by aqua regia was found unsuitable for the analysis of these metals in the samples because it recovers relatively little heavy metals and more analysis time.

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1. Introduction

Electronic waste or e-waste products contain intricate blends of plastics and chemicals, which when not properly handled can be harmful to people and the environment (Leung et al., 2006). The composition of e-waste is very diverse and differs in products across different categories. It contains more than 1000 different substances, which fall under 'hazardous' and 'non-hazardous' categories. The presence of elements like lead, mercury, arsenic, cadmium, selenium and hexavalent chromium and flame retardants beyond threshold quantities in e-waste classifies them as hazardous waste (<http://www.cpcb.nic.in>). Consequently, exactly analyzing the contents of heavy metal in e-waste is very important for the routine monitoring and risk assessment and regulation of environment. The level of heavy metal concentration in e-waste may be evaluated from the level of dust deposition per unit area and metal concentrations in the deposit (Krolak, 2000). This is because most e-wastes often contain dust particles embedded within their various components and as such poses health risks when dismantled and piled up in stores without proper disposal.

Low concentrations of trace metals, particularly in geological and environmental samples require pre-concentration prior to detection. The problem of

choosing the procedure for the digestion of the examined samples remains a fundamental one in spite of the huge amount of work done to develop accurate methods for the determination of trace metals in different materials (Maria, 2002). The effect of the sample preparation steps on the quality of the analytical result is universally recognized. The application of an appropriate digestion procedure and its effective combination with the separation and detection methods are of major importance in the analysis of trace metals samples (Maria, 2002).

Many techniques employed for elemental analysis require the conversion of the sample matrix into a solution form (Twyman, 2005). The ultimate choice of decomposition method is influenced by the amount of sample available, the nature of the sample, the sample matrix and the analysis time available (Adelolu, 1989). The approaches for destroying organic material and dissolving heavy metals fall into two groups-wet digestion by acid mixtures prior to elemental analysis and dry ashing, followed by acid dissolution of the ash (Zarcinas et al., 1987; Hseu, 2004). Concentrated acids such as HNO₃, HCl, H₂SO₄, and HClO₄ as well as dual or triple mixtures of them with or without other oxidants (e.g. H₂O₂) have been used extensively for such purposes (Maria, 2002; Hseu, 2004; Zachariadis et al., 1995; Ming and Lena,

1998; USEPA, 1996). Also, many efficient dry ashing methods have been developed and applied to soil sample analysis. These sample preparation techniques for total metal analysis can require several hours, or even several days, to complete. They use acid digestion and thermal decomposition steps, which can result in analyte losses, incomplete recoveries, and/or sample contamination (Smith, 1994; Smith and Arsenault, 1996). These limitations are well known to the analytical community and to end users of these methods (Binstock, 1991).

Though a lot of digestion methods have been published for trace metal analysis in soil samples, no one method has been found to be efficient in recovering all the heavy metals. Analytical Laboratories are particularly interested in reproducible and absolutely efficient digestion techniques for sample treatment prior to analysis (Zachariadis et al., 1995). Hence, over the years, research has been geared towards finding efficient digestion techniques for different sample types. This has been mainly achieved by modifying existing digestion techniques. Therefore, the aims of this study are to (1) evaluate the contents of Cd, Cr, Fe, Pb and Zn in surface dust from an e-waste site using different digestion methods; and (2) recommend the most appropriate digestion method for determining the five heavy metals in surface dust from an e-waste site.

2. Material and Methods

2.1. Study Area

Westminster Electronic Market is situated in Apapa Local Government Area of Lagos, Nigeria, close to the Lagos Tincan Island Port. Its location has made it an attractive point for disembarking and selling Used Electrical and Electronic Equipment (UEEE). The market has about 300 outlets where all types of UEEE are sold. Additionally, the market also has large storing facilities, which make it a big hub for storing UEEE before being redistributed to other markets or exported to neighbouring countries (Odeyingbo, 2011).

2.2. Sample Collection and Preparation

Three categories of dust samples were randomly collected between November 2010 and January 2011 during the dry season, when the prevalence of dust was expected to be high. Dust samples were collected from the surfaces of printed circuit boards, plastic casings, cathode ray tubes and other internal and external components of e-waste across different stores within the market by careful brushing with plastic brushes into plastic containers. This was tagged indoor dust. Surface dust was collected randomly from bare ground across the market area outside the workshops. This was tagged Outdoor dust. Surface dust was also collected 100 meters away from the market area where

heavy metal contribution from e-waste is likely not to be present. The samples were homogenized and mixed. This was used as the control sample. Each representative sample was stored in polyethylene bags which had been previously treated overnight with dilute HNO₃. They were then placed in desiccators to get rid of moisture and ground into fine powder. Dry samples were sieved with 0.125mm sieve and homogenized. This particle size range was chosen to facilitate comparison of heavy metal concentration with soil guidelines.

2.3. Digestion Methods

2.3.1. Method A: Hot Plate Aqua-regia Digestion

1g of a well homogenized sample obtained from sample preparation procedure above was weighed into a Kjeldahl flask and 12ml of freshly prepared aqua regia (3ml HNO₃ + 9ml HCl i.e. ratio 1:3) was added. The beaker was covered and the contents heated for 2 hours on the medium heat of a hot plate. The mixture was allowed to cool and then filtered through a Whatman No. 42 filter paper into a 50ml standard volumetric flask. The filtrate was diluted to 50ml with de-ionized distilled water. Blank solutions were also prepared.

2.3.2. Method B: Dry Ashing Followed By Aqua-regia Digestion

1g of each dust samples were accurately weighed into different crucibles and placed inside a Vecstar Furnace (serial No. F191600, model- LF3, 250V, 13A, 3000W) and ashed at 460°C for 12 hours. The ash was digested in a 12ml freshly prepared aqua regia solution on a hot plate within a fume cupboard for 2 hours. The digests were transferred into clean centrifuge bottles and placed inside a centrifuge which was set at 3000 revolutions per minute for 15 minutes. The mixture was finally transferred into a 50ml standard volumetric flask and filtered through a Whatman No. 42 filter paper. The filtrate was made up to mark with 10% HNO₃. The procedure was repeated and blank was also prepared.

2.3.3. Method C: Digestion with HNO₃ followed by Extraction with HCl

1g of each dust sample was accurately weighed into a 250ml Kjeldahl flask and 3ml of concentrated Nitric acid was added. It was evaporated to dryness without allowing it to boil. After cooling, another 3ml of nitric acid was added and placed on a hot plate with the flask covered with a wash glass. The temperature was increased until a gentle reflux action was taking place. Heating was continued until the digestion was complete which is indicated by a light coloured residue. 15ml of 1:1 HCl/Nitric acid was added and the beaker again gently heated for 15 minutes. The

wash glass and flask were washed down with de-ionized water into a Whatman No. 42 filter paper and filtered into a 50ml volumetric flask. The filtrate was made up to mark with de-ionized water. Blank solutions were also prepared.

2.4. Heavy Metal Analysis

The concentrations of Pb, Cd, Fe, Cr and Zn in the final solutions after the digestions of the indoor, outdoor and control dust samples were determined by an atomic absorption spectrometer (AAS) (Perkin Elmer 1100).

3. Results

Table 1 illustrates the mean concentration (from four sub-samples) of the elements determined in indoor dust, outdoor dust and control dust samples expressed in mgKg^{-1} . The mean heavy metal concentrations in indoor dusts were higher than that of dust collected from the outdoor environment and control dust. This is due to the interaction between e-waste and dust deposited on them over time (Adaramodu, et al., 2011). The results of the three methods of digestion showed large standard deviations indicating the highly heterogeneous nature of the dust samples. Generally, concentrations of heavy metals in control dust were relatively lower than the rest (indoor and outdoor) with the three methods of digestion, indicating less impact of heavy metal pollution activities within the area. Method B gave the lowest results for all the heavy metals analysed in the three samples except for chromium in outdoor dust sample. 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). Katz et al (1981) obtained low

recoveries with dry ashing in comparison with other methods of digestion. Method B also gave the lowest precision of the three digestion methods used; signaling it's unsuitability for the analysis of these heavy metals in the samples studied.

3.1. Statistical Analysis

Significant differences between concentrations of heavy metals, following different digestion methods were analyzed by ANOVA (table 2). Statistical significance was defined as $p < 0.05$. The one-way ANOVA showed sufficient evidence to conclude at the 95% confidence level that the means of the three digestion methods for the three samples analysed were not equal except for Cr in the outdoor sample. However, results of the Student's t-test for the significance of differences of the mean values obtained between methods A and B, and methods C and A at a probability level of 95% ($t_{\text{critical}} = 3.18$) showed no difference for most metals analysed in the three samples. Table 3 lists the mean values obtained from methods C and B, the pooled standard deviation of both of them, the calculated $t_{\text{experiment}}$, and the result of the t-test against $t_{\text{critical}} = 3.18$ (95% probability level). In comparison with method B, method C gave significantly higher recoveries in cases of lead, iron and zinc in both the indoor and control samples. Only for cadmium in indoor sample; iron, chromium and zinc in outdoor sample; and zinc in control sample the results didn't differ significantly at this probability level. Table 4(a – c) shows the comparison of the precision of the three methods using F-test (one-sided test) at 95% probability level. In comparison with method B and C, method A gave better precision for most of the metals analysed in the three samples while method B gave the lowest.

Table 1: Results of the concentration of Pb, Cd, Fe, Cr and Zn in mgKg^{-1} found in indoor, outdoor and control dust samples using the three different methods of digestion. The results are the mean values calculated from four replicate measurement of each sample for the different metals.

	INDOOR DUST			OUTDOOR DUST			CONTROL DUST		
	Methods								
	A	B	C	A	B	C	A	B	C
Pb	22.5	9.3	27	15.9	6.4	21.3	9.4	4.7	10.5
Cd	1.8	0.5	1.25	1.9	ND*	1.9	ND	ND	ND
Fe	108	103.3	131	103.3	74.7	106.5	62	12.3	65
Cr	0.35	ND	ND	0.1	2	0.3	ND	ND	ND
Zn	295.5	231	63.5	213	142.5	184	78	63.5	63.5

* Not Detected

Table 2 indicated a one-way analysis of the variances (ANOVA) for comparing methods A, B and C for the heavy metals analysed in the three samples. The between-treatment (BT) represents the three different digestion methods while the within-treatment (WT) represents the replicate measurements of each method. The F-experimental values should be compared to F-critical values for 2x9 degrees of freedom. The F-critical values for $P = 0.05$ (95%) is 4.26 and the result of the hypothesis if the variations differ significantly is expressed by yes or no.

Table 2. A one-way analysis of the variances (ANOVA) for comparing methods A, B and C for the heavy metals analysed in the three samples.

Metal	Source of Variation	Indoor Dust F- 95% Experimental value	Outdoor Dust F- 95% Experimental value	Control Dust F- 95% Experimental value
Pb	BT/WT	56.99	42.71	12.65
Cd	BT/WT	9.47	-	-
Fe	BT/WT	10.45	5.39	375.59
Cr	BT/WT	-	2.91	No
Zn	BT/WT	129.77	120.15	52.9

Table 3. Results of the Student's t-test for the significance of differences of the mean values between methods C and B at a probability level of 95% ($t_{critical} = 3.18$)

	Element	Mean Method CMg/kg	of Mean Method BMg/kg	of Pooled s	t-value	Significant difference
Indoor Dust sample	Pb	27	9.3	1.77	14.14	Yes
	Cd	1.25	0.5	0.72	1.47	No
	Fe	131	103.3	11.18	3.50	Yes
	Cr	-	-	-	-	-
	Zn	63.5	231	25.74	86.44	Yes
Outdoor Dust sample	Pb	21.3	6.4	5.93	3.55	Yes
	Cd	-	-	-	-	-
	Fe	106.5	74.7	14.21	3.16	No
	Cr	0.3	2.0	1.58	1.52	No
	Zn	184	142.5	54.71	1.07	No
Control Dust sample	Pb	10.5	4.7	1.12	7.32	Yes
	Cd	-	-	-	-	-
	Fe	65	12.3	8.25	9.03	Yes
	Cr	-	-	-	-	-
	Zn	63.5	63.5	7.91	0	No

Table 4(a-c). The comparison of the precision of the three methods using F-test (one-sided test) at 95% probability level. The F-experimental values should be compared to the F-critical values for 3x3 degrees of freedom. The F-critical values for P = 0.05 (95%) is 9.28 and the result of the hypothesis if the variances differ significantly is expressed by yes or no.

(a) INDOOR DUST SAMPLE

	Method AxB F-value	95%	Comment	Method BxC F-value	95%	Comment	Method AxC F-value	95%	Comment
Pb	5.14	No	-	1.78	No	-	2.89	No	-
Cd	25	Yes	Method A more precise	25	Yes	Method C more precise	1	No	-
Fe	11.11	Yes	Method A more precise	9	No	-	100	Yes	Method A more precise
Cr	-	-	-	-	-	-	-	-	-
Zn	1225	Yes	Method A more precise	12.25	Yes	Method C more precise	100	Yes	Method A more precise

(b) OUTDOOR DUST SAMPLE

	Method AxB F-value	95%	Comment	Method BxC F-value	95%	Comment	Method AxC F-value	95%	Comment
Pb	4.84	No	-	10.24	Yes	Method B more precise	2.12	No	-

Cd	-	-	-	-	-	-	2.25	No	-
Fe	178	Yes	Method A more precise	100	Yes	Method C more precise	1.78	No	-
Cr	1.78	No	-	4	No	-	2.25	No	-
Zn	10.30	Yes	Method A more precise	3.89	No	-	2.65	No	-

(c) CONTROL DUST SAMPLE

	Method AxB F-value	95%	Comment	Method BxC F-value	95%	Comment	Method AxC F-value	95%	Comment
Pb	21.78	Yes	Method B more precise	9	No	-	196	Yes	Method C more precise
Cd	-	-	-	-	-	-	-	-	-
Fe	1.83	No	-	1.13	No	-	2.07	No	-
Cr	-	-	-	-	-	-	-	-	-
Zn	100	Yes	Method A more precise	4	No	-	25	Yes	Method A more precise

3.2. Comparison of the Digestion Methods

Method C showed higher mean lead concentration than method A for the three samples analysed. The Student's t-test showed no significant difference ($p < 0.05$) in terms of the recovery of lead from the three samples using both methods. The comparison of the precision of both methods in the analysis of the three samples also showed no significant difference in their variances except for the control dust sample where method C was found to be more precise than method A. Hence, Digestion with nitric acid followed by Extraction with HCl (method C) was found most suitable for the analysis of lead in the three samples. Sastre et al. (2002) stated that nitric acid digestion was an optimum method for estimating heavy metal content in soil samples with high organic matter content, being superior to microwave-assisted and aqua regia digestions.

The higher mean cadmium concentration (1.9mg/kg) recorded in outdoor dust indicates a high contamination of cadmium outside the stores. This might be due to e-waste dumping and dismantling within the environment. Cadmium wasn't detected in the control dust sample. In comparison with method C, method A recorded higher mean cadmium concentration in the indoor dust but gave the same mean concentration in the outdoor dust sample. There was a significant difference ($p < 0.05$) in terms of the recovery of cadmium in the indoor dust sample between methods A and C and no significant difference in the outdoor dust sample. The comparison of the precision of both methods in the analysis of the three samples for cadmium also showed no significant difference in their variances.

Method C gave the highest recovery for Fe than the other two methods in the three samples. The high concentration of Fe in the samples maybe due to the huge amount of Fe found in electronics. There was

no significant difference ($p < 0.05$) in mean concentrations of Fe in the three samples using methods A and C. There was also no significant difference in their variances except for the indoor dust sample where method A was found to be more precise.

The mean Cr concentration in the samples was generally low and was undetected in the control dust sample with the three digestion methods and in the indoor dust sample with method B and C. This might be due to the fact that Cr is present in small amount in e-waste and also in nature. There was no significant difference in mean concentrations of Cr and in their variances in the outdoor dust sample using methods A and C. Method B gave the highest mean Cr concentration in the outdoor dust sample. Zeng-Yei Hseu (2004) reported the highest Cr recovery by dry ashing method for different composts when compared with other methods. It is worthy to note that the duration of the ashing used was far less than the one used in this experiment. Morales et al. (1989) obtained greater values for Cr by USEPA method 3051 than by the dry ashing method for sewage sludge samples. Further Cr analysis in these samples is required.

Zn was the most abundant of the heavy metals in the dust samples. This might be due to the presence of Zn in metal casings and also because of the low melting point of Zinc. Overall, method A gave highest recoveries of Zn. There was a significant difference in mean concentrations of Zn in the indoor and control dust samples using methods A and C. In comparison with method B and C, method A gave better precision for Zn in all three samples.

4.0. Conclusion

Digestion with nitric acid followed by Extraction with HCl (method C) was found most

suitable for the analysis of lead and iron in the three samples. Aqua regia (method A) could also be used reproducibly for these metals in the samples. Methods A and C could be used reproducibly for the efficient recovery of Cd in the samples. Method A was the most efficient method for recovering Zn in the samples. Dry ashing followed by aqua regia digestion gave the lowest recovery for all the heavy metals analysed except for Cr in outdoor dust sample. Further investigation would be carried out with the dry ashing method mostly in the area of reducing the ashing period. In summary, method C is recommended as the method for digesting surface dust in the recovery of Pb and Fe from e-waste site based on recovery efficiency. Method A with comparable cost and time effectiveness with method C can be used as an alternative in the pretreatment analysis of Pb and Fe. Method A is recommended as the method for recovering Zn in these samples while methods A and C are the recommended methods for the recovery of Cd in the samples. Method B is not recommended for the analysis of these heavy metals in the samples because of its little recovery and longer analysis time.

Corresponding Author:

Ehi-Eromosele C.O
Department of Chemistry
Covenant University
P.MB. 1023, Ota, Nigeria
E-mail: cyril_720@yahoo.com

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