Elemental Analysis of Discarded Printed Circuit Boards using Different Analytical Techniques and Recovery of Silver

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Received: 16.6.2024, Revised: 21.7.2024, Accepted: 22.7.2024

Abstract:
The rapid advancement of technology and the demands of our consumer-driven society significantly contribute to the growing volume of e-waste generated annually. This category includes all discarded components and products from electronic and electrical equipment that are not intended for reuse. Among these, Printed Circuit Boards (PCBs) are essential elements in all electrical and electronic devices and are difficult to reuse or recycle considering the complex structure of PCB. This study focuses on analyzing PCBs for their elemental content and the recovery of precious metal, silver. Elemental concentration was analysed using Neutron Activation Analysis (NAA), nano-colorimetry, potentiometry and Atomic Absorption Spectrometry(AAS) techniques .The findings reveal that Non -metallic part in analysed PCBs is about 80-84 % while among metallic concentrations, copper concentration was found to be highest (42.88-90.80 mg/g) and that of lead lowest (0.26-0.75mg/g).The total amount of silver in three PCB samples is approximately 2 mg/g, with a recovery rate was about 66%. However, the fourth sample contains a lower total amount of silver, with a recovery rate of 52.79%.

Key words:
E-waste ,PCB, recovery of silver, NAA, Potentiometry, nano-colorimetry

Introduction:

Electronic waste (E-waste) is produced when electronic devices are disposed of once they reach the end of their operational life. The rapid advancement of technology and our consumption-oriented culture contribute significantly to the rising volume of e-waste generated annually. This category includes all discarded components and products from electronic and electrical equipment (EEE) that were not designed for reutilization[1] Printed Circuit Boards (PCBs) are essential components in all electrical and electronic devices. The materials in PCBs can be

 DOI: 10.59143/isas.jisas.3.1.DKBG9369

broadly classified into Metallic Fractions and Non-metallic Fractions. From a recycling perspective, PCBs are particularly valuable due to their metal content, which is typically over 28-30% [2,3].PCBs are varied and intricate regarding their types, sizes, shapes, components, and compositions. Furthermore, as technology advances, the composition of PCBs continuously evolves, complicating the achievement of consistent material compositions. The intricate mix of plastics, ceramics, and metals in PCBs makes the process of liberating and separating each component highly challenging. Metals within PCBs include numerous base and rare earth metals, as well as hazardous metals [4,5] Traditionally, valuable metals are reclaimed from waste printed circuit boards (WPCBs) through hydrometallurgy and pyrometallurgy methods. This involves primary leaching using substances like aqua regia or various acids. Electronic waste, or electro-waste, is rich in valuable metals such as copper, silver, palladium, nickel, aluminium, zinc, gold, iron, lead, among others [6-8]

Discarded PCBs are a treasure trove of valuable materials, interspersed with plastics and various other components. By meticulously analyzing their composition, we can innovate more efficient and effective methods to extract these precious resources. This not only minimizes our dependence on costly virgin materials but also significantly lowers the environmental impact associated with their mining and processing.Improper disposal of PCBs poses a severe threat, as they can release harmful chemicals into the environment, leading to soil and water contamination. Through detailed analysis of the materials in PCBs, researchers can identify these environmental hazards and develop strategies to mitigate them. This paves the way for safer and more sustainable recycling practices for e-waste, safeguarding both our ecosystems and public health.

Present work deals with the elemental analysis of discarded printed circuit boards and recovery of precious metal: Ag. For this different analytical techniques such as Neutron Activation Analysis, Nano-colorimetry, potentiometry and Atomic Absorption Spectrometry were used.

Experimental:

Printed circuit boards were collected from discarded computer equipments like hard disc, mother board, other cards etc. from computer hardware shop and scrap market. These were then broken down in smaller pieces of 1cm x 1cm dimension, by using plyer. Each piece was weighed and then digested by using aqua-regia to analyse the metal concentration. By maintaining waste to aqua-regia ratio 1:1.5 for 3 h at 100 ^{o}C. After digestion solution was filtered by using Whatman filter paper no. 1. The whole solution was kept in refrigerator for

hastening crystal formation of silver chloride. Crystals were separated by filtering the solution through Whatman filter paper no.42 Filtrate was diluted to 250 ml for further experiments.

Elemental analysis of Printed circuit boards

Silver metal in PCBs was estimated by Neutron Activation Analysis (NAA) while other metals by nano-colorimetry. NAA is a non-destructive technique which was used for determination of silver in various matrices [9-11].

Silver estimation using NAA

The quantitative determination of Silver in PCB samples was done by NAA technique using Cf-252 neutron source available in department of chemistry, University of Pune. The neutron flux of the source determined by standard method was found to be ~ 10^6 n cm^{-2} s^{-1}. The arrangement of facility is such a way that it gives uniform geometry of flux at the position of irradiation. One can irradiate 18 samples simultaneously, 6 in the inner core and 12 in the outer core. The flux of inner core being 1.6 times greater than the outer. It is to be noted that all the irradiations were done in the inner core.

The activity of ^{108}Ag formed after irradiation was measured using NaI (Tl) detector coupled to single channel analyser. The activity at the end of the irradiation was calculated using the half -life of silver-108 and time lapse between the end of irradiation and the time of counting. The activity in terms of counts per 30 sec for silver was used to calculate amount of element in the sample.

The induced Activity is given by following equation

$$A_t = W \times L \times r \times \phi \times \sigma \times (1-e^{-\lambda t}) / M \times 100 \quad (1)$$

Where,

W = Weight of the element, g

L = Avogadro constant, 6.022×10^{23}

ϕ = Neutron flux, n $cm^{-2}s^{-1}$

σ = The capture cross section, cm^2

r = Percentage abundance of the target ,%

λ = Decay constant of the radioactive product formed, $time^{-1}$

t = Time of irradiation, time

A_t = Activity of the nuclide at the end of irradiation, dps

Silver was estimated by comparator method of analysis, wherein sample and standard are irradiated and counted under identical conditions.

Analysis of Aluminium, Copper, Nickel, Zinc and Lead by using Nano-colourimeter (Nano colour 500 D).

The elements Al, Cu, Ni, Zn and Pb were analysed by kits supplied by Nano colour 500 D

Determination of recovered silver from PCB and amount of silver remaining in solution

Weighed recovered silver chloride was dissolved in water by adding 2-3 drops of concentrated HNO_3. This resulted in formation of $AgNO_3$. For calculating the normality of silver nitrate solution, the following cell was constructed for estimation of silver:

$^{+}$ Ag | $AgNO_3$ (0.001M) | KNO_3 Bridge | Recovered $AgNO_3$ | Ag $^{-}$

Potentiometric titration of Recovered silver (silver nitrate) solution was carried out using KI as titrant. The amount of silver in the recovered solution was calculated by plotting EMF versus volume of $AgNO_3$ curve.

Remaining Silver in the solution was determined by using Atomic Absorption Spectrometer (varian sectra AA 220 AAS).

Results and Discussion:

In printed circuit boards many heavy metals are present which has potential to pollute the environment. When PCBs are not treated properly, it pollutes the environment. Therefore, it is essential to analyse the heavy metals in PCBs from which the potential hazard of PCB can be studied. In this work, PCB samples were digested using aqua regia (solid to liquid ratio 1:1.5). In the acid digestion process harmful brominated substances are evolved which were confirmed using starch iodide paper.

Analysis of non- metallic part of printed circuit boards

Fibre optics, ceramics, epoxy resin, brominated flame retardants are the non-metallic parts present in printed circuit boards which is used as base for the metallic part to be installed. In printed circuit boards 70-80 % part is non- metallic[4]. Table 1 shows weight of PCB before and after digestion from which % of non-metallic part was calculated which is about 80-84 %.

Presence of non-metallic part in printed circuit boards depends on the use and manufacturing processes of the printed circuit boards.

Analysis of Cu, Ni, Zn, Al and Pb in PCBs by using nano-colorimeter

The elements Cu, Ni, Zn, Al and Pb in PCBs were estimated with the help of nano-colouimeter using supplied kits. The results are shown in Table 2. Following are the important findings:

- **Copper** : The concentration ranges from 45.28 mg/g to 90.8 mg/g. This is consistent with previously reported amounts of 60 mg/g to 240 mg/g [12,13]
- **Nickel** : The concentration ranges from 7.03 mg/g to 12.49 mg/g, which is higher than the previously reported range of 0.5 mg/g to 2 mg/g [13]
- **Zinc** : Detected for the first time in this study, the concentration ranges from 5.65 mg/g to 9.79 mg/g. There are no previous reports on zinc concentrations in printed circuit boards.
- **Aluminium** : The concentration ranges from 10.03 mg/g to 14.28 mg/g, which falls within the previously reported range of 15 mg/g to 30.1 mg/[13]
- **Lead** : The observed concentration ranges from 0.26 mg/g to 0.75 mg/g, significantly lower than the previously reported range of 20 mg/g to 30 mg/g [13].

The findings reveal that while the concentrations of copper and aluminium align with existing data, nickel levels are elevated, zinc is newly identified, and lead concentrations are significantly reduced. A detailed examination of the data shows that copper concentration in PCBs varies according to design and functionality. High-performance PCB designs necessitate higher copper concentrations. Additionally, the number of layers in a PCB impacts the overall copper levels. In contrast, nickel, zinc, and lead in PCBs are primarily present as solder alloys, with manufacturers optimizing soldering to maintain PCB quality within acceptable ranges, resulting in relatively stable concentrations of these metals across different PCBs. Aluminium is predominantly located in the capacitors of PCBs, leading to consistent concentrations across all samples.

Analysis of silver in PCBs by NAA

PCB samples were analysed by NAA wherein during irradiation of sample, (n,γ) reaction takes place on Ag present in the sample which results in ^{108}Ag. Presence of Ag was confirmed by measuring the half -life of ^{108}Ag by plotting log activity versus time curve, which was found to be 2.27 min confirming the presence of Ag in PCB. Quantitative determination of Ag in the PCB sample and in recovered Ag sample was estimated by comparator method of analysis by

irradiating and counting Ag activity of the sample and standards under identical conditions. The results are shown in Table 3

Estimation of recovered silver by Potentiometry

The recovery of silver from PCBs was determined using a potentiometric method. A graph of electromotive force (e.m.f) versus the added volume of potassium iodide (KI) is shown in Figure 2. From this curve, the amount of silver (Ag) was calculated (Table 3). The results indicate that the amount of silver recovered through potentiometric titration closely matches the results obtained from Neutron Activation Analysis.

The total amount of silver was calculated by combining the recovered silver with the remaining silver in the solution (Table 3). As illustrated in the table, the total amount of silver in the first three PCB samples is approximately 2 mg/g, with a recovery rate of about 66%. However, in the fourth sample, the total amount of silver is lower, with a recovery rate of 52.79%. Silver chloride with low solubility can't be recovered completely, hence % recovery of Ag is less. However, electrolysis method can be used further to recover remaining silver.

Conclusions:

Elemental analysis of discarded PCBs showed presence of Ag, Cu, Ni, Zn , Al and Pb amount of which varies from element to element. In printed circuit boards 80-84 % part is non- metallic. The copper and aluminium concentrations align with existing data while that of nickel concentration is found to be higher than reported. Estimation of zinc is newly reported, and lead concentration is substantially lower. Amount of precious metal, Ag , and its recovery was determined using NAA, Potentiometry and AAS techniques. The total amount of silver in the three PCB samples is approximately 2 mg/g, with a recovery rate of about 66%. However, in the fourth sample, the total amount of silver is lower, with a recovery rate of 52.79%. The results obtained by NAA and potentiometry match well with each other.

Acknowledgement:

Author is thankful to Head, Environmental Science Department and Head, Chemistry Department, SPPU for providing infrastructural facilities. He is grateful to Dr. Nilima Rajurkar, Former Head, Chemistry Department and Environmental Science Department , SPPU for her guidance and cooperation during the work.

Figures:

Fig. 1 Collected printed circuit boards scrap

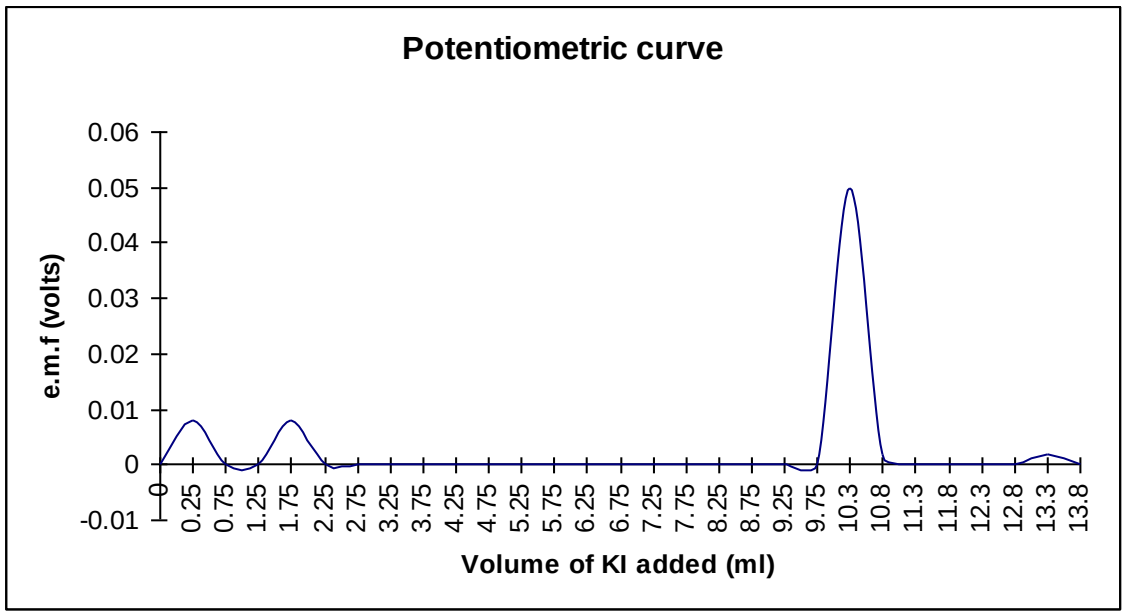

Fig. 2 E.M.F Vs added volume of KI

Tables:

Table 1 Acid digestion of Printed Circuit Boards

Printed circuit boards	Weight of PCB before digestion/g	Weight of PCB after digestion/g	Non- metallic part in PCB %
Sample 1	78.191	62.789	80.31 %
Sample 2	80.457	65.761	81.74 %
Sample 3	84.013	67.371	80.19 %
Sample 4	81.703	68.863	84.73 %

Table 2 Elemental Analysis of Printed Circuit Boards by nano-colourimeter

Printed circuit board	Concentration of metals mg/g				
	Copper	Nickel	Zinc	Aluminum	Lead
Sample 1	90.80	9.59	8.31	10.23	0.75
Sample 2	79.54	11.49	6.18	12.30	0.26
Sample 3	61.89	12.49	5.65	14.28	0.44
Sample 4	45.28	7.04	9.79	10.03	0.27

Table 3 Recovery of silver from Printed Circuit Boards

Printed circuit boards	Recovered silver mg/g (potentiometric analysis)	Recovered silver mg/g (by NAA)	Silver remaining in solution Mg/g	Total Silver mg/g	Recovery of silver %
Sample 1	1.324	1.335	0.6957	2.02	65.54
Sample 2	1.342	1.330	0.6674	2.01	66.76
Sample 3	1.384	1.370	0.613	2.04	67.84
Sample 4	0.717	0.720	0.6413	1.358	52.79

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