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Evaluation of Wet Digestion Methods for Quantification of Metal Content in Electronic Scrap Material

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Abstract: Recent advances in the electronics sector and the short life-span of electronic products have triggered an exponential increase in the generation of electronic waste (E-waste). Effective recycling of E-waste has thus become a serious solid waste management challenge. E-waste management technologies include pyrometallurgy, hydrometallurgy, and bioleaching. Determining the metal content of an E-waste sample is critical in evaluating the efficiency of a metal recovery method in E-waste recycling. However, E-waste is complex and of diverse origins. The lack of a standard digestion method for E-waste has resulted in difficulty in comparing the efficiencies of different metal recovery processes. In this study, several solid digestion protocols including American Society for Testing and Materials (ASTM)-D6357-11, United States Environment Protection Agency Solid Waste (US EPA SW) 846 Method 3050b, ultrasound-assisted, and microwave digestion methods were compared to determine the metal content (Ag, Al, Au, Cu, Fe, Ni, Pb, Pd, Sn, and Zn) of electronic scrap materials (ESM) obtained from two different sources. The highest metal recovery (mg/g of ESM) was obtained using ASTM D6357-11 for most of the metals, which remained mainly bound to silicate fractions, while a microwave-assisted digestion protocol (MWD-2) was more effective in solubilizing Al, Pb, and Sn. The study highlights the need for a judicious selection of digestion protocol, and proposes steps for selecting an effective acid digestion method for ESM.

Keywords: electronic waste; acid digestion; heavy metal; precious metal; metal recovery; sequential extraction

1. Introduction

Rapid industrialization and urbanization have resulted in an exponential increase in the generation of hazardous industrial and municipal solid wastes (MSW) including electronic wastes (E-wastes), fly ash, spent catalyst, and battery wastes [1–3]. According to a report by the World Bank, MSW is generated globally at a rate of 1.3 billion tonnes per year, and is expected to increase to 2.2 billion tonnes annually by 2025 [4]. These solid wastes generally contain mixtures of hazardous chemicals including polymers and heavy metals (such as cadmium, mercury, and lead) [1,5]. Toxic leachates from these wastes pollute groundwater and have detrimental effects on the environment and human health [6,7]. Rapid technological advancement has also resulted in the growing consumption of heavy metals (for instance copper, nickel, zinc, chromium, iron, etc.) in various industries such as automobile, electronics, steel, chemical, and even medicine fields [8]. Such increasing demand has caused massive depletion of natural ore reserves, thus making it extremely crucial to search for alternative sources of these metals. The presence of high concentrations of heavy metals in solid wastes such as E-wastes, fly ash, and spent catalyst have made them attractive secondary sources of metals [2,6,9]. Indeed, metal recovery through such urban mining not only delays the depletion of natural ores, but may provide a sustainable solution to the disposal problems of these hazardous solid wastes [10,11]. Knowledge of the metal contents of the wastes is critical in evaluating the efficiency of metal recovery by different recycling methods such as chemical leaching and bioleaching [12].

The current study evaluates the recovery efficiency of several digestion protocols to determine the metal content in E-wastes, using electronic scrap material (ESM) from printed circuit boards (PCBs) as an example. PCBs are present in electrical and electronics devices such as televisions, computers, and mobile phones. In general, PCBs contain about 40% metals, 30% plastics, and 30% ceramics [13]. Rapid product obsolescence has reduced their effective lifespan, and high market penetration has resulted in the generation of a colossal amount of E-waste [5,14]. The volume of E-waste generated worldwide was nearly 41.8 million tonnes in 2014 and is expected to reach 50 million tonnes annually by 2018 [15]. To tackle the growing menace of E-waste, especially in countries that lack clear legal framework for E-waste collection and recycling, a proper structure for optimized E-waste management is required based on a lifecycle perspective [16]. Studies have shown that E-wastes are loaded with toxic heavy metals such as Al, Cu, Fe, Ni, Pb, Sn, and Zn [6] as well as significant quantities of precious metals such as Au, Ag, and Pt, which makes the recycling of E-wastes economically profitable and environmentally sustainable [17–19]. Unfortunately, different digestion protocols have been adopted for sample preparation, thus rendering it difficult for comparison in metal recovery [11,12,20–24]. A standard acid digestion method is important for evaluating the effectiveness of a metal recovery process. Metals in the waste matrix form soluble metal salts when subjected to oxidative acid digestion reactions [19,25]. Since most of these wastes are heterogeneous in composition, knowledge of the chemical forms of the metals present in the waste matrix is highly important to standardize the digestion protocol.

Using selective extraction reagents, sequential extraction methods (SExM) may be employed to determine the chemical nature of the heavy metals present in the waste matrix [26–28]. During a SExM process, selective liberation of the heavy metals into the solution occurs when different extraction reagents are used. In an SExM process, metal extraction takes place in decreasing order of mobility, with metals of highest mobility being extracted in the very first step of the treatment. In the second step, salt solutions are used through ion-exchange to release ion-exchangeable metal fractions present on the bare surfaces of the solid wastes. In the subsequent step, the carbonate-bound metal fractions are extracted using acidic solution. Following that, metals associated with iron (Fe) and manganese (Mn) oxides are dissolved under reducing conditions, after which metals bound to the organic phase are mobilized by incorporating oxidizing agents to oxidize the organic matter. Finally, the residual fraction would contain metals bound to silicates [29].

Previously, acid digestions were performed in open systems by heating the solid waste with an appropriate acid [19]. Over time, however, other methods such as microwave-assisted digestion and high-pressure bomb digestion have become increasingly adopted due to their higher metal recovery rate [19,20,30,31]. In general, an acid digestion reaction of a solid waste depends on the following factors: the acid used and its concentration, reaction time, external driving forces (heat, ultrasound, agitation, microwave, etc.), reaction conditions (temperature, solid-liquid ratio, etc.), and the chemical form of the metals present in the solid waste matrix [32]. The choice of an acid or acid mixture in digestion is critical and is largely dependent on the nature of the metals present in the waste [29]. In theory, metals associated with carbonates, phosphates, borates, and some oxides and sulphides may be extracted using hydrochloric acid, while nitric acid is applied to release metals from a vast range of metal salts [32]. However, noble metals are not soluble in both hydrochloric acid and nitric acid, and are extracted using aqua regia. Hydrofluoric acid is used to release metals bound to silicate fractions [29]. To improve metal recovery and increase reaction kinetics, oxidizing agents such as hydrogen peroxide are added during the digestion [33].

The current study compares the effectiveness of different wet digestion methods for the solubilization and quantification of metals present in ESM derived from PCBs, in order to select the most effective acid digestion protocol for ESM. In this study, two different batches of ESM obtained from different sources were used to evaluate 11 acid digestion protocols which include the ASTM Method D 6357-11, US EPA (United States Environmental Protection Agency) methods, as well as ultrasound-assisted and microwave digestion methods.

2. Materials and Methods

2.1. Equipment

ESM solid samples were digested on either a hot plate (Thermoscientific, model Cimarec SP Model: 131320-33, Singapore), a Chemical Oxygen Demand (COD) reactor (Rocker, Model: CR25, Linkuo Dist., New Taipei City, Taiwan), an ultrasonic bath (ELMA Model: P30H, Frankfurt, Germany), or a microwave digester (Milestone Microwave Laboratory System MLS-1200 MEGAFour, Sorisole (BG), Italy). To remove moisture and organic compounds, the solid samples were heat-treated in a Carbolite muffle furnace (Model: CWF 110, Hope Valley, UK). Metal concentrations were determined using an Inductively-Coupled Plasma Mass Spectrometer (Agilent 7500a ICP-MS, Singapore).

2.2. Digestion Reagents and Electronic Scrap

The chemicals used were of analytical grade and were obtained from Merck Pte. Ltd. (Singapore,) and Alfa Aesar (Singapore). Reagents used included concentrated nitric acid (conc. HNO_3) (69% w/w), concentrated hydrochloric acid (conc. HCl) (37% w/w), concentrated hydrofluoric acid (conc. HF) (49% w/w), and hydrogen peroxide (H_2O_2) (30% w/w). All glassware and polyethylene flasks were washed with dilute HNO_3 (5% v/v), followed by rinsing with copious amount of deionized water (dH_2O). E-waste samples were provided by Cimelia Resource Recovery Pte. Ltd. (Singapore) and TES-AMM Singapore Pte. Ltd. (Singapore). The dust-like E-waste samples were derived from processed and shredded PCBs. The ESM was ground (using an IKA M20 batch mill, with tungsten carbide blade) to decrease the particle size for more effective acid digestion [23]. The ground ESM particles were sieved to a particle size smaller than 250 μm.

2.3. Characterization of ESM

2.3.1. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX)

SEM analysis provides images of a sample's surface topography, while EDX provides elemental analysis of the sample. Dried ESM samples were transferred onto copper stubs using carbon tapes and were sputter-coated with platinum nanoparticles using a JEOL JFC-1300 Auto Fine Coater under vacuum at 40 mA for 60 s. The morphology of the ESM samples was analyzed using a JEOL JSM-5600LV Scanning Electron Microscope (SEM). Surface elemental composition of the ESM samples was examined using an Energy-dispersive X-ray Spectroscopy (EDX) (OXFORD Instruments 6647). The EDX data were analyzed using INCA Suite Version 4.01.

2.3.2. X-ray Diffraction (XRD)

X-ray diffraction (XRD) of the ESM samples was performed in a SHIMADZU X-ray Diffractometer (XRD-6000, Shimadzu, Kyoto, Japan) to analyze the chemical composition of ESM samples. The diffraction spectra were recorded using Cu radiation (40 kV, 60 mA) over the range of 5–80° (2θ). DIFFRAC.EVA software (Version 2.1, Copyright @ Bruker AXA 2010–2012, Singapore) was used to match the sample peaks with data from the Powder Diffraction File published by The International Centre for Diffraction Data (ICDD).

2.4. Digestion Protocols

2.4.1. US EPA Solid Waste 846 Method 3050 B

This method is commonly used for extracting various metals such as aluminum, antimony, arsenic, barium, beryllium, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silver, sodium, thallium, vanadium, and zinc from solid waste matrix [33]. The reagents used include 1:1 HNO_3-dH_2O mixture (v/v), conc. HNO_3, conc. HCl and H_2O_2, with digestion at 95 ± 5 °C. Although this method is not effective in extracting silicate-bound metals, it has been widely used for digesting various solid wastes such as ashes, sludge, sediments, and soils [34].

This protocol for the digestion of ESM was chosen owing to its popularity (Table S1). Different driving forces affecting the digestion process such as ultrasound and microwave were also evaluated in this study to improve metal recovery.

2.4.2. ASTM D6357-11

This protocol was developed for determining the concentration of trace metals such as antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, gold, lead, manganese, molybdenum, nickel, vanadium, and zinc present in fly ash residues from coal combustion process. The use of this protocol was reported in a study on medical waste incinerator fly ash for metal leachability. With strong reagents (aqua regia and conc. HF) and reaction conditions (ashing at 500 °C and digestion at 150 °C), this method can be effective for the digestion of ESM due to the presence of a high concentration of silicates fraction [34].

2.4.3. Digestion Reactions in Microwave Digesters

All microwave digestion experiments were carried out in a microwave digester (Milestone Microwave Laboratory System MLS-1200 MEGAFour).

- Microwave-Assisted Digestion Method 1 (MWD-1)

The US EPA SW 846 Method 3051a [35] is effective in the solubilization of metals including aluminum, arsenic, barium, cadmium, calcium, chromium, cobalt, copper, iron, and lead. Digestion is conducted at 175 °C (with an initial ramp rate of 20 °C/min) in a microwave digester using conc. nitric acid and hydrochloric acid. This protocol is commonly used for solid wastes with matrices similar to soil and sediments. The US EPA SW 846 Method 3051a requires 0.5 g of the sample in 12 mL of aqua regia with 60 min of digestion.

- Microwave-Assisted Digestion Method 2 (MWD-2)

The US EPA SW 846 Method 3052 [36] is capable of solubilizing all metals extractable using US EPA SW 846 Method 3051a, and is specifically effective in digesting solid waste with matrices containing silicates, organics, and other complex materials. The method employs conc. HNO_3 and conc. HF as digestion reagents to unlock the metals by complete digestion of the solid waste matrix at 180 °C (with an initial ramp rate of 20 °C/min). The US EPA SW 846 Method 3052 requires 0.5 g of the sample in 9 mL of nitric acid and 3 mL of hydrofluoric acid with 60 min of digestion.

- Microwave-Assisted Digestion Method 3 (MWD-3)

This protocol is not a standard digestion method but has been reported in earlier studies for the digestion of fly ash [29,36,37]. In this method, 0.25 g of the ESM sample is kept in Teflon digestion crucibles followed by the sequential addition of 5 mL conc. HNO_3, 3 mL conc. HCl, and 2 mL conc. HF. The ESM sample is digested at 250 °C for 60 min (with an initial ramp rate of 20 °C/min).

2.4.4. Digestion Reactions in an Ultrasonic System

Ultrasound-assisted digestions were performed in an ultrasonic bath (ELMA Model: P30H, Frankfurt, Germany). These non-standard protocols were adopted and specifically tailored to be conducted in an ultrasonic bath. In all the modified protocols, the digestion mixtures were shaken gently once every two minutes for improved digestion efficiency. UD-1 and UD-2 are customized protocols of standard digestion methods for use in an ultrasonic bath. UD-3 and UD-4, however, are non-standard methods, and have been adapted from a previous report on fly ash digestion [29]. Both UD-3 and UD-4 were found to be efficient in solubilizing copper, nickel, lead, and zinc, and hence were extended for digesting ESM samples.

- Ultrasound-Assisted Digestion Method 1 (UD-1)

The current method was employed to determine the elemental composition of ESM samples using a modified US EPA SW 846 Method 3050 B, incorporating an ultrasound-assisted digestion protocol. Briefly, 0.2 g of ESM sample is placed in a 15-mL polypropylene tube, followed by the addition of 2 mL of 1:1 conc. HNO_3:dH_2O (v/v). The mixture is sonicated for 5 min at 60 °C. Then, 3 mL of conc. HNO_3 is added to the digestion mixture and sonicated again at 60 °C for 10 min. Lastly, the digestion mixture is topped up with 2 mL of conc. HCl and sonicated for 5 min at 60 °C, after which the digestion mixture is cooled and diluted to 10 mL with deionized water.

- Ultrasound-Assisted Digestion Method 2 (UD-2)

In this method, ASTM D6357-11 was modified for use in an ultrasonic system. Briefly, 0.5 g of ashed ESM sample is placed in a 50-mL polypropylene tube. Then, 5 mL of aqua regia and 5 mL of conc. HF are added, and the digestion mixture is sonicated for 10 min at 60 °C. Following this, 3 mL of 5% (w/w) nitric acid is added to the digestion mixture and sonicated again for 15 min at 60 °C. The resulting slurry is cooled and diluted to 25 mL with dH_2O.

- Ultrasound-Assisted Digestion Method 3 (UD-3)

In this method, 0.5 g of ESM sample is weighed and placed in a 50-mL polypropylene tube. Then, 15 mL of conc. HNO_3 is added and the digestion mixture is sonicated for 10 min at 60 °C. Following this, 5 mL conc. HF is added to the reaction mixture and the resulting mixture is sonicated again at 60 °C for 10 min. The final digestate is cooled and diluted to 30 mL using dH_2O.

- Ultrasound-Assisted Digestion Method 4 (UD-4)

In this method, 0.5 g of ESM sample is introduced in a 50-mL polypropylene tube. Then, 8 mL of conc. HNO_3 is added and the slurry is sonicated at 60 °C for 10 min. To the reaction mixture, 5 mL conc. HNO_3 and 5 mL conc. HF are added, and the slurry if again sonicated for 10 min at 60 °C. The final digestion mixture is cooled and diluted to 25 mL using dH_2O.

2.4.5. Sequential Extraction Method (SExM)

The Modified Tessier sequential extraction method was employed in this study to determine the various chemical forms of the metals present in ESM [26,28]. The method employs water (step 1), 0.1 M magnesium chloride ($MgCl_2$) (step 2), 0.1 N sodium acetate or acetic acid (step 3), 0.1 N hydroxyl amine hydrochloride (step 4), 2% HNO_3:H_2O_2 and a combination of concentrated nitric acid (step 5), and finally hydrogen peroxide and hydrofluoric acid (3:5:2 mL, % v/v) (step 6) as the extraction reagents in six sequential steps [27,38]. Subsequently, 0.5 g of ESM sample is used and sequentially extracted with 100 mL of each leaching solution for 3 h. Steps 1 to 3 are performed at 25 °C, step 4 is performed at 60 °C, step 5 is carried out at 85 °C, and the final extraction step is completed at 95 °C [27].

2.4.6. Digestion Using Different Acids

ESM samples were digested with different acids and/or combinations of acids including (i) conc. HNO_3, (ii) conc. HCl, (iii) conc. HNO_3 + conc. HCl, (iv) aqua regia, (v) conc. $HNO_3 + H_2O_2$, (vi) conc. HCl + H_2O_2, (vii) conc. HNO_3 + conc. HCl + conc. H_2O_2, (viii) aqua regia + H_2O_2, (ix) conc. HNO_3 + conc. HF, (x) conc. HCl + conc. HF, (xi) conc. HNO_3 + conc. HCl + conc. HF, and (xii) aqua regia + conc. HF. Moreover, 0.25 g of ESM sample was used for each of the acid digestion experiments. With a final working volume of 12 mL, the slurry was heated for 2 h at 60 °C in a water bath. When a combination of two acids were used, the sample was treated for 60 min with the first acid (6 mL) at 60 °C, and then the next acid (6 mL) was added and treated for another 60 min at 60 °C. When a combination of three acids was used, 4 mL of each acid was added sequentially at an interval of 30 min. A final reaction volume of 12 mL was used for the process for all digestion experiments with a total reaction time of 120 min at 60 °C.

2.5. Digestate Analysis

The digestate was centrifuged at 15,000 rpm for 10 min and filtered (45 μm) to remove suspended particulates. The residue after centrifugation was dried and weighed, and the amount of metal solubilized was determined gravimetrically. The metal concentration in digestate liquor collected after filtration was analyzed using ICP-MS (Agilent 7500).

2.6. Loss on Ignition

Three grams of ESM was placed in ceramic capsules and heated at 800 °C in a muffle furnace. The inorganic fraction obtained after the heating contained ceramics and metallic portion of the ESM. The organic fraction was calculated gravimetrically.

2.7. Statistical Analysis

All the experiments were repeated ($n = 3$), and the results are reported as the mean ± standard deviation. Statistical analysis (one-way ANOVA) was done using Microsoft Excel with the level of significance set at $p < 0.05$.

3. Results

3.1. ESM Characterization

3.1.1. Morphology of ESM

SEM micrographs of ESM samples as-received from the two sources (Cimelia Resource Recovery Pte. Ltd. (CRR) and TES-AMM Singapore Pte. Ltd. (TES-AMM)) before digestion are shown in Figure 1a,b. The samples were heterogeneous in nature, with particles of varying sizes, shapes, and textures. Many smooth rod-shaped particles with rough and uneven crystals and flakes were found attached to the surfaces. EDX analyses of the samples from both sources revealed a high concentration of silicon (Figure 1). Apart from gold and copper, the samples contained significant amount of metals such as aluminum, iron, lead, nickel, silver, tin, and zinc. The copper content was lower in the sample from TES-AMM, in comparison to that from CRR.

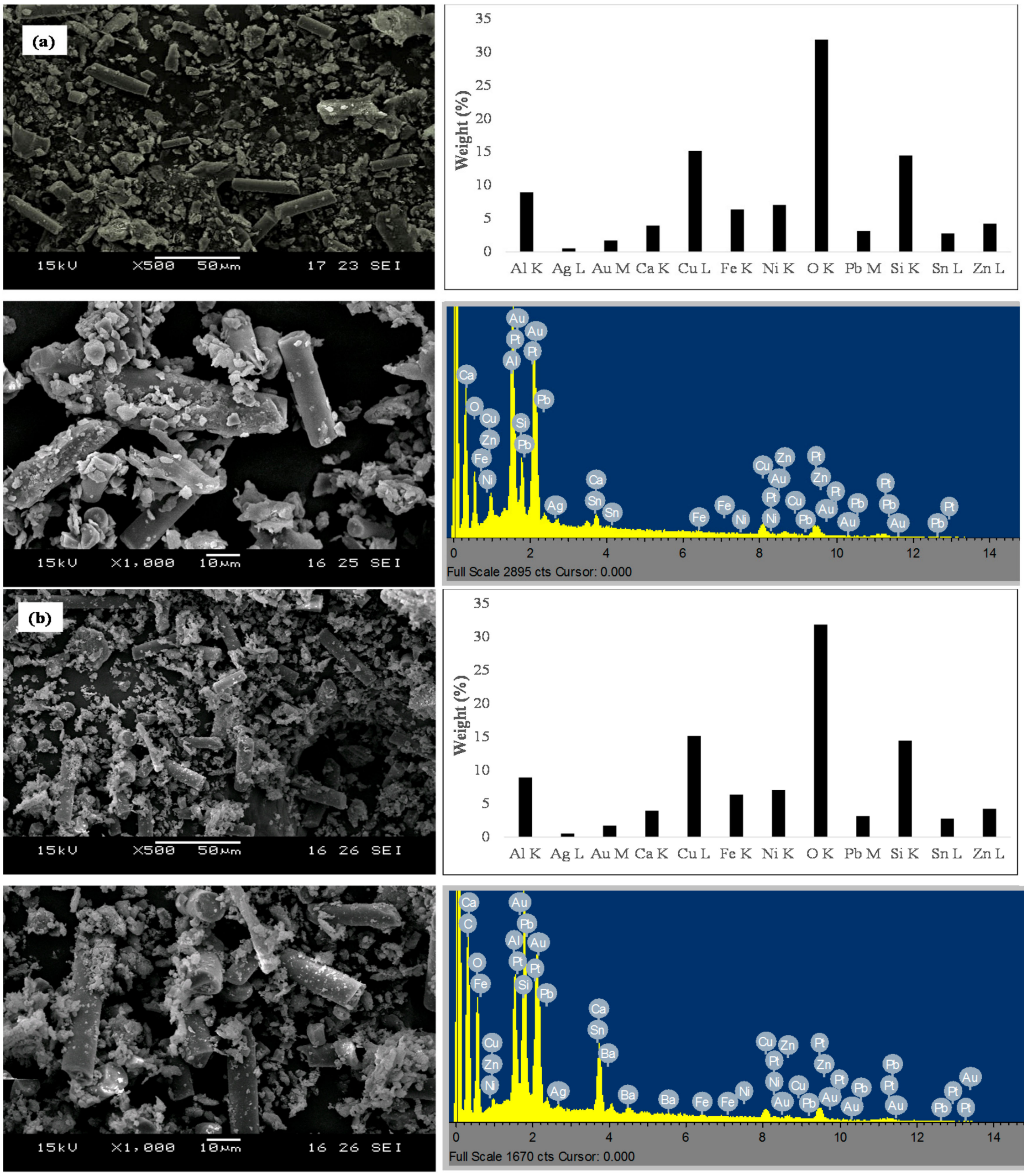

Figure 1. SEM-EDX micrographs of untreated ESM samples obtained from (**a**) TES-AMM and (**b**) CRR.

3.1.2. X-ray Diffraction Analysis (XRD) of ESM

Figure 2 shows the XRD peak analysis of ESM samples from the two different sources. The major elements identified by the semi-quantitative analysis include mainly metals such as copper, lead, tin, zinc, nickel, aluminum, magnesium, and silicon. XRD analyses of both the samples corroborate the EDX analysis; base metals form the major component in the samples.

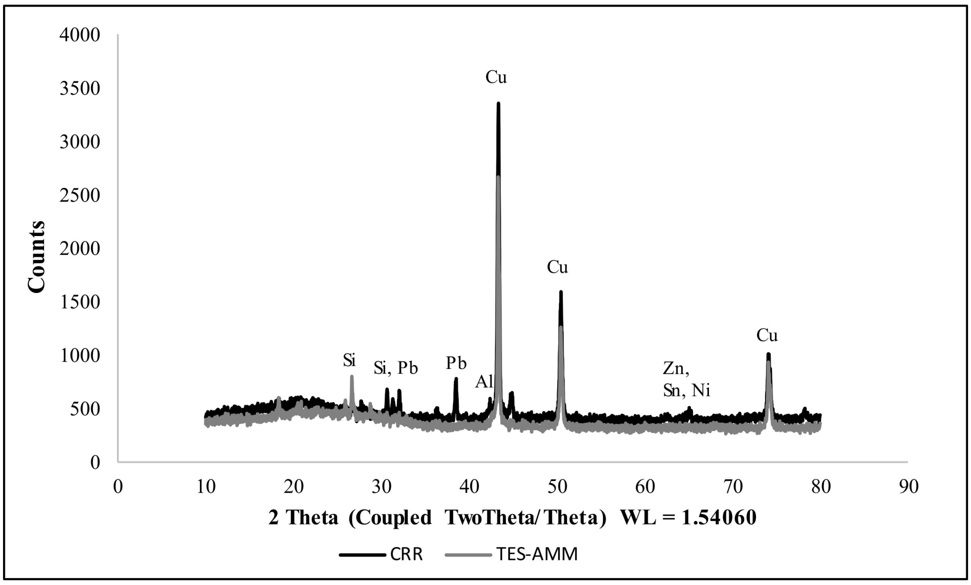

Figure 2. XRD analysis of untreated ESM samples obtained from CRR and TES-AMM.

3.2. Comparison of Elemental Metal Compositions of ESM after Different Acid Digestion Protocols

Elemental composition of the two ESM samples following various acid digestion methods are given in Table 1. For both the ESM samples from different sources, the highest digestion efficiency for Cu, Fe, Ni, Zn, Pd, Au, and Ag was obtained using the ASTM Method D6357-11 while the microwave-assisted digestion Method 2 (MWD-2) was more efficient in solubilizing Pb, Al, and Sn. XRD and SEM-EDX analysis confirmed the presence of a significant amount of silica in both samples (Figures 1 and 2) and is consistent with previous work [17–19]. Both the most effective acid digestion methods utilize conc. hydrofluoric acid (a non-oxidizing acid) along with other acids for solubilizing the metals from the waste matrix. Hydrofluoric acid is efficient in dissolving silicate fractions and its use with other acids in both the methods validated their superior performance for metal recovery over other acid digestion protocols. The heterogeneity in the metal composition in the E-wastes could be attributed to the diverse source of PCBs and the different physical segregation methods employed during E-waste grounding [39].

3.3. Efficacy of Different Acids for Metal Dissolution from ESM

The effectiveness of a digestion method depends largely on the judicious selection of acids for the process and the chemical form of the metals in the substrate. Figure 3 shows the effect of various acids and acid combinations for solubilizing metals from solid waste. Two acid digestion protocols, (i) aqua regia + conc. HF and (ii) conc. HNO_3 + conc. HCl + H_2O_2, were more effective than other combinations in digesting the ESM. Digestion with aqua regia and hydrofluoric acid, when added stepwise, gave the best solubilization of aluminum, copper, gold, lead, nickel, palladium, silver, and zinc ($p < 0.05$) (Figure 3). The highest recovery of iron and tin was observed with the digestion of ESM using the stepwise addition of conc. nitric acid, conc. hydrochloric acid, and hydrogen peroxide ($p < 0.05$) (Figure 3). Digestion with aqua regia and conc. HF resulted in almost 21% higher extraction of Cu, 17% higher recovery of Al and Pb, 14% higher recovery for Zn and Ni, and 10% higher recovery for Ag, Au, and Pd, while digestion with conc. HNO_3 + conc. HCl + H_2O_2 resulted in 12% and 9% higher recovery of Fe and Sn respectively, compared to the next best digestion protocol. Acid combinations with hydrofluoric acid showed higher recovery, which confirmed the effectiveness of ASTM D6357-11 and MWD-2 digestion methods (Table 1). However, the application of hydrofluoric acid singly did not result in significant metal solubilization due to the non-oxidative nature of the acid.

Table 1. Comparison of metal recovery using different acid digestion protocols for ESM.

Sample	**ESM from TES-AMM**									
Method	**Concentration (mg/g)**									
	Ag	**Al**	**Au**	**Cu**	**Fe**	**Ni**	**Pb**	**Pd**	**Sn**	**Zn**
ASTM method D 6257-11	0.89 ± 0.01	33.03 ± 1.22	0.52 ± 0.01	282.41 ± 1.11	14.45 ± 1.42	5.34 ± 0.12	3.89 ± 0.11	0.27 ± 0.01	0.47 ± 0.02	16.46 ± 1.13
US EPA SW 846 Method 3050B	0.78 ± 0.03	30.53 ± 1.53	0.41 ± 0.01	237.13 ± 3.42	11.68 ± 3.12	4.04 ± 0.08	2.31 ± 0.21	0.18 ± 0.03	0.41 ± 0.04	12.93 ± 2.31
MWD-1	0.54 ± 0.01	23.81 ± 0.91	0.31 ± 0.03	221.42 ± 2.44	10.11 ± 1.45	3.28 ± 0.31	2.84 ± 0.08	0.21 ± 0.02	0.32 ± 0.03	9.34 ± 1.12
MWD-2	0.81 ± 0.04	39.11 ± 0.74	0.49 ± 0.02	247.35 ± 3.61	12.56 ± 3.11	4.43 ± 0.23	5.32 ± 0.18	0.24 ± 0.04	0.67 ± 0.01	14.57 ± 1.45
MWD-3	0.73 ± 0.02	23.45 ± 1.32	0.36 ± 0.01	251.67 ± 3.15	11.32 ± 1.45	4.74 ± 0.34	2.46 ± 0.13	0.23 ± 0.05	0.53 ± 0.03	11.54 ± 1.23
UD-1	0.67 ± 0.01	19.89 ± 0.65	0.38 ± 0.02	256.41 ± 1.52	10.11 ± 2.12	4.37 ± 0.31	4.11 ± 0.19	0.16 ± 0.02	0.55 ± 0.04	13.45 ± 2.34
UD-2	0.57 ± 0.01	10.95 ± 0.21	0.37 ± 0.02	247.38 ± 5.46	12.56 ± 1.22	4.42 ± 0.41	4.02 ± 0.14	0.25 ± 0.04	0.51 ± 0.06	11.79 ± 1.87
UD-3	0.73 ± 0.04	19.59 ± 1.15	0.38 ± 0.04	251.44 ± 3.82	10.62 ± 2.42	4.25 ± 0.12	3.89 ± 0.07	0.15 ± 0.01	0.51 ± 0.07	11.84 ± 2.09
UD-4	0.61 ± 0.05	13.52 ± 1.46	0.36 ± 0.03	210.78 ± 2.61	9.56 ± 1.78	3.66 ± 0.37	4.95 ± 0.11	0.13 ± 0.02	0.53 ± 0.03	10.78 ± 2.34
Sample	**ESM from CRR**									
Method	**Concentration (mg/g)**									
	Ag	**Al**	**Au**	**Cu**	**Fe**	**Ni**	**Pb**	**Pd**	**Sn**	**Zn**
ASTM method D 6257-11	1.18 ± 0.05	53.23 ± 1.42	0.18 ± 0.01	449.24 ± 5.32	31.45 ± 1.31	10.56 ± 0.11	6.45 ± 0.07	0.12 ± 0.01	1.68 ± 0.02	22.45 ± 1.23
US EPA SW 846 Method 3050B	1.08 ± 0.01	61.49 ± 2.45	0.18 ± 0.02	416.63 ± 7.82	28.61 ± 2.12	8.45 ± 1.22	6.34 ± 0.28	0.11 ± 0.05	1.56 ± 0.04	20.13 ± 2.56
MWD-1	0.83 ± 0.07	42.33 ± 2.34	0.16 ± 0.04	405.35 ± 8.12	23.33 ± 1.13	9.33 ± 1.09	5.87 ± 0.12	0.10 ± 0.01	1.43 ± 0.01	18.56 ± 1.78
MWD-2	0.96 ± 0.04	64.22 ± 3.12	0.17 ± 0.01	428.23 ± 4.98	30.45 ± 1.42	10.12 ± 1.13	7.12 ± 0.54	0.11 ± 0.01	1.96 ± 0.05	21.44 ± 3.09
MWD-3	0.92 ± 0.05	58.78 ± 1.87	0.16 ± 0.03	407.36 ± 5.28	27.56 ± 3.12	9.67 ± 0.88	6.88 ± 0.15	0.11 ± 0.03	1.87 ± 0.04	17.56 ± 2.67
UD-1	0.88 ± 0.07	50.34 ± 2.45	0.16 ± 0.02	362.53 ± 4.12	24.34 ± 1.15	8.22 ± 0.76	6.56 ± 0.65	0.09 ± 0.02	1.56 ± 0.03	16.45 ± 4.12
UD-2	0.76 ± 0.05	48.56 ± 3.24	0.17 ± 0.02	387.88 ± 2.08	22.17 ± 0.87	7.85 ± 0.56	6.05 ± 0.34	0.10 ± 0.02	1.78 ± 0.09	19.78 ± 2.67
UD-3	0.79 ± 0.03	49.34 ± 2.68	0.18 ± 0.01	378.65 ± 5.65	23.56 ± 0.98	8.08 ± 0.53	6.48 ± 0.23	0.11 ± 0.03	1.62 ± 0.06	21.65 ± 4.87
UD-4	0.82 ± 0.06	42.46 ± 3.45	0.16 ± 0.02	364.78 ± 2.44	20.98 ± 1.11	7.45 ± 1.32	6.22 ± 0.12	0.08 ± 0.03	1.61 ± 0.07	18.12 ± 2.44

All experiments were conducted in triplicates and results are reported as the mean ± SD. SD: standard deviation; MWD: microwave-assisted digestion; UD: ultrasound-assisted digestion. The coefficient of variation was less than 10%.

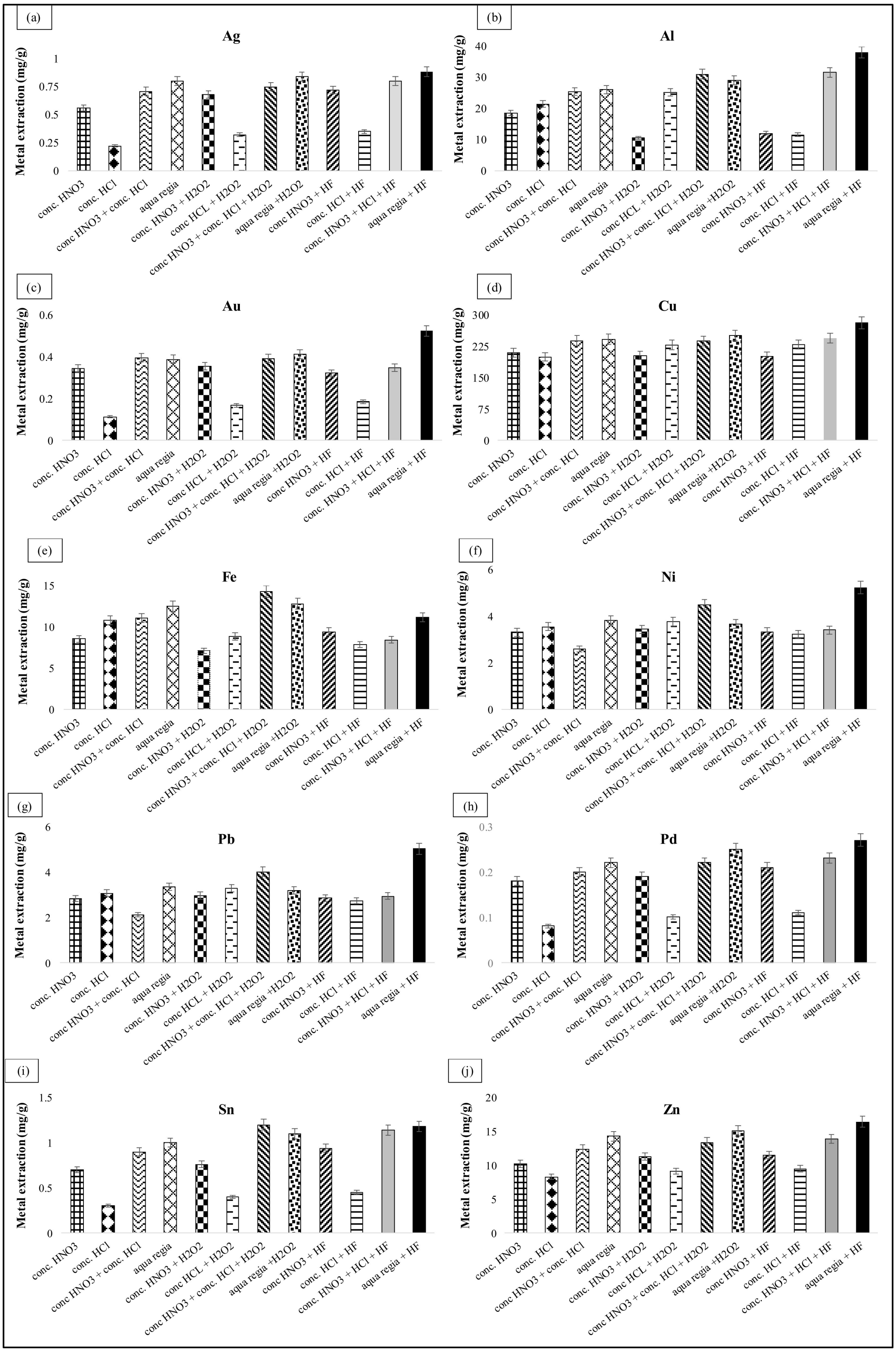

Figure 3. Dissolution of metals (**a**) Silver (Ag); (**b**) Aluminum (Al); (**c**) Gold (Au); (**d**) Copper (Cu); (**e**) Iron (Fe); (**f**) Nickel (Ni); (**g**) Lead (Pb); (**h**) Palladium (Pd); (**i**) Tin (Sn); (**j**) Zinc (Zn) using different acids (*n* = 3).

The use of different extraction reagents in SExM effectively segregates the various metals present in a solid waste matrix into different fractions, based on their chemical forms [29]. In the present study, the Modified Tessier sequential extraction protocol was used to determine the chemical form of the metals in the matrix (Figure 4). SExM utilizes different extraction reagents to mobilize metals into the solution in decreasing order of mobility. Copper and lead were found to be mainly bound to carbonates and organic fractions, with a small fraction attached with Fe-Mn oxide fractions (Figure 4). A significant portion of zinc remained attached to organic matter. A lower fraction of zinc was also found to be attached to carbonates and silicates (Figure 4). Since copper, lead, and zinc mainly remained as carbonates and organic, the solubilization of these metal fractions required acids and oxidizing agents respectively; the acids effectively digest the carbonate fractions, while the oxidizing agents oxidized the organic matters for efficient metal solubilization. The efficacy of aqua regia with hydrogen peroxide in the dissolution of copper and lead thus can be explained based on the binding states of the metals (Figure 3). Zinc was present as carbonate and as organic and silicate fractions. Since HF is effective in dissolving silicates, a combination of aqua regia and HF resulted in higher recovery of zinc compared to any other acid combination.

Nickel remained mainly bound to organic matter, while iron was found in both organic and silicate fractions. As shown from Figure 3, aqua regia with HF gave the highest metal recovery for nickel. E-waste contains large fractions of silicate, which may hinder the oxidizing agents from reaching the metal fractions. Thus, HF may have assisted the dissolution of the silicate fractions to enhance the metal extraction process. On the other hand, iron and tin, which remained bound to both organic and silicate fractions, were recovered maximally by the stepwise addition of the conc. HNO_3 + conc. HCl + H_2O_2, resulting in 12% and 9% higher recovery than aqua regia with hydrogen peroxide, respectively (Figure 3). Aluminum remained bound mainly to organic and silicate fractions (Figure 4). Thus, aqua regia with conc. HF resulted in the higher dissolution of Al compared to the sequential addition of conc. HNO_3, conc. HCl, and H_2O_2. Precious metals (gold, silver, and palladium) remained bound mainly to organic and silicate fractions (Figure 4) and were effectively recovered using a combination of aqua regia and conc. HF (Figure 3).

The use of sequential extraction procedures is central to determining the most effective acid digestion protocol for a specific type of waste, as it provides insight into the chemical forms of the various metals in the waste. Metals bound to water soluble components require a digestion protocol that incorporates water as one of the extraction agents. The US EPA SW 846 Method 3050b with 1:1 HNO_3-dH_2O mixture (v/v) is thus effective in targeting water-soluble components. However, from Figure 4, it is evident that the substrate contains an insignificant amount of metals bound to water-soluble fractions. This is also illustrated by the lower effectiveness of the US EPA SW 846 Method 3050b for the metal extraction of E-waste samples (Table 1). As aqua regia is efficient in removing both carbonates and Fe-Mn oxides, a combination of aqua regia with conc. HF resulted in higher metal recovery since these reagents oxidize the organic fractions and remove the silicate fractions, respectively. This strategy explains why ASTM D6357-11 resulted in the highest metal dissolution efficiency for E-waste (Table 1). The presence of an adjuvant oxidizing agent such as hydrogen peroxide augmented the digestion process by dissolving the organic fractions. On the other hand, the addition of conc. HF enhanced the disintegration of the silicate structure [40] and released the metals bound to the silicate fractions. However, both hydrogen peroxide and conc. hydrofluoric acid in isolation were not effective in solubilizing metals from the ESM solid matrix. Thus, judicious selection of the most effective acid digestion protocol requires knowledge of the chemical nature of the metals present in the solid waste matrix.

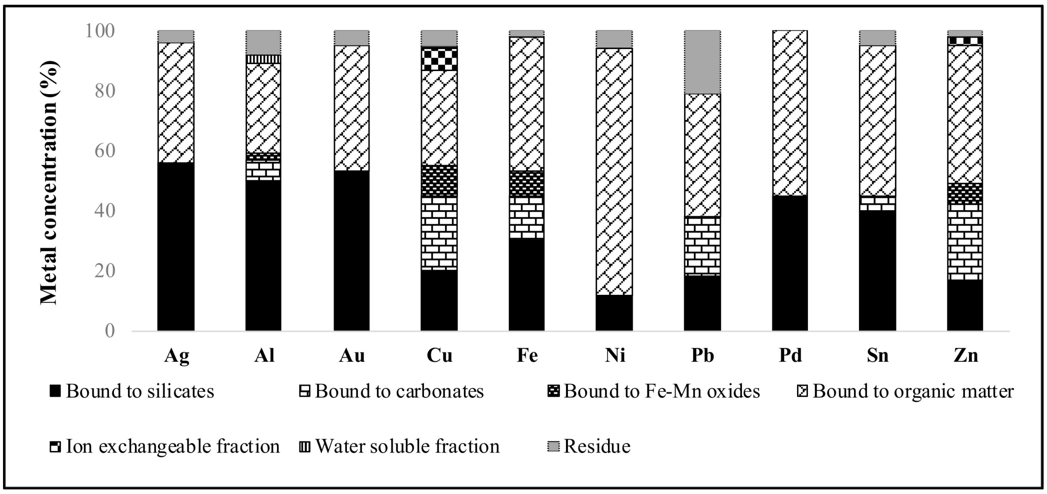

Figure 4. Sequential extraction of metals using various extraction reagents ($n = 3$).

3.4. Improved Metal Solubilization through Pre-Treatment of ESM

Pre-treatment of ESM may significantly enhance metal recoveries from its solid matrix during a digestion process [1]. In the present study, TES-AMM samples were ashed in a muffle furnace at 550 °C for 2 h. The effect of the heat pre-treatment on the metal solubilization was determined using acid digestion (ASTM D6357-11 Method) with the pre-treated samples. Figure 5 shows that pre-treatment significantly increased the metal recovery efficiency of several metals (Ag by 10%, Al by 15%, Au by 8%, Cu by 13%, Fe by 10%, Ni by 15) ($p < 0.05$). Ashing pre-treatment removed the volatile matter in the ESM solid matrix, and resulted in a concentration of trace metals and an increase in the oxidation state of the metals, and thus enhanced the solubilization of the metals by acids in the subsequent step [22,41].

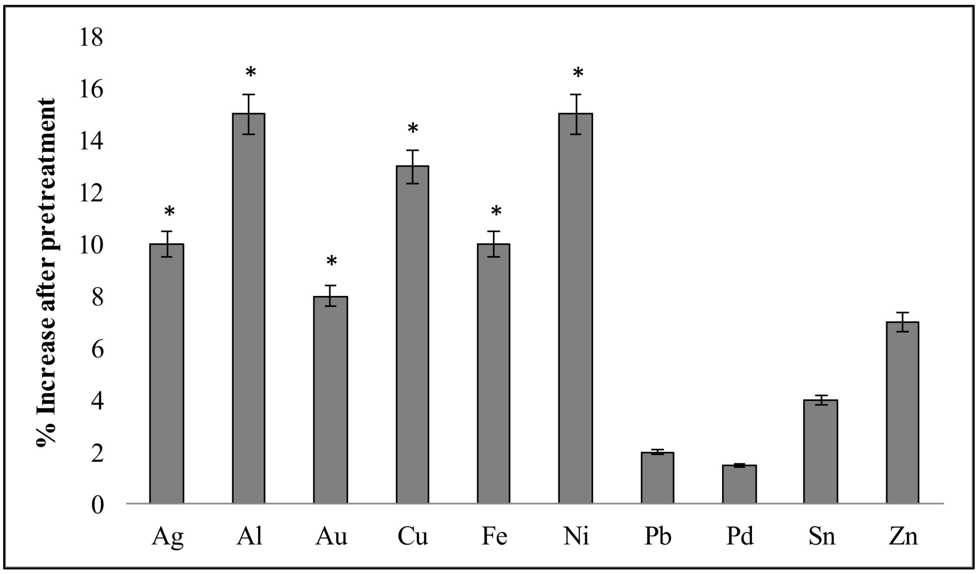

Figure 5. Impact of pretreatment on recovery of metal from ESM using ASTM D6357-11 Method, ($n = 3$, $p < 0.05$, one-way ANOVA, "*" indicates significant effect of pretreatment).

3.5. Effect of Different Driving Forces on Metal Recovery from ESM

To improve the digestion efficiency of the US EPA SW 846 Method 3050b, different driving forces such as microwave-based and ultrasound-based heating were applied (at 150 °C and 60 °C, respectively).

Using the US EPA SW 846 Method 3050b, the microwave-based closed heating system resulted in higher metal dissolution compared to the ultrasonic system ($p < 0.05$) (Figure 6). Similar observations have been reported previously [29,42]. Apart from higher metal recovery, the microwave-based digestion protocol was faster than the traditional method; the US EPA SW 846 Method 3050B at 95 °C required a treatment time of 270 min, while the ultrasound- and microwave-modified protocols required 40 min and 20 min, respectively. Ultrasound- and microwave-based heating increased the rates of reaction. It is generally recognized that ultrasound-assisted digestion is safer to operate, and a higher volume of solid waste may be treated, compared to microwave or bomb digestion methods [28]. However, less reagents are needed for microwave digestion, thus making it a more environmentally friendly process.

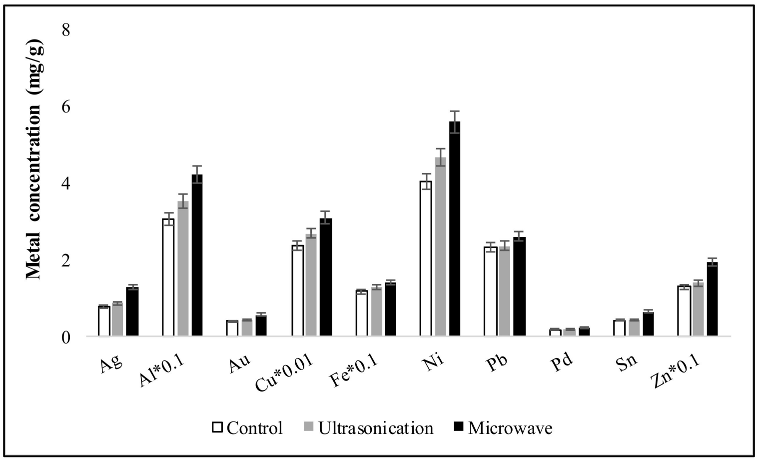

Figure 6. Effect of different driving forces on metal recovery from TES-AMM samples using the US EPA SW 846 Method 3050b, ($n = 3$). (For instance, the Cu*0.01 value of 3 denotes a Cu concentration of 300 mg/g.)

3.6. Fractional Composition of ESM

The composition of the ESM samples obtained from the two sources was evaluated using results obtained from the acid digestion and loss-on-ignition (Figure 7). The polymeric fraction was obtained indirectly using the loss-on-ignition results, and the ASTM D6357-11 acid digestion method was used to determine the metal fraction.

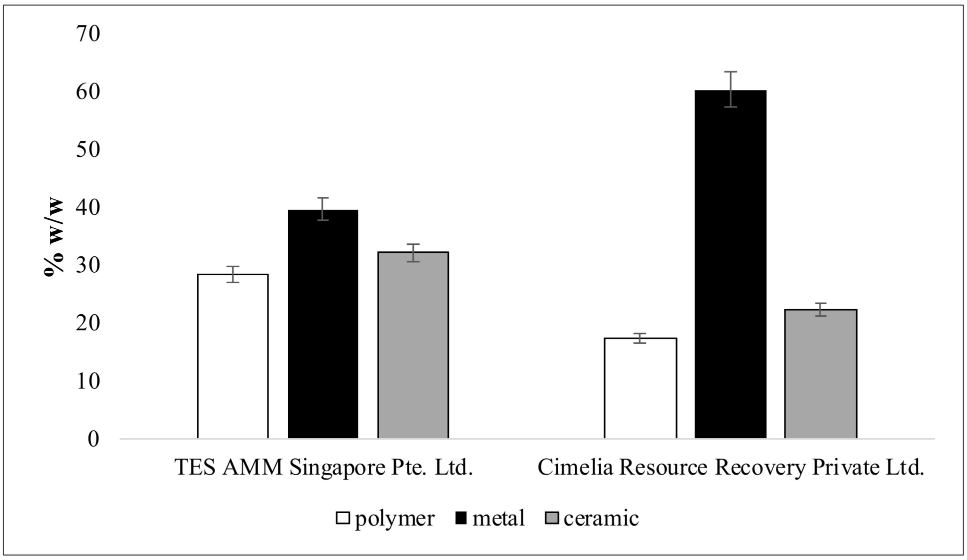

Figure 7. Fractional composition of TES-AMM and CRR samples ($n = 3$).

The polymeric fractions are comprised mainly of non-conductive materials. The TES-AMM and CRR samples contained 28.3% *w*/*w* and 17.34% *w*/*w* of polymeric fractions, respectively. Similar results have been reported by Yamane [19] using different sources of ESM samples. The polymeric fractions of ESM comprised mainly solid residues of carbon and fiberglass. The ceramic fraction constituted 32.1 and 22.4% *w*/*w* of the TES-AMM and CRR samples, respectively. The ceramic materials found in the ESM samples were primarily silica, alumina, mica, and barium titanate [19]. Figure 7 also reveals the heterogeneous nature of the E-waste stream; variation in the composition of the ESM mainly depends on the place of origin, application, type, age, and weld types [19].

4. Conclusions

The efficiency of a digestion protocol for solid waste is dependent on the waste matrix, the chemical form of the metals in the waste matrix, and the acids used in the digestion process. Results from the present study showed that ASTM D6357-11 is best suited for the determination of the metal composition of the E-waste samples examined. Selective extraction procedures provided a better understanding of the chemical form of the metals present in the matrix and the heterogeneous nature of the ESM sample. A mixture of aqua regia and HF was found to be the most effective combination for maximum metal extraction, and revealed the presence of silicate, organic, and carbonate fractions in the waste. Pre-treatment of ESM solid waste by ashing (at 550 °C) resulted in a significant increase in metal recovery. The microwave-assisted digestion method was faster and more effective in solubilizing metals from the waste compared to the traditional protocol or ultrasonication. Unfortunately, the heterogeneity of ESM samples and the different chemical form of the metals present in the solid matrix renders standardization of acid digestion protocol difficult. However, the use of SExM protocol (to determine the chemical form of the metals in the ESM matrix) and the concentration of the solid waste by heat pre-treatment, coupled with improved reaction kinetics by employing different driving forces, is useful in the selection of an effective acid digestion protocol for a specific type of ESM.

Supplementary Materials: The following are available online at www.mdpi.com/2079-9276/6/4/64/s1, Table S1: Operating parameters for different digestion methods.

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Author Contributions: Y.-P.T. conceived the project; both authors designed the experiments; S.D. performed the experiments and analyzed the data; both authors wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; and in the decision to publish the results.

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