Analysis of the content of germanium, tellurium and thallium in the grounded waste of electronic equipment

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Abstract
The article draws attention to the problem of the presence of selected metals in waste electrical, electronic equipment (WEEE). These metals belong to the group of critical metals (germanium), strategic metals (tellurium) and highly toxic elements (thallium). Due to low content of these metals in e-waste, they are usually ignored during e-waste analysis, therefore they belong to the least-known metals in the literature regarding waste recycling. Their presence in WEEE can cause them to be concentrated in the environment during improper e-waste processing. The article presents the applications of Ge, Te, Tl in electronic equipment, quantities identification of these metals in a variety of electronic equipment elements, paying special attention to the ability to accumulate/concentrate Ge, Te, Tl in individual fractions after the e-waste shredding and grinding process This research aims to determine possibility getting of these metals into the environment, during the storage and processing of e-waste (especially in the unit processes of disassembly, separation, shredding), in the case of uncontrolled electronic waste handling and disposal.
Keywords: e-waste processing, waste electrical, electronic equipment (WEEE), Technology Critical Element (TCE)

1. Introduction

Currently, german, tellurium and thallium belong to Technology-Critical Elements (TCE) in European Union (European COST Action TD1407: Network on Technology-Critical Elements). These metals are widespread in waste electrical and electronic equipment (WEEE) and therefore should be considered as significant source of pollution. The possible presence of these metals in the environment and the impact on environmental processes should be particularly taken into account, especially if they constitute potentially toxic compounds. (Cobelo-García and 2018). Tellurium is used in the production of cadmium telluride (CdTe) solar cells, which is it's major application (40% of global consumption), next to thermoelectrics (30%). The most important application of germanium currently is infrared optics - lenses and windows for infrared image recording devices (30%), optical materials - optical fiber cables (20%). Transistors, photodiodes, photo-resistors, radiant solar energy transducers, and X-ray spectroscopy analyzers account for 15% of the germanium supply. Today, approximately 70% of thallium production is used in electronic devices. Thallium is used, among others, in semiconductor materials, photocells, infrared measuring devices or in glass lenses, prisms, and windows for optical fibers (Paul and Krzak 2015, MCS 2017). In the unit weight of waste electrical and electronic equipment, in the context of primary and minor constituents (e.g. plastic, glass, ceramics, and other metals as Cu, Fe, Al, Zn) Ge, Te and Tl are micro or trace constituents (<0.1%). However, considering the possibility of recycling these metals, it should be taken into account the fact that millions of tons of waste electronic equipment is in circulation. Its recycling and unitary processes of disassembly, separation, grinding, and milling can be the source of uncontrolled emissions of metals to water, soil, and air. In addition, they may cause the migration of these metals to the nearest environments and/or expose workers to the harmful effects of metals through inhalation, skin contact or ingestion (Julander et al., 2014). In particular, thallium is highly toxic metal, listed by the European Water Framework Directive (Directive 2000) and United States Environmental Protection Agency (USEPA 2015) as a priority pollutant, which penetration into surface environments and its dispersion in soils, sediments and waters can occur relatively easily due to high volatility and solubility of thallium compounds (Belzile N. and Chen, 2017).

In the article, elements and electronic subassemblies that are carriers of Ge, Te, Tl, were subjected to separation and mechanical treatment (cutting, grinding) and then their quantitative analysis was made. The aim of the research was to determine the distribution of metals in the milled mass of waste in individual fractions and to determine the possible tendency to accumulate/ concentrate metals in a given fraction. The granulometric distribution of metals in the ground fraction of waste is crucial knowledge in the analysis of the possible migration of pollutants in the form of metal dust raised during the processing of e-waste.

2. Materials and Methods

The electrical and electronic equipment in the form of garden solar lamps, a portable solar panel and in the form of unitary electronic components such as photoresistors and photodiodes were analysed. The combined photovoltaic cell elements were manually removed to separate them from the housing, electronic control systems. Then selected carriers of metals Ge, Te and Tl were subjected to fragmentation in the blade mill. Ground fractions obtained from milling were weight and subjected to further grain size separation. Materials were sieved with sieves of the standard series: 0.5, 0.2 and 0.1 mm (MULTISERW-Morek). Total content of Tl, Te Ge and other metals (Co, Ni, Mn, Sr, Ba, Cu, Zn, Cd, Pb, Cr) in each fraction was determined by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS Elan 6100 DRC-e Perkin Elmer), after digestion in a hot aqua regia.

3. Results and Discussion

The content of Ge, Te, Tl and other metals in analysed elements and electronic subassemblies are presented in Table 1. The concentration of Ge, Te, Tl differs depending on the type of electronic element. The highest thallium content is found in photovoltaic cells: 0.077-0.015 ppm. The main germanium carriers are photoresistors (0.934 ppm), while tellurium - solar cells (1.472 ppm). Among other metals, which are minor constituents, the dominant ones are copper and cadmium, chromium and lead - other toxic heavy metals.

Table 1. Concentration of metals in electronics equipment subassemblies

Metals ppm	Photovoltaic cell solar lamp	Photovoltaic cell solar panel	Photo-resistors	Photo-diodes
Tl	0,077	0,015	0,006	0,001
Ge	0,401	0,047	0,934	0,260
Te	0,070	1,472	0,343	0,032
Ni	227,774	241,3	2685,700	114,490
Cu	91,471	78863	1093,950	347505
Zn	37,270	82,4	31,605	506,2
Cd	0,853	340,4	1789,300	98,88
Pb	7,715	6335,5	9,620	25,12
Cr	449,385	487,5	6199,100	89,84

In the separated material, the tendency to concentrate critical metals in fine fractions was observed. Figure 1 shows Ge, Te, Tl content of separated fractions received from the photovoltaic cell. The concentration of Ge decreases with decreasing granulometric size of the material. In the fraction of 0.2-0.1, (that was only 12% of the total mass), was the highest germanium (1,139 ppm) and thallium concentration (0,274 ppm). In the analysed material, (after sieving) the share of the thickest grain fraction (above 0.5) was the largest and it was 49.9% of the total material. The share of other fractions was respectively: 27.6% for fraction 0.5-0.2, 12% for fraction 0.2-0.1 and 10.5% for the fine fraction (less than 0.1).

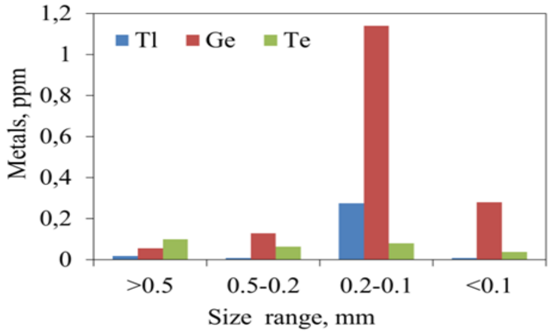

Figure 1. Tl, Ge and Te distribution in different grain fraction of ground photovoltaic cell supplied from solar lamps

4. Summary

The processes of grinding, crushing, grinding of e-waste create conditions in which metals may be released to the environment. In addition, the activities of collecting and transporting the fragmented fraction may lead to the dispersion and migration of dust pollutants. Knowledge of the composition of the fractionated material is a significant quantitative factor identifying the most metal-bearing fractions. Ge, Te and Tl can concentrate in fine fractions of grounded e-waste. The content of toxic metals (Tl) in the smallest fractions, which can easily be released into the environment, is particularly dangerous.

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