

The content of heavy metal ions in ash from waste incinerated in domestic furnaces

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Abstract: The article presents the results of preliminary tests obtained from the analysis of ash coming from the combustion of various types of waste in household furnaces. The aim of this work was to examine the influence of various types of waste burned in household furnaces on the elemental composition of the generated ash. As part of the research, analyses of ash generated from the incineration of mixed waste, plastics, wood, textiles, rubber waste and paper were made. The content of selected metal ions: Mn, Cu, Mo, Zn, Cd, Tl, Cr, Co, Ni, As, Sn, Sb, Pb, V was determined in the tested samples, according to PN-EN ISO 17294-2: 2016-11 standard. The highest concentrations of zinc were found in the large-sized waste, rubber and textile ash samples and highest concentrations of copper were found in the plastic and paper ash samples. The highest concentrations for elements such as copper, lead, cobalt and chromium were recorded for samples of rubber and large-sized waste containing e.g. varnished furniture boards. The obtained results showed that depending on the waste incinerated, the content of selected metals was significantly different, and the highest concentrations were noted for samples of large-sized waste, waste from segregated plastics and waste from rubbers.

Aim of the study

Waste management is mainly aimed to protect human health and, secondly, to protect the environment. Humanity has been producing waste for centuries, however along with the rapid civilization development, the amount of generated waste has drastically risen. A lot of legal regulations have been introduced to reduce waste generation as well as a rational management of already generated waste, e.g. separate collection of waste and recycling, thermal utilization with energy recovery, and natural use, thus avoiding the inadvisable storing. The rise in the living costs (increased fuel and energy prices) and, consequently, impoverishment of society and low ecological awareness caused the common usage of high-calorie waste as fuel in household furnaces, thus causing environmental pollution with uncontrolled emission of hazardous substances and producing dangerous furnace waste (ash/slag) (Zajac A. 2016). Such waste utilization is carried out in uncontrolled conditions, as opposed to utilizing in professional energy, cement or waste incineration plants. Incineration of waste in specially adapted equipment, endowed with exhaust aftertreatment devices, reduces dioxin emissions by over 700 times more than during the combustion of waste in a domestic furnaces.

In Poland, it is forbidden to incinerate waste in equipment which is not adapted to it. In accordance with the Waste Act and the Code of Offenses, it is prohibited to burn waste in furnaces, domestic boiler rooms as well as in the open air. These issues are regulated by the following documents:

- Directive 2000/76/EC of the European Parliament and of the Council of 4 December 2000 on the incineration of waste
 - Waste Management Act 14 of December 2012:
 - Article 155. Thermal treatment of waste shall be carried out only in waste co-incineration plants or in waste co-incineration plants, subject to Article 31.
 - Article 191. Who, contrary to the provisions of Article 155, thermally transforms waste outside the waste incineration plant or waste co-incineration plant shall be subject to the arrest or a fine.
- The combustion process in a domestic environment takes place at low temperatures, which results in high emission of toxic gases into the environment, including: carbon and sulfur oxides, hydrogen chloride, hydrogen fluoride and hydrogen cyanide, as well as metals such as cadmium, thallium, mercury and others. Waste such as polyvinyl chloride (PVC), from which liners, bottles, cable casing, foils, shoes, clothing, furniture, plywood or chipboards are made, is burnt in domestic furnaces in an uncontrolled way. It is also extremely unhealthy to incinerate PET plastics, rubber waste or varnished materials. As a result of domestic thermal utilization of this group of products, carcinogenic dioxins are introduced to the atmosphere, whose toxic effects on health are manifested only after several dozen years, for example in the form of cancer.
- Waste management issues are regulated by the Waste Management Act of 14 December 2012 (Journal of Laws

2013, item 21) (Waste Management Act 2012). According to the provisions of art. 155. “thermal waste treatment is carried out only in waste incineration plants or waste co-incineration plants (...)”, which explicitly prohibits the incineration of waste in uncontrolled conditions, e.g. in household furnaces (Sobolewski A. at al. 2019, Waste Management Act 2012, Zając A. 2016).

In Poland, storage of ash in landfills is still the basic form of managing them. However, ash from domestic furnaces is often dumped into fields and gardens, due to the belief in their beneficial fertilizing properties. This is the case with the combustion of pure biomass, while in the case of ash from conventional fuels or mainly from waste, large amounts of toxic elements get into the soil along with the ash, causing its permanent pollution (Kajda-Szcześniak M. 2014).

All these aspects have recently led to an increase in the interest of authorities controlling the emission of pollutants over the possibility of identifying incineration in waste furnaces basing on the chemical composition of furnace waste (ash).

Material and methods

The research material consisted of ash coming from the incineration of waste such as plastics, textiles, rubber, paper and large-sized waste. From the collected waste, ash was prepared in laboratory conditions by burning each of the waste samples at the temperature of $550^{\circ}\text{C} \pm 25^{\circ}\text{C}$ in such a way as to obtain samples of ash from total combustion and from combustion

with limited oxygen access. The analytical samples prepared in this way were then mineralized by mixture of nitric acid and hydrogen peroxide in an Anton Paar microwave oven. Microwave mineralization was carried out at programmed boundary conditions: maximum temperature measured with IR sensor – 210°C , maximum internal temperature – 230°C , maximum microwave power 650 W, maximum pressure 50 bar, maximum pressure increase 0.3 bar/s. After mineralization, the samples were subjected to multi-elemental analysis by ICP-MS technique, according to PN-EN ISO 17294-2: 2016-11 standard. The analysis of the content of such elements as: Mn, Cu, Mo, Zn, Cd, Tl, Cr, Co, Ni, As, Sn, Sb, Pb, V was conducted in the samples.

Results and discussion

The test results of metals content in ash samples from waste are presented in Table 1.

The content of individual elements in various types of ash from waste was very diverse. The highest concentrations were recorded for metal ions such as zinc in samples of waste from rubber, plastics and large-sized waste, in which the content reached even 24738 mg/kg d.m. in rubber waste (Table 1).

High concentrations were also noted for copper, whose content in one of the ash sample from plastic waste was 23203 mg/kg d.m. Another element characterized by a high concentration in the tested samples is lead, whose concentration in ash samples from waste plastics was 10883 mg/kg d.m. High



Fig. 1. Ash from waste

levels of manganese, nickel and chromium were also noted for plastic ash samples (Table 1).

The highest cobalt concentration was determined in samples of large-sized waste – 9237 mg/kg d.m.. The lowest concentration was recorded for thallium, whose concentration in ash samples from large-sized waste and plastic waste was below the limit of quantification of the method (<0.25 mg/kg d.M.). The maximum concentration of thallium in ash samples from textile waste is 0.399 mg/kg d.m., in ash samples from paper waste – 0.575 mg/kg d.m., in ash samples from rubber waste – 1.73 mg/kg d.m. The concentration of molybdenum was between 1.76 mg/kg d.m. in ash samples from rubber wastes to 32.1 mg/kg d.m. in ash samples from large sized wastes. The minimum concentration of cadmium was determined in ash samples from paper – 0.452 mg/kg d.m., and maximum in ash samples from large-sized waste 15.7 mg/kg d.m. The lowest concentration of arsenic was noted for ash samples from textiles waste – 1.29 mg/kg d.m., and highest concentration for ash from paper waste – 15.8 mg/kg d.m.. The concentration of vanadium fluctuate between 5.23 mg/kg d.m. in ash samples from large-sized waste and about 39 mg/kg d.m. in ash samples from plastic and rubber wastes. The concentration of tin was the highest for ash samples from plastic waste – 857 mg/kg d.m., and the lowest in ash samples from large-sized and rubber wastes – about 10 mg/kg d.m. The maximum concentration of antimony was determined in ash samples from plastic waste – 24 mg/kg d.m., and the minimum concentration in ash samples from large-sized (1.35 mg/kg d.m.) and paper waste (1.90 mg/kg d.m.).

The existing literature provides little information on the composition of ash coming from domestic furnaces fired with other fuels than conventional or biomass (Czop M. and Kajda-Szcześniak M. 2010, Wasielewski R. and Radko T. 2018). The composition of ash from fossil fuels and wood biomass is discussed widely in the literature, in view of the former being used for the production of building materials and for road

foundation (Choi M.J. at al. 2019, Rissanen J. at al. 2018, Czop M. and Kajda-Szcześniak M. 2010). The latter, in turn, is often a direct mineral fertilizer or is used as an addition to fertilizers or soil conditioners (Czop M. at al. 2016), although some authors also indicate the possibility of its use as an ingredient in mortars or cements (Fuller A. at al. 2018, Rissanen J. at al. 2018). Fly ash can also be used to produce geopolymers (Novais R. M. at al. 2018).

The results obtained from the tests can be compared with the ones already available in the literature for ash obtained under controlled conditions, e.g. from commercial fluidized bed boilers or waste incineration plants (Shakya P.R. at al. 2006, Cieślik E. at al. 2018).

The results obtained in own research indicate that in most of the ash tested the highest concentration was recorded for zinc, lead, manganese and copper, which is confirmed by other authors. (Shakya P. R. at al. 2006, Smółka-Danielowska D. at al. 2019, Szcześniak-Kajda M. 2014, Czop M. and Kajda-Szcześniak M. 2010, Wang P. at al. 2019, Poykio R. at al. 2016).

The metal concentration in the different kind of ash from waste followed such order:

- Large-sized waste: Tl<Sb<As<V<Cd<Sn<Mo<Ni<Cu<Cr<Mn<Pb<Co<Zn
- Plastic waste: Tl<Cd<As<Mo<V<Co<Sb<Sn<Mn<Ni<Cr<Zn<Pb<Cu
- Rubber waste: Tl<Mo<As<Co<Cu<Sn<Cd<Sb<Ni<V<Cr<Pb<Mn<Zn
- Paper waste ash: Tl<Cd<Sb<Co<Mo<V<As<Pb<Ni<Sn<Cr<Mn<Zn<Cu
- Textile waste: Tl<As<Mo<Co<V<Cd<Sn<Ni<Cu<Sb<Cr<Mn<Pb<Zn

Figures 2 to 6 present in a graphical way the test results of the content of 14 elements in ash resulting from the incineration of waste.

Table 1. Results of the analysis of metals in ash samples [mg/kg_{d.m.}]

Ions of metals	Ash from waste				
	large-sized waste	plastic waste	rubber waste	paper waste	textiles waste
	concentration mg/kg dry mass				
Mn	1093–2904	598–841	123–169	102–157	258–272
Cu	296–740	3206–23203	9.15–10.4	200–416	56.4–62.2
Mo	5.49–32.1	11.7–18.8	1.76–1.79	3.95–4.15	2.82–3.63
Zn	3461–10609	2019–5406	18755–24738	114–148	1519–1812
Cd	5.62–15.7	1.85–2.94	10.9–12.5	0.452–0.640	8.32–9.15
Tl	<0.250	<0.250	1.54–1.73	0.297–0.575	0.353–0.399
Co	3343–9237	41.5–157	3.17–3.40	2.06–4.52	4.68–5.09
Ni	146–407	633–1801	22.6–28.0	28.1–41.9	43.9–47.7
As	2.55–7.71	6.44–11.3	2.40–2.49	10.1–15.8	1.29–1.48
V	5.23–13.3	24.8–39.1	30.0–39.3	8.63–15.1	5.47–5.49
Cr	515–1420	528–1787	59.3–77.4	49.5–99.5	96.8–98.9
Sn	10.1–11.9	11.9–857	10.4–11.3	36.5–49.4	45.0–45.4
Sb	1.35–2.95	27.7–240	11.7–14.0	1.90–1.95	79.1–80.4
Pb	2192–5212	229–10883	83.3–94.9	20.6–30.1	342–357

The characteristic features of such a graph can be seen for each type of ash. Based on the obtained test results, it is possible to determine with some probability the type of waste burned in the furnace. However, it is necessary to carry out tests of the content of the same 14 elements in ash coming from mixed waste and ash from conventional fuel and biomass, due to the fact that the waste is often not burned alone, but together with conventional fuel or wood biomass.

Conclusions

The authors of numerous papers on the use and research of various types of ash (Shakya P. R. at al. 2006, Cieřlik E. at al. 2018, Smořka-Danielowska D. at al. 2019, Szczeřniak-Kajda M. 2014, Czop M. and Kajda-Szczeřniak M. 2010, Czop M. at al. 2016, Wang P. at al. 2019) most often studied ash from known sources, with a constant and known composition

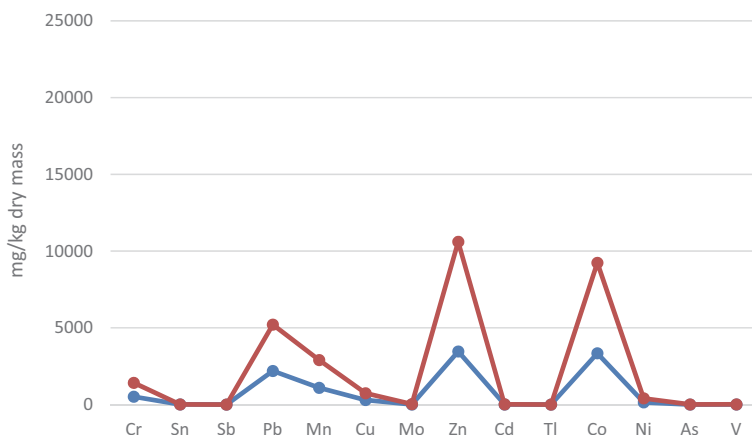


Fig. 2. Results of elements contents in 2 samples of large-sized waste ash tests

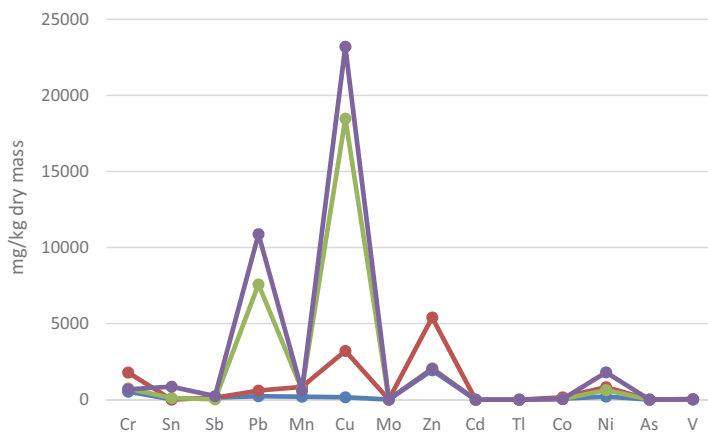


Fig. 3. Results of elements contents in 4 samples of plastic waste ash tests

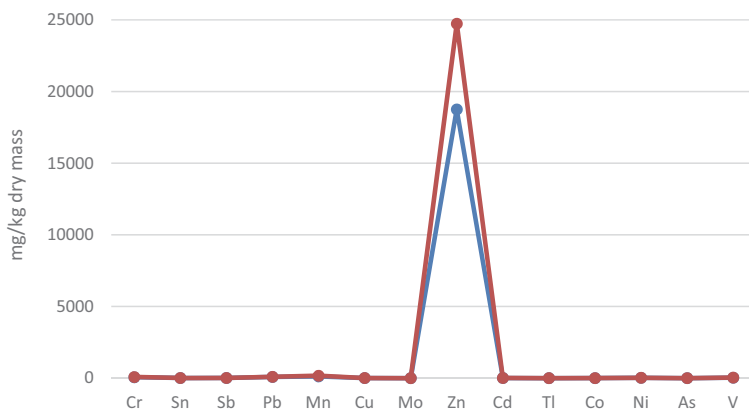


Fig. 4. Results of elements contents in 2 samples of rubber waste ash tests

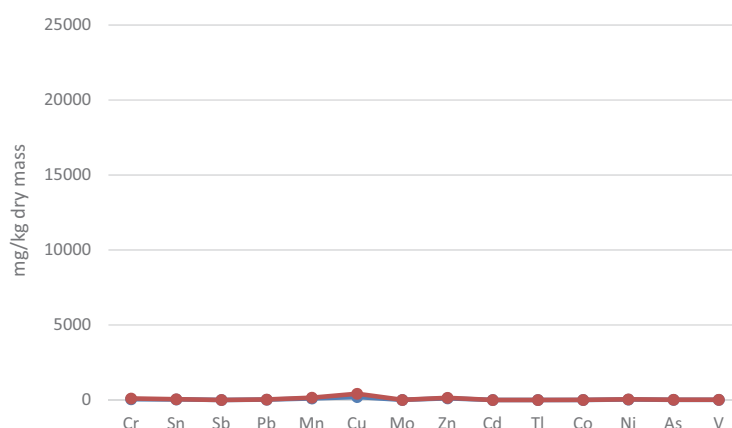


Fig. 5. Results of elements contents in 2 samples of paper waste ash tests

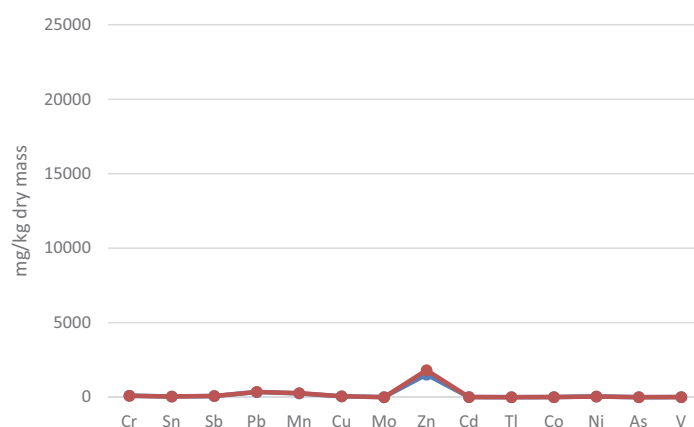


Fig. 6. Results of elements contents in 2 samples of textile waste ash tests

towards their specific use. However, there is no data in the literature on the composition of ash from waste burned in domestic furnaces. This is mainly due to the fact that the incineration of waste in uncontrolled conditions is prohibited. These issues are regulated by law and the prohibition of incineration and co-incineration of waste in individual heating devices, results from the provisions of the Waste Management Act from 14 December 2012 (Journal of Laws 2013, item 21). According to the provisions of art. 155. “thermal waste transformation takes place only in waste incineration plants or waste co-incineration plants (...)” (Sobolewski A. at al. 2019, Waste Act 2012).

On the basis of the performed tests, it can be stated that:

- The highest concentrations of zinc were found in the samples of ash from large-sized, rubber and textile wastes and highest concentrations of copper were found in the plastic and paper ash samples.
- The highest concentrations of elements such as copper, lead, cobalt and chromium were recorded for ash samples of rubber and large-sized waste containing e.g. varnished furniture boards.
- The obtained results showed that depending on the waste incinerated, the content of selected metals in ash was significantly different, and the highest concentrations were noted for ash samples of large-sized waste, waste from segregated plastics and waste from rubbers.

- Basing on preliminary research, it can be stated that it might be possible in the future to identify waste utilized in household furnaces on the basis of chemical analyses of ash coming from incinerated waste. However, a broader physicochemical analysis should also be carried out including leachability tests, which are the subject of further research.

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