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Analysis of Heavy Metals in Blister Pack and Medical Gloves Samples

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Incineration is a common method to treat medical wastes. Whereas pathogens and environmentally problematic organic compounds are destroyed, toxic heavy metals cannot be ruined. In this study heavy metal concentrations of two types of medical wastes were analyzed. Four different blister pack layers (polyvinyl chloride (PVC), polyvinyl chloride/polyvinylidiene chloride with pigment (PVC/PVdCp), polyvinyl chloride/polyvinylidiene chloride transparent (PVC/PVdCt) and polyethylene (PE)) and blister pack as a unit, and three types of medical gloves (latex powdered and powder-free medical gloves, nitrile powder-free medical gloves and vinyl powdered and powder-free medical gloves) were digested using high pressure digestion methods. Different acid mixtures were used to digest the samples. Heavy metal concentrations were analyzed by the inductively coupled plasma – optical emission spectrometry (ICP-OES). As, Fe, Na, P, Sn, Sr and Zn were detected in blister pack and different blister pack layers. Ca, Fe, K, Mg, Na, P, Sr and Zn were detected in three different types of medical gloves. No environmentally relevant elemental concentrations were detected except for Sn and Zn.

Keywords: *Heavy metals, medical gloves, blister packs, inductively coupled plasma spectroscopy.*

1. Introduction

Medical wastes are an issue of global concern. Medical wastes are defined as solid or liquid wastes originating from treatment of human beings in hospital or clinic, from clinical diagnosis and pathological testing and from medical research (Patwary et al. 2011). Their danger potential originates from pathogens and infectious components. Moreover, medical waste can consist of radioactive and toxic substances from hospitals, clinical laboratories and medical research institutions. They include sharps (syringes and needles), blood products, human tissues, body parts, pharmaceuticals, cytotoxins, and heavy metals, in addition to the item of general use such as paper, food, plastics, etc (Javied at al. 2008). Medical plastic wastes consist of packing containers, pharmaceutical packages and various medical devices, i.e. gloves, syringes, catheters, etc. Therefore, medical wastes cannot be treated as other municipal wastes.

The USA Environmental Protection Agency (EPA) research data and industry operating experience indicate that incineration has historically been the most widely used treatment technology for the disposal of medical waste (Alagoz et al. 2008). Incineration is a high-temperature dry oxidation process that converts the waste into residual ash and gases. The numerous advantages of incineration (reduction of waste volume, production of energy, saving in landfill cost) have led to its world wide use as a preferred means of treating and disposing of medical solid waste (Alagoz et al. 2007). It is particularly useful in the treatment of pathological waste and sharps. It is usually selected to treat wastes that cannot be recycled, reused, or disposed of directly in a landfill site, such as medical wastes (Alagoz et al. 2007, Xie et al. 2009).

Increasing amounts of medicines packaging in blister packs and growing numbers of medical gloves usage lead into investigation of this kind of waste. Most of the blister consists of two - four different types of materials, such as: most common polyvinyl chloride (PVC) and others polyvinyl chloride/polyvinylidiene chloride (PVD/PVdC), polyvinyl chloride/polyethylene/polyvinylidiene chloride (PVC/PE/PVdC), polyvinyl chloride/ polychlorotrifluoroethylene (PVC/ACLAR), polyvinyl chloride/aluminum (PVC/Alu), polyvinyl chloride /cyclic olefin copolymer (PVC/COC), etc (Pilchik 2000, Christopherson R2001). Chosen layers of blister pack quantities and thicknesses can vary to have the best protection properties and excellent barrier against water vapor, oxygen, gas, aroma and taste properties (Jena et al. 2011, Christopherson Ret. al. 2001). Medical gloves can be made of a few different polymers: natural rubber latex, nitrile and vinyl. All medical gloves can be powder-free, or powdered with cornstarch, rice starch or talc ($Mg_3Si_4O_{10}(OH)_2$) to lubricate the gloves (STRECH 2011).

The emission of toxic metals from medical waste combustion devices is a potential threat to human health. Metals may exit the waste combustion system either from bottom or filter ashes, or directly via exhaust gases into the environment. Metals cannot be destroyed by incineration, but may be transferred into different compounds. Most of the metals are transferred into the residual ashes. A fraction of the metals originally in the waste may also be found in the exhaust gases emitted from the system (Trouve et al. 1998). Recently, the formation and fate of metal containing nanoparticles originating from waste materials or formation in the incinerator were discussed (Roes et al. 2012, Walser et al. 2012).

The aim of this research is to determine heavy metal concentrations in four types of blister pack layers and blister pack as a unit, and three types of medical gloves using inductively coupled plasma spectroscopy. This is a first step towards the whole assessment of their fate during and after incineration.

2. Methods

2. 1. Instrumentation

In this study a microwave Multiwave 3000 (Perkinelmer, Anton Paar) was used for material digestion. Multiwave 3000 is a versatile and powerful microwave sample digestion system for safe high-pressure acid digestions of all types of organic and inorganic samples. For all the above specified materials microwave-assisted acid digestion procedures were performed using a high-pressure digestion system with eight 100 mL teflon digestion vessels. Different acid mixtures were used for specific material. These procedures were adapted according to the manufacturer's recommendations for various materials.

The digested samples were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian Liberty 110). Analytical ICP-OES operating conditions are listed in

Table 1. ICP-OES operating parameters

ICP-OES operating parameters	Value
Power	1.2 kW
Plasma flow	12 L/min
Nebulizer flow	160 kPa
Auxiliary flow	1,5 L/min
Pump speed	15 rpm
Stabilization time	25 s
Rinse time	0 s
Sample delay	8 s
Element wavelength	nm Sn (189.926), As (193.696), Mo (202.03), Ag (328.068), Sr (346.446), Tl (351.924), Al (396.152), Ba (413.066), Ni (231.604), Be (234.861), Co (237.862), Si (251.611), Fe (259.837), Cr (267.716), Mn(279.482), Mg (279.553), V (292.402), Na (588.995), Li (610.362), B (208.893), Ca (317.933), P (213.618), Zn (213.856), Cu (324.754), Sb (217.581), Pb (220.353), Cd (228.802), K (769.896)

2. 2. Samples and reagents

Tested materials used in this study were four blister pack layers (polyethylene (PE), polyvinyl chloride (PVC), polyvinyl chloride/polyvinylidiene chloride with pigment (PVC/PVdCp), polyvinyl chloride/polyvinylidiene chloride transparent (PVC/PVdCt)), blister pack as a unit, latex powder-free (pf) and powdered (p), two types of nitrile pf and vinyl pf and p medical gloves. Blister pack as a unit and four blister pack layers (Fig. 1.) were collected from Perlen Corverting AG, Switzerland. Medical gloves were obtained from different companies. Nitrile pf, latex pf and vinyl p and pf glove were obtained from TOP gloves (Malaysia), nitrile pf gloves from Sempercare (USA) and latex p gloves from Baxter (USA) (Fig. 2.). Ultra-high-quality water (18 MΩ cm), analytical-grade reagents (HNO_3, HCl, HF, H_2O_2, and HBO_3), control elemental stock standard solutions were used in this study.

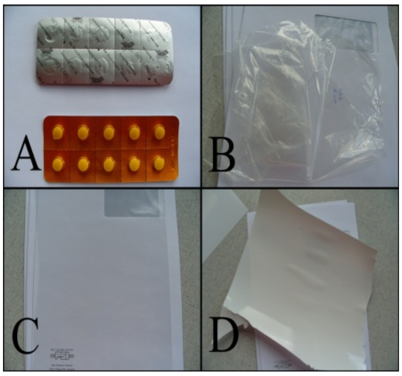

Fig. 1. A - Blister pack; B - PE layer; C - Transparent PVC; D - PVC/PVdC with pigment;

Fig. 2. E - Nitrile pf gloves; F - Latex p, pf gloves; G - Vinyl p, pf gloves;

2. 3. Sample digestion

Each sample was shredded to small pieces. Approximately 300 mg of cut material was placed into 100 mL teflon digestion vessels. Two samples were analyzed in parallel.

PVC digestion: Vinyl p and pf gloves, blister pack, PVC layer, PVdC/PVCp and PVdC/PVCt layer were filled with 5 mL of HNO_3, 1mL of HCl and 1 mL of H_2O_2.

Polyethylene digestion: PE layer material was filled with 7 mL of HNO_3 and 1 mL of HF.

Rubber digestion – method 1: Latex p, pf and nitrile pf gloves were filled with 6 mL of HNO_3 and 2 mL of H_2O_2.

Rubber digestion – method 2: Latex p, pf and nitrile pf gloves were filled with 8 mL of HNO_3 and 1 mL of HF.

Vessels were tightly closed, placed in a special holder, and heated in the microwave digestor. The operation program is given in

Table *2*. After digestion each vessel was carefully opened to release the pressure. The digestate solution was filled with 40 mL of HBO_3 to complex the hydrofluoric acid, diluted with de-ionized water and transferred to a 100 mL plastic bottle for further analysis by ICP-OES.

After each run, the cleaning process was carried out. Digestion vessels were filled with 6 mL concentrated HNO_3 and cleaning program had been performed. After that all vessels were rinsed with water.

Table 2. Program for microwave Multiwave 3000 digestion of samples

Material	Method	Program						
		Power, W	Ramp	Hold, min	Fan	Pressure increase rate, bar/s	IR, °C	Pressure, bar
PVC, PVC/PVdC, PVC/PVdC transparent and with pigment, vinyl powdered and powder-free gloves	PVC - I	800 0	15	30 20	1 3	0,2	220	50
Polyethylene	PE	700 0	5	45 20	1 3	0,2	200	45
Latex powdered and latex, nitrile powder-free	Rubber - I	600 0	20	15 20	1 3	0,1	200	40
	Rubber - II	600 0	15	30 20	1 2	0,2	220	60
Cleaning	-	800 0	10	5 20	1 2	0,5	240	60

3. Results

Four different blister pack layers and blister pack as a unit were analyzed. Blister pack layers were PVC, PE, PVC/PVdCp and PVC/PVdCt. Analytical results are presented in

As was found only in blister pack – 278.58 $mg \cdot kg^{-1}$. It means that this element comes from other material, like glue, but not from in this paper analyzed materials. The highest quantity of Fe – 1604.44 $mg \cdot kg^{-1}$ was measured in blister pack, while the lower quantity was seen in PE layer. The highest quantity of Na – 591.93 $mg \cdot kg^{-1}$ was measured in PVC/PVdCp layer, its lower quantities were seen in PVC, PVC/PVdCt layers and in blister pack. P was measured in both PVC/PVdCp layer and blister pack and it consisted of 124.36 $mg \cdot kg^{-1}$ and 33.39 $mg \cdot kg^{-1}$, respectively. The highest quantity of Sn – 2873.05 mg·kg^{-1} was measured in PVC layer, while its lower quantities were seen in PVC/PVdCp, PVC/PVdCt layers and in blister pack. Sr was found only in PVC layer – 1.58 mg·kg^{-1}. A small content of Zn was discovered in blister pack and PE.

In this study blister pack is made of some quantities of the above analyzed blister pack layers. The P result shows that our hypothesis is correct and the blister pack is made of PVC/PVdCp layer. The P is found just in blister pack and PVC/PVdCp layer that shows that PVC/PVdCp layer was used in making an analyzed blister pack. Zn and Fe were detected in the blister pack and it shows that it is made of PE, too.

It is not allowed to sum up the content from original subfractions, as we have no information about the quantity of these fractions used in the blister production. The concentrations can only be used to interpret possible origins of the elements.

Table 3. Metal quantity in blister pack and in layers (mg·kg^{-1})

Method	PVC-1	PVC-1,	PVC-1	PVC-1	PE
Material	Blister pack	PVC	PVC/PVdC without pigment	PVC/PVdC with pigment	PE
As	278.58	n.d.*	n.d.*	n.d.*	n.d.*
Fe	1604.44	n.d.*	n.d.*	n.d.*	45.98
Na	192.33	222.2	338.51	591.93	n.d.*
P	33.39	n.d.*	n.d.*	124.36	n.d.*
Sn	1668.13	2873.05	1690.51	1559.45	n.d.*
Sr	n.d.*	1.58	n.d.*	n.d.*	n.d.*
Zn	9.44	n.d.*	n.d.*	n.d.*	6.24

*– not detected;

Just few of the measured heavy metals were detected in medical gloves. Analytical results are presented in

Table 4. Metal quantity in medical gloves (mg·kg^{-1})

Method	Rubber-1,	Rubber-1	Rubber-1,	Rubber-1
Material	Latex powdered	Latex powder-free	Nitrile powder-free (SC)	Nitrile powder-free (TG)
Ca	7372.71	156915.9	7258.12	50701.48
Fe	n.d.*	46.28	n.d.*	23.72
K	n.d.*	n.d.*	n.d.*	n.d.*
Mg	112.63	636.38	37.34	266.58
Na	n.d.*	n.d.*	233.74	1305.58
P	182.81	137.00	292.12	354.09
Sr	n.d.*	20.67	6.29	n.d.*
Zn	1087.44	2589.97	5225.53	5534.50

*not detected;

The highest quantity of Ca – 168917.5 mg·kg^{-1} was measured in latex pf using the rubber-2 method. A similar quantity was found in latex pf using the rubber-1 method. Lower quantities of Ca were detected in latex p and nitrile pf using both rubber methods. The highest quantity of Fe – 68.80 mg·kg^{-1} was comparably small and measured in latex pf using the rubber-2 method. Its similar quantity is seen in latex pf using the rubber-1 method, in TG nitrile pf using both rubber methods and in vinyl pf and p gloves. In latex p and SC nitrile pf no Fe was found. K was found only in SC nitrile pf gloves – 206.51 mg·kg^{-1}. The highest quantity of Mg – 677.61 mg·kg^{-1} was measured in latex pf using the rubber-2 method.

Table 4. Metal quantity in medical gloves (mg·kg^{-1}) (Table 4 continued)

Method	Rubber-2	Rubber-2	Rubber-2	Rubber-2	PVC-1	PVC-1
Material	Latex powdered	Latex powder-free	Nitrile powder-free (SC)	Nitrile powder-free (TG)	Vinyl powder-free	Vinyl powdered
Ca	6853.51	168917.5	7183.84	52517.9	n.d.*	n.d.*
Fe	n.d.*	68.80	n.d.*	37.50	29.13	20.61
K	n.d.*	n.d.*	206.51	n.d.*	n.d.*	n.d.*
Mg	127.52	677.61	36.12	273.11	n.d.*	64.92
Na	n.d.*	n.d.*	240.07	1241.88	368.02	312.60
P	115.15	148.81	233.08	376.32	36.78	n.d.*
Sr	n.d.*	21.93	n.d.*	6.59	n.d.*	n.d.*
Zn	1002.03	2748.08	5103.13	5584.98	109.31	52.83

* - not detected;

The similar quantity is obtained with the rubber-1 method. Lower quantities of Mg were detected in all other gloves. The highest quantity of Na – 1305.58 mg·kg^{-1} was measured in TG nitrile pf using the rubber-1 method, and its similar quantity was detected in TG nitrile pf obtained with the rubber-2 method. Lower quantities of Na were detected in SC nitrile pf using both methods and in both vinyl gloves. The highest quantity of P – 376.32 mg·kg^{-1} was measured in TG nitrile pf using the rubber-2 method. A similar result was obtained using the rubber-1 method. Lower quantities of P were detected in SC nitrile pf using both methods, in both latex gloves using both methods and in vinyl pf gloves. The highest quantity of Sr – 21.93 mg·kg^{-1} was measured in latex pf using the rubber-2 method, its similar quantity was detected in latex pf using the rubber-1 method. Its lower quantities were detected in SC nitrile pf using the rubber-1method and in TG nitrile pf gloves using the rubber-2 method. The highest quantity of Zn – 5584.98 mg·kg^{-1} was measured in TG nitrile pf using the rubber-2 method, its lower quantity was detected in all other types of glove.

4. Discussion and conclusions

Use of Multiwave 3000 was a rapid and efficient way to digest the blister pack and medical gloves samples studied. By means of ICP-OES, different heavy metals (*Table 1*) were detected in all analyzed materials.

Various quantities of As, Fe, Na, P, Sn and Zn were found in blister pack. Fe – 1604.44 mg·kg^{-1} and Sn – 1668.13 mg·kg^{-1} constituted the biggest quantities. The following quantities of the elements were found in PVC layers: Na – 222.2 mg·kg^{-1}, Sn – 2873.05 mg·kg^{-1} and a small amount of Sr – 1.58 mg·kg^{-1}. Na – 591.93 mg·kg^{-1}, P – 124.36 mg·kg^{-1} and Sn – 1559.45 mg·kg^{-1} were found in PVC/PVdCp layers. In PVC/PVdCt Na – 338.51 mg·kg^{-1} and Sn – 1690.51 mg·kg^{-1} were found. In PE Fe – 45.98 mg·kg^{-1} and Zn – 6.24 mg·kg^{-1} were found.

Various quantities of Ca, Fe, K, Mg, Na, P, Sr Zn were detected in medical gloves. By means of both methods the highest concentrations of Ca and Zn were detected in p and pf latex gloves. In nitrile gloves we can see a similar trend, but higher quantities of Na and P were detected there compared to latex gloves. The highest concentration of Na and Zn was found in vinyl gloves.

From the obtained data it is seen that heavy metals concentrations in original blister packs are generally low. A high As content should be verified in future studies in order to confirm that such high As concentrations may only exceptionally occur. However, similar high values are confirmed for ashes obtained from incineration of medical wastes (Singh 2007). The Sn concentrations were found one order of magnitude higher than in average municipal solid waste samples (Ludwig 2003, Belevi 2000).

In gloves Sn was not detected, however, Zn concentrations were found to be about four times higher than in average municipal solid waste (Belevi 2000, Ludwig 2003) what is comparable with the concentrations found in highly contaminated waste wood (Wellinger 2012). It should be considered that a small inorganic content of gloves results in small amounts of ash residues. Therefore, it is expected that they contain elevated concentrations compared to residues from MSW incineration. This may be of particular concern if such ashes are disposed of in landfills without further treatment. Chlorine from PVC is strongly influencing the volatility of metals in incineration (Ludwig 2003). However, PVC gloves contain much lower Zn concentrations in contrast to the other gloves tested. Mixing different types of gloves could therefore influence the fate of Zn in an incinerator and its concentration in ash residues.

In this study only clean materials were investigated and contamination occurring during their use was not considered. In addition to Zn and Sn, other toxic heavy metals may have to be considered to assess real medical wastes.

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Sunkiųjų metalų medicininių pirštinių ir vaistų pakuotės mėginiuose analizė

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Terminis apdorojimas yra vienas plačiausiai ir dažniausiai taikomų medicininių atliekų apdorojimo būdų. Taikant šį apdorojimo būdą, stabilizuojamos pavojingos medicininės atliekos, sumažinamas jų kiekis ir svoris. Straipsnyje buvo analizuojamas sunkiųjų metalų kiekis dviejų rūšių medicininėse atliekose: blisterio pakelyje ir keturiuose jo sluoksniuose (polivinilo chloridas (PVC), polietilenas (PE), permatomas polivinilo chloridas, dengtas polivinilideno chloridu (PVC/PVdCt), ir polivinilo chloridas, dengtas polivinilideno chloridu su pigmentu (PVc/PVdCp)), bei trijų rūšių medicininėse pirštinėse (lateksinės medicininės pirštinės su milteliais ir be jų, dviejų rūšių nitrilinės medicininės pirštinės be miltelių ir vinilinės medicininės pirštinės su milteliais ir be jų). Visi išvardyti mėginiai buvo skaidomi naudojant aukšto slėgio skaidytuvą *Multiwave 3000* (Perkinelmer, Anton Paar). Kiekvienai medžiagai buvo naudojami skirtingi rūgščių mišiniai, kurie buvo parinkti pagal gamintojo rekomendacijas. Suskaidyti ir ištirpinti mėginiai buvo toliau analizuojami indukuotos plazmos optinės emisijos spektrometru (ICP-OES, Varian Liberty 110). As, Fe, Na, P, Sn, Sr ir Zn kiekiai buvo rasti lizdiniame pakelyje ir jo sluoksniuose, o Ca, Fe, K, Mg, Na, P, Sr ir Zn – medicininėse pirštinėse. Tik aplinkosauginiu požiūriu reikšmingi elementai – Sn ir Zn – buvo rasti tirtuose mėginiuose.