

What goes around comes around?

High levels of cadmium in low cost jewelry

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Abstract—Low-cost silver jewelry is sold for example in European open-air markets and in specialized shops for traditional handicrafts. While analyzing the material composition of such jewelry, high levels of cadmium were detected. The material composition of 21 samples was analyzed. 12 samples contained 20 percent of cadmium or higher levels (the highest value being 43.9 percent). Lower levels of nickel, copper, zinc and lead were also found. All samples were analyzed for metal migration into artificial sweat solution and 0.07 M hydrochloric acid. Due to the lack of threshold values for cadmium migration in Swiss law, the results were compared to nickel migration (artificial sweat solution) and lead (gastric acid). Compared to this threshold, the measured values for metal migration were excessively high. The vast majority of produced cadmium is used in Nickel/Cadmium cells and other components or substances used in electronic industries. It is out of the question that the observed levels of cadmium could originate from natural cadmium sources (ores). Therefore, it is very likely that inappropriate recycling techniques of electronics and/or Nickel/Cadmium cells account for the cadmium found in jewelry. A further analysis of cadmium isotopes will equally not clarify the origin of cadmium, as the isotopic fractionation of specific processes or cadmium ores is not accurate enough. In the end, evidence can only be found by describing the production chain of such low cost jewelry.

Index Terms—Cadmium, low cost jewelry, metal migration, gastric acid, artificial sweat solution, nickel-cadmium cells, lead silver solder

I. INTRODUCTION

At present, e-waste management systems in affluent societies differ greatly from those in developing countries and emerging economies. In affluent societies, e-waste

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management systems are built on the already existing municipal waste management systems. In contrast, extensive informal waste recycling sectors which only focus on waste fractions with economic value predominate in developing countries and emerging economies. Non valuables or even hazardous substances or waste fractions are ignored, left aside or simply dumped. This particularly applies to e-waste produced in circumstances in which all activities are entirely driven by economic valuable waste fractions. The final material recovery processes applied in the informal sector are of concern, as crude methods are applied to certain e-waste fractions, resulting in:

- Emission of hazardous substances to the detriment of the environment and human health [1-5].
- very low material recovery efficiency, not to mention the recovery of energy [6].
- Continuous dilution and blending of secondary materials -either intentionally or unintentionally.

As informal e-waste sectors are only driven by market incentives, it is logical that informal or semiformal businesses produce outputs which can be sold. Manual separation of e-waste can produce very pure material fractions. But if inappropriate methods are applied -such as chemical leaching of components containing precious metal, solder recovery on open fires, or other chemical or thermal methods- output fractions of metals from the informal sector are impure and of poor quality. Such methods are also limited in their degree of recovery efficiency. Nevertheless, there seems to be a demand for such relatively unrefined amalgams.

Until now, it has been difficult to trace where these unrefined metal fractions go to. For some metals; however, the market demand is clear: in India and numerous other countries private savings are frequently kept in the form of gold and silver jewelry. This creates a demand for precious metal recovery from electronics. It is worth noting that precious metal extracted from e-waste in the informal sector enters the market tax-free. Some indications for the whereabouts of other metals have been published. Weidenhamer has shown that lead from lead batteries has been used in the production of low cost jewelry from China [7]. His findings also indicate that some lead might originate from lead solder used in electronics [8]. But lead is a ubiquitous metal, present in many products, substances and fluids. Consequently, using lead as a trace metal from electronics is risky.

In contrast, cadmium is almost exclusively used in Nickel/Cadmium cells (Ni/Cd cells). 79% [9] to more than 95% [10] of worldwide cadmium production is used in such cells. Other applications of cadmium in electronics rely on the good thermal and electrical conductivity—a reason for which cadmium is used in switches for high current circuits and silver-cadmium solders. Almost all applications are components and parts of electronic or electrical equipment. This enables the metal to serve as a tracer for the whereabouts of recovered metals from e-waste.

Apart from the above mentioned applications of cadmium in electronics, cadmium can also be found as anti-corrosive protection (in form of amalgam) or as pigments and stabilizers in plastics (mainly in oxidized form). Cadmium oxides are bright yellow, orange or red. Compounds which contain cadmium are highly resistant to temperature and ultraviolet light. Primary cadmium is produced as a by-product from the extraction, smelting and refining of the nonferrous metals zinc, lead and copper.

The noble metal control department of Zurich airport in Switzerland carries out regular controls of imported jewelry. Silver jewelry from India has shown (1) considerable high levels of cadmium and (2) a level of silver content which is too low for precious metal control mechanisms -including higher import taxes- to be applied. As no regulation applies to such imports, the border authorities can do nothing to stop such products entering the country. The jewelry is typically sold on open-air markets and in specialized shops for traditional handicrafts. The skill and design of the jewelry is often considerable, with much of the work being done by hand. Fig 1 shows samples of the jewelry.



Fig 1 Sample of low cost silver jewelry

II. METHODS

Four different analytical methods have been applied (1) to analyze the metal content in the jewelry by atomic absorption spectroscopy (AAS) and the total content of all present elements with inductively coupled plasma mass spectrometry (ICP-MS), (2) to simulate the release of toxic metals onto the skin in an artificial sweat solution, (3) to simulate the release of metals to gastric acids in a hydrochloric acid. (4) In addition to the above, the layer structure of certain samples was examined by electronic raster microscopy.

To analyze the total metal concentration in the jewelry (1)

or the concentration of the migrated metal into different solutions (2, 3), either atomic absorption spectroscopy (AAS) or inductively coupled plasma mass spectrometry (ICP-MS) were used. The choice of the applied technique is dependent on the concentration which has to be measured. To simulate the migration of toxic metals onto the skin, an artificial sweat solution was used (2). To simulate the migration to gastric acids, a 0.07 M hydrochloric acid was used (3).

A. Total metal content of jewelry

The noble metal control at the custom offices detected—by means of desktop or handheld X-ray fluorescence (XRF) instruments- high cadmium levels within imported jewelry. Those samples which showed high levels were confiscated and sent for detailed analysis to the Official Food Control Authority of the Canton of Zurich. There, the total content of the elements: lead, cadmium, silver, copper and nickel, were examined. To do this, 500 mg of sample material was dissolved in concentrated nitric acid. The concentration of the various metals in solution have been analyzed either by AAS or ICP-MS, depending on the concentration level.

B. Simulation of metal migration by submersion in an artificial sweat test solution

As jewelry is designed to come in contact with skin and clothing, a simulation of the metal migration onto the skin was conducted according to the European Standard test method for release of Nickel [11]. This procedure is equivalent to the standard operation procedure for lead in the United States [12]. The artificial sweat test solution was composed of 0.5 % sodium chloride, 0.1 % lactic acid and 0.1 % uric acid in unionized, oxygen enriched water. The solution was buffered on a pH-value of 6.5 with ammonia solution of 1 % concentration. The jewelry was immersed in the sweat solution for 7 days at 30 °C, thus simulating the migration of metal in jewelry when worn on the skin. After seven days the concentration of dissolved metals in the sweat solution was measured by AAS, allowing the hypothetical amount of migrated metal onto the skin to be gauged. These values give a first base value from which the uptake of toxic metals through the skin can be estimated.

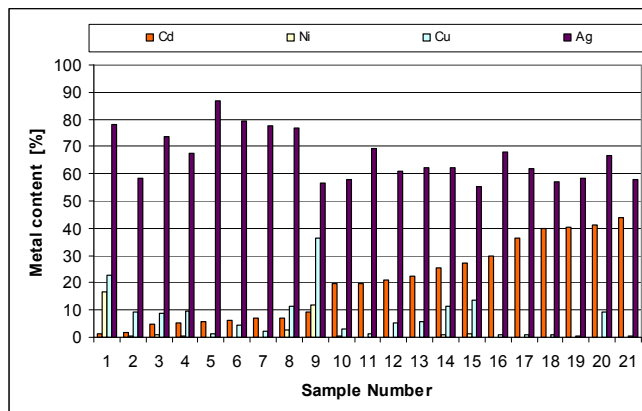


Fig 2. Metal content in percentage of the weight of 21 samples, sorted according to their cadmium content

C. Simulation of metal migration by submersion in hydrochloric acid

It is important to know which amount of metals may migrate when jewelry or parts of jewelry are swallowed. To simulate the solution of metals in gastric acid, the samples were submerged in a 0.07 molar hydrochloric acid solution of 37 °Celsius. The volume of solution was 50 times bigger than the sample mass. The migrations of lead, cadmium, silver and nickel were tested with ICP-MS after one, three and six hours. This procedure is also equivalent to the standard operation procedure for lead in the United States [12].

III. RESULTS

The metal concentrations of cadmium, silver, nickel and copper in the 21 drawn samples are shown in Fig 2. The average of cadmium concentration is 20 percent (standard deviation: 14.6), of silver 66 percent (standard deviation: 9), nickel 2 percent (standard deviation 5) and copper 6 percent (standard deviation 9). The average of lead concentration is below 0.1 percent and therefore not shown in Fig 2. The cadmium concentrations of the samples range from 1.4 (lowest value) to 43.9 percent (highest value).

After silver, cadmium was the metal most commonly found in the majority of samples. The results for metal migration into artificial sweat solutions and solutions of hydrochloric acid are only shown for cadmium, its concentration being exorbitantly high. Lead migration was also measured, but as the migration was very low (maximum 1.5 $\mu\text{g}/\text{cm}^2/\text{week}$), the detailed results are not shown. Fig 3 shows the release of cadmium into the artificial sweat solution after 7 days at 30 °Celsius as a function of the cadmium concentration of the samples. The results are shown in milligram release of cadmium per square-centimeter and week. The results do not show a clear correlation between concentration in the sample and migration into solution ($r^2 = 0.24$). Some of the samples with 20-25 percent of cadmium migrates more than 100 microgram per square-centimeter, whereas the majority of samples containing above 25 percent of cadmium released less than this amount.

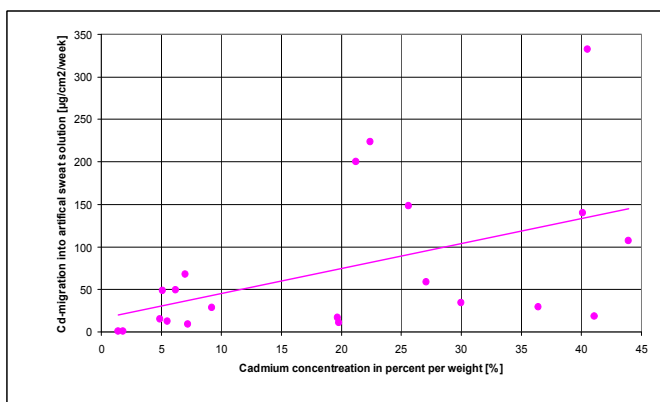


Fig 3 Cadmium migration in artificial sweat solution as function of cadmium concentration in sample

Fig 4 shows the migration of metal into hydrochloric acid

also as a function of the cadmium metal concentration of the samples. The migration of cadmium was measured after one, three and six hours -shown in Fig 4 as three different values. The migration of cadmium was measured in part per million (ppm). The results of cadmium migration into 0.07 M hydrochloric acid, also do not show a clear correlation between cadmium concentration in the sample and migration into the solution ($r^2=0.32$). The results of cadmium migration over a period of time (after one, three and six hours) vary between the samples too.

In general the migration after one, three and six hours shows a linear increase. Therefore, it can be concluded that the material of the jewelry is more or less homogeneous and that no sandwich structure with different alloys is present. The assumption that the jewelry has no sandwich structure is supported by the pictures of the light-optical microscope measurement. Seven samples have been orthogonally cut and analyzed with the light-optical microscope. Beside from some inclusions, no relevant changes in the structure of the jewelry material were to be seen on the pictures.

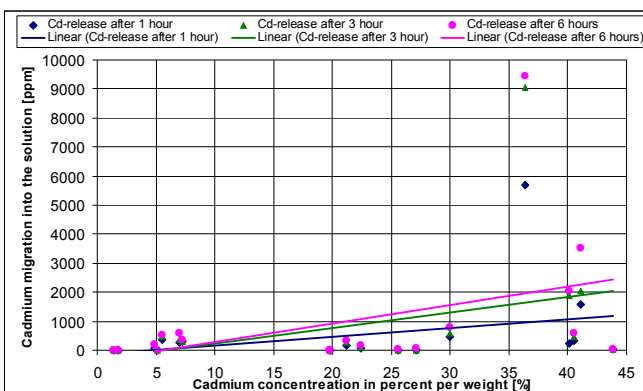


Fig 4 Cadmium migration in 0.07 M hydrochloric acid as function of cadmium concentration in sample

A. Origin of cadmium in jewelry

The applications of cadmium are Ni/Cd cells (79%), pigments (11%), coatings (7%), stabilizers (2%) and minor applications including special alloys (1%). Cadmium alloys include electrical conductivity alloys, heat conductivity alloys, and electrical contact alloys [9].

Silver cadmium alloys are frequently used as contact materials for make and break switches. Silver Cadmium Oxide contacts have good arc extinction and protect against contact welding while making contact, particularly for currents in the range of 100-3000 ampere [13]. The alloying of silver with cadmium produces materials with good corrosion resistance and low contact resistance characteristics. This process also provides them with good switching capability in AC circuits. The silver-cadmium alloy contacts are ductile materials and can be supplied in shapes and sizes similar to silver. [14]

Primary cadmium is a by-product of the zinc production. After the final purification steps for zinc, cadmium is left over as dust (distillation), or as filter cake (leaching).

IV. DISCUSSION

The cadmium concentrations of the samples range from 1.4 (lowest value) to 43.9 percentages (highest value). The migration into an artificial sweat solution lies between 0.8 and 332 $\mu\text{g}/\text{cm}^2/\text{week}$. As neither the Swiss, EU or US regulation have a threshold value for cadmium in jewelry coming into contact with human skin, these values are compared to the threshold value for nickel given in the Swiss and EU regulations [15]. Nickel should not exceed 0.5 $\mu\text{g}/\text{cm}^2/\text{week}$, hence, the cadmium migration is far above these values. As nickel has an allergenic potential this comparison has its limitations. It is worth mentioning that the metal migration into the solution is not proportional to the metal content in the samples (also indicated by the trend-line in Fig 3).

The migration of cadmium into hydrochloric acid after a submersion of the samples for one hour ranges between 0.08 mg/kg – 5.6 g/kg. After six hours, 0.19 mg/kg – 9.5 g/kg of cadmium migrate into the solution. These values greatly exceed the threshold values for cadmium migration of the European Norm for toys [16] which limit the migration to a maximum of 75 mg/kg. As expected, the migration increases with the exposure of time of the sample, indicated by the trend lines in Fig 4. However, like the migration of sweat solution, metal concentrations of the sample are not proportional to the migration values.

The release of metal also depends on the presence of other elements and the resulting hardness of the amalgam. In general one can say the harder the amalgam, the less metal is released.

The exact means by which the cadmium found its way into the silver jewelry must be determined and is the subject of further research. The sources of human cadmium exposure originate mainly from fertilizers, fossil fuels, iron/steel production [17] as well as through the smoking of cigarettes. Since July 2006, the EU directive on the reduction of hazardous substances bans the use of lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) in electronic products. [18]. The same substances are also forbidden to be used in electronics by the so called “China RoHS” [19]. Consequently, cadmium exposure from electronics can be expected to decrease in the future. But, primary produced cadmium, which is a by-product of the zinc mining industry, is mostly used in Ni/Cd cells [9] [10]. Yet batteries in general –including Ni/Cd cells- are explicitly excluded from both regulations. To encourage the returning and recycling of Ni/Cd cells, many efforts and voluntary measures have been discussed [20]. Ni/Cd cells will continue to be a source of cadmium emission to the environment as long as closed loop recycling is not installed.

One possible source of cadmium in silver jewelry might come from the recycling of Ni/Cd cells. However, the volumes are considerable as recovering cadmium from Ni/Cd cells requires a pyrolytic process to remove water and organic components, as well as an evaporation/condensation process to separate and recover cadmium and nickel as metals. Such processes are unlikely to occur in informal recycling

businesses as they do not apply industrialized processing techniques. A simple incineration of Ni/Cd cells would leave cadmium oxide as residue –most likely not the source of cadmium in jewelry.

Two other possible sources come into question:

- Input of primary cadmium from zinc refining processes
- Collection and blending of silver-cadmium solders into silver for jewelry production

The authors of [21], [22] and [23] suggest that the origin of cadmium, either from ores or anthropogenic sources, can be determined by the isotopic fractionation. According to the studies, the isotopic composition of cadmium is fractionated when high temperature processes, such as evaporation/condensation processes, are involved. As a result, cadmium and the characteristic isotopic composition is suggested as a tracer to determine a contamination of anthropogenic or geogenic origin. Primary cadmium can be gained by evaporation/condensation processes or by leaching and electrolytic deposition of residues from zinc and, to minor extends, of copper and lead refineries. Because isotopic fractionation certainly occurs during such processes, cadmium from e-waste recycling processes can not be distinguished by this means.

V. CONCLUSION

At present, neither the total cadmium content, nor the cadmium migration of consumer goods is regulated anywhere. Only the Canadian Children’s Jewellery Regulations under the Hazardous Products Act foresees a migration level of lead in jewelry. Nevertheless, article 37 of the Swiss act for food and consumer goods [24] stipulates that consumer goods which come in contact with skin, hair or mucous membrane may only release limited amounts of substances which are of no danger to human health. Which amount of cadmium is tolerable under this ordinance? In the two months during which the sample-collection was made, jewelry with up to 44% of cadmium was found to be imported. There is no reason to believe that such products will not continue to be imported. At some point in time this jewelry is discarded, dismantled or lost. It is unacceptable that a hazardous substance, such as cadmium, is allowed to come in direct contact with consumers in the form of jewelry. Nor is it acceptable that after use cadmium is disposed in an uncontrolled manner into the environment.

Metal content of imported jewelry will continued to be monitored. Once further evidence is found to support the evidence that cadmium and lead are substantial alloys in low cost jewelry, legal measures will be considered to limit such imports into Switzerland.

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