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ORIGINAL PAPER

Determination of allergy-causing metals from coins

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Abstract The majority of everyday items contain metals and their alloys, although many of them may be harmful to human health. Nickel, originating from different sources such as coins, jewelry, or buttons, represents the most common cause of contact allergy dermatitis. Therefore, the aim of this research work was to estimate the possible risk of allergy resulting from skin exposure to coins. In order to obtain information on the amounts of metals released by their daily use, extraction experiments of coins were performed applying an artificial acidic sweat solution during varying extraction periods. After extraction, the mass of the metals released (copper, iron, nickel, and zinc) were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES). The mass rate of Ni extracted per area considerably exceeded the permissible values according to the European norm: 50 times for 50-lipa coins, 80 times for 20-lipa coins, and 110 times for 1-kuna coins. This indicates that nickel-containing coins may represent a serious health hazard, especially to sensitive people.

Keywords Alloys · Spectroscopy · Transition metal compounds · Allergy · Coins

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Introduction

Nickel, gold, mercury, and chromium are today recognized as a frequent cause of allergic contact dermatitis. Allergy to nickel is a phenomenon with growing importance in the last years: 20% of the female population and 5% of the male population are estimated to be nickel-allergic. Elemental nickel and its salts cause dermatitis during solubilization in sweat occurring after prolonged contact with the human skin. This is characterized by a broad range of skin symptoms ranging from dryness, chapping, and inflammation to eczema and blisters. The mechanism of these effects is not well explained and not yet understood, but the reactions by nickel have been positively correlated with the expansion of specific $CD8^{+}$T cells [1].

Many researchers report the impacts of nickel-containing objects on human health, such as skin allergies and nickel-induced carcinogenesis [2, 3]. Some recent studies concluded that 1-euro and 2-euro coins release up to 320 times more nickel during a prolonged contact with the metal than the European standards permit, because of a galvanic reaction [4]. Further investigations proved the risk of nickel allergy by the manipulation of Euro coins [5]. Since allergic diseases are reaching epidemic proportions in the world [6], it is important to understand their mechanisms [7] and to quantify the possible effects of exposure to different allergens.

In Denmark, nickel is still the most frequent contact allergen, even though the nickel sensitivity in young women has decreased due to reduced exposure [8]. The physiological response in humans to nickel depends on the following factors: the physicochemical properties of the Ni compounds, the effective concentration, the duration and type of exposure, and the sensitivity and well-being of the individual exposed [9].

Some people develop dermatitis from even brief contact with nickel-containing items, while others observe problems only after many years of skin contact. The European directive, “The Dangerous Substances and Preparations (Nickel Safety) Regulations,” adopted in 2000 forbids selling of any products that come into prolonged contact with the skin, if those release more than 0.5 μg Ni/cm^2 per week [10]. The new directive also stipulates that analysis should be carried out in accordance to other norms, such as BS EN1811:1999 for nickel release and BS EN12472 for nickel release from coated products [11–14]. A Swedish study published before 2000 revealed that 25% of the objects that were supposed to come into skin contact showed a positive nickel test [15].

The clinical significance of nickel release from coins was taken into consideration when deciding the composition of euro coins [16, 17]. The world’s first coin was the “Lydian Lion,” minted around 800 BC in Lydia [18], but one of the first nickel-alloy coins was issued in ancient Bactria, today Afghanistan, in 139 BC. The appearance of nickel coins in modern history can be linked to the nickel Belgian coins produced in 1860 and the United States’ five-cent coin, commonly called a “nickel” (made of 25% nickel and 75% copper) that was produced in 1865 [19]. The first nickel coin of the pure metal was made in 1881 [20]. The Croatian National Bank issued coins in denominations of 1, 2, 5, 10, 20, and 50 lipa and 1, 2, 5, and 25 kuna in 1993 containing nickel.

Not only nickel, but also other metals in coins may cause allergic skin problems. For example, copper was identified as the cause of dermatitis on the fingertips and eyelids of a bingo-hall worker with exposure to 2-euro coins [21]. For this reason, nickel, copper, and iron were determined by Fournier in euro coins by inductively coupled plasma-optical emission spectrometry (ICP-OES) [22]. Recently, a case of a taxi driver was reported who exhibited itchy, erythematous,occurring scaly plaques on his thumb [23]. The aim of this work was to estimate the possible risk of nickel allergy resulting from exposure to different Croatian coins, in which the nickel part can vary between 0 and 23% of the alloy used for minting of the coin. Furthermore, the release of copper, iron, and zinc was investigated.

Table 1 Average composition, diameter, and weight of the investigated metal coins

Coins	5 lipa	10 lipa	20 lipa	50 lipa	1 kuna
Diameter/mm	18	20	18.5	20.5	22.5
Mass/g	2.50	3.20	2.90	3.65	5.00
Cu/%	72.5	72.5	0	0	65
Fe/%	0	0	95	95	0
Ni/%	0	0	5	5	23.2
Zn/%	27.5	27.5	0	0	11.8

Results and discussion

In this research work, five different coins used in Croatia were investigated (Fig. 1, Table 1).

Three of the five investigated coins contain 5–23% of nickel; thus, they may provoke nickel allergy. Determination of copper, nickel, iron, and zinc was performed by ICP-OES, since it offers the possibility for a simultaneous determination of many elements of interest. Working parameters are given in the Experimental.

By performing measurements using the chosen axial-viewed torch system, many advantages can be observed, such as reduced interferences, improved detection limits, and a broader achievable linear dynamic range [24]. The calculated limits of detection and the selected spectral lines (bold values) used for ICP-OES analyses are presented in Table 2.

The concentration ranges of the elements investigated in the sweat extracts (minimum–maximum in μg cm^{-3}) after 1 h of extraction were: Cu 0.54–4.68, Fe 0.06–0.27, Ni 0.81–3.37, and Zn 1.55–6.51, and at the end of the experiments (240 h): Cu 110–750, Fe 105–133, Ni 35–240, and Zn 22–113. The measured concentrations of copper, iron, nickel, and zinc after extraction during different time periods are presented in Fig. 3. The exhibited positive reactions to the provocative patch test on the human skin ranged from erythema to eczema, spreading papules, and vesicles. A severe skin reaction, occurring after the patch test, is presented in Fig. 2.

The picture of the arm of the volunteer was taken 12 h after the coins’ removal. It clearly demonstrates the occurring allergenic reaction caused by nickel-containing coins. This research work showed that these three coins

Fig. 1 Pictures of the Croatian coins investigated: 5, 10, 20, 50, and 1 kuna

Table 2 Detection limits in artificial acidic sweat solution

Element	Limits of detection/ng g^{-1} in acidic sweat solution (λ/nm)
Cu	1.7 (324.754), 0.1 (327.396), **0.1 (224.700)**,
Fe	19.7 (259.940), 1.7 (238.204), **1.9 (239.562)**,
Ni	**6.4 (221.647),** 3. 8 (232.003), 2.8 (341.476),
Zn	4.7 (202.548), 7.9 (206.191), **3.0 (213.856)**,

Bold values indicate the selected lines

Fig. 2 Allergic skin reaction caused by 45-h exposure to coins; the picture was taken 12 h after the removal of the coins

caused allergic reactions (20, 50 lipa, and 1 kuna coins), while the other two did not (5 and 10 lipa). The allergic skin reactions (erythema, spreading papules, and vesicles) remained several days after the removal of the coins.

All heavy metals including nickel were strongly extracted from the coins by sweat after 240 h. For this reason, nickel as well as the other metals under study extracted from the coins may have an important impact on the immune system. The calculated mass release rates expressed as µg Ni/cm^2 per week are presented in Table 3.

The nickel release rates for the coins under study exceed the permissible value 50 times for 50-lipa coins, 80 times for 20-lipa coins, and 110 times for 1-kuna coins. Those results were compared to the amounts of other heavy metals released (Table 4).

According to our results (Fig. 3), handling of metal coins transfers significant amounts of nickel, copper, iron, and zinc to the skin.

People sensible to nickel or some other element should protect themselves from allergic reactions by wearing gloves or by preventing a prolonged contact with the skin. The rate of extractable Ni from coins exceeded the permissible value from 50 (50 lipa coins) to 110 times (1-kuna coins). This is much less than the values found for Euro coins, with the limits exceeded 320 times [4]. It is important to emphasize that the normal use of coins does not involve prolonged skin contact. Therefore, nickel present in the investigated coins represents a possible health hazard only to sensitive individuals and to people being exposed to the coins for a prolonged time. In such cases, protective equipment like gloves should be used.

Table 3 Ni release calculated according to the EU nickel directive regarding to the surface area of the coins and the time of exposure

Coin	5 lipa	10 lipa	20 lipa	50 lipa	1 kuna
Diameter/mm	18	20	18.5	20.5	22.5
Mass/g	2.50	3.20	2.90	3.65	5.00
Ni in coin/%	0	0	5	5	23.2
Ni in µg/(cm^2 week)	0	0	39.42	24.25	56.70

Week refers to a 40-h working week

Table 4 Ni release compared to Zn, Cu, and Fe amounts

Coin	5 lipa	10 lipa	20 lipa	50 lipa	1 kuna
Diameter/mm	18	20	18.5	20.5	22.5
Mass/g	2.50	3.20	2.90	3.65	5.00
Cu in µg/(cm^2 week)	38.93	14.32	0	0	52.40
Fe in µg/(cm^2 week)	0	0	8.19	6.67	0
Ni in µg/(cm^2 week)	0	0	39.42	24.25	56.70
Zn in µg/(cm^2 week)	13.47	5.67	0	0	6.80

Experimental

Samples

The tests covered five different samples of coins (5, 10, 20, 50 lipa, and 1 kuna coins presented in Fig. 1) used in Croatia. The characteristics of the coins, such as the composition of the alloy used, weight, diameter, and thickness, are presented in Table 1. The coins may be used as a model items for estimating the harmful impact of metal objects, due to their metal composition with 0–23% Ni.

Chemicals and standard solutions

All chemicals (nitric acid, sodium chloride, ammonium chloride, sodium hydroxide, acetic acid, lactic acid, and urea) and the 1,000 µg cm^{-3} standards used were of p.a. grade, supplied by Merck, Darmstadt, Germany. The acidic sweat solution was prepared according to EN 1811 standard.

Instrumentation

The inductively coupled plasma-optical emission spectrometer used was a Perkin Elmer Optima® 3000 XL. The instrument was equipped with a standard one-piece extended torch with a quartz injector tube, a cyclone spray chamber, and a concentric nebulizer. ICP-OES measurements were performed using an axial view. Optical system: Echelle; detector: solid-state detector; RF frequency: 40.68 MHz; power: 1,300 W; plasma gas flow: 15.0 dm^3/min; auxiliary gas flow: 0.5 dm^3/min; sample flow rate: 0.8 cm^3/min.

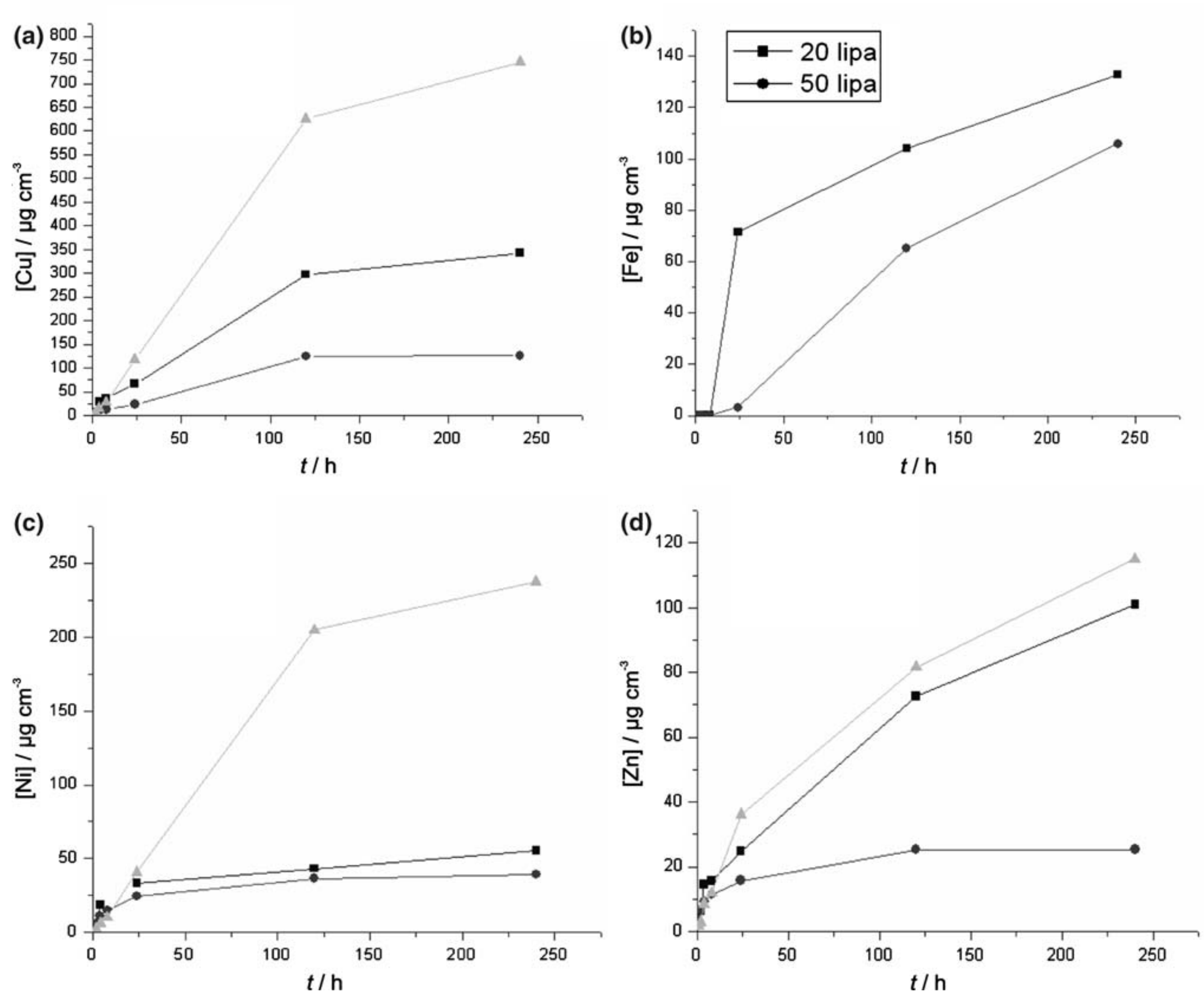

Fig. 3 Metal concentrations measured in extracts from coins in the artificial acidic sweat solution: **a** Cu concentrations in the sweat solution (*filled square* 5 lipa, *filled circle* 10 lipa, *filled triangle* 1 kuna); **b** Fe concentrations in the sweat solution (*filled square* 20 lipa, *filled circle* 50 lipa); **c** Ni concentrations in the sweat solution (*filled square* 20 lipa, *filled circle* 50 lipa, *filled triangle* 1 kuna); **d** Zn concentrations in the sweat solution (*filled square* 5 lipa, *filled circle* 10 lipa, *filled triangle* 1 kuna)

Sample preparation

All samples were taken from different containers after different time periods in the artificial sweat solution. The extracts were taken after 1, 2, 4, 8, 24, 120, and 240 h and analyzed by ICP-OES for copper, iron, nickel, and zinc. According to the "EU nickel directive," the mass of extractable Ni was calculated regarding the surface area of the coins and the time of exposure.

Patch test

The patch study was performed with the volunteer's permit. For a skin allergy test, the coins were attached by adhesive tape to the subject's arm, so that the skin area was completely covered. The contact time was 45 h; thereafter the elicited reaction was monitored. The result of the patch test study is presented in Fig. 2.

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