



A pilot study on the content and the release of Ni and other allergenic metals from cheap earrings available on the Italian market

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Abstract

The capability of alloys used in cheap jewellery to release metal ions on contact with the skin causing allergic contact dermatitis (ACD) is generally acknowledged. To reduce the diffusion of the Ni-induced ACD the Council Directive 94/27/EC [Council Directive 94/27/EC of 30 June 1994. Official Journal L 188, 22/07/1994, 1.] limited the total Ni content in alloys and its release rate in artificial sweat. In this work, three different aspects were explored: i) the frequency of skin sensitization to Ni-containing earrings in patients before and after the introduction of the Directive's limit; ii) metal composition of alloys by X-ray analysis; iii) metal leaching in artificial sweat followed by Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS) quantification. Well-known allergenic metals, as Ni, Cr and Co, and possible emergent allergens, as Al, Ag, Au, Cd, Cu, Fe, Ir, Mn, Pb, Pd, Pt, Rh, Sn, V and Zn, were studied.

Results showed that the frequency of allergy due to earrings did not decrease after the introduction of the Ni limit: in 1994 and in 2005 patients positive to Ni patch tests were 54.3% and 53.5%, respectively. The earring components analyzed were Fe-based or alloys of Cu/Zn or Fe/Cr/Ni, plated with a thin film of precious metal (Ag, Au) which, in several cases, was combined with a Ni layer beneath. Five out of 10 items were not in compliance with the Ni Directive 94/27/EC having a total Ni content $>0.05\%$. In three cases the release of Ni concentrations was higher than the safe sensitizing limit given by the above mentioned Regulation (*i.e.*, $<0.5 \mu\text{g}/\text{cm}^2/\text{week}$). The release of Cu and Zn was very variable among the different pieces (Cu: $0.134\text{--}30.9 \mu\text{g}/\text{cm}^2/\text{week}$; Zn: $0.141\text{--}160 \mu\text{g}/\text{cm}^2/\text{week}$); two objects released high amounts of Fe (358 and $586 \mu\text{g}/\text{cm}^2/\text{week}$) and one released considerable Mn ($21 \mu\text{g}/\text{cm}^2/\text{week}$). Lead was released from 70% of the objects, while Ag, Al, Cd, Co, Cr and Sn from *ca.* 30% of the items and concentrations of these elements were well below $0.5 \mu\text{g}/\text{cm}^2/\text{week}$. Vanadium was released by only one item whereas Au, Ir, Pd, Pt and Rh were never leached.

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1. Introduction

Ni is a chemical element considered as one of the primary sources in causing allergic contact dermatitis (ACD). In fact, 10–15% of women and 2–5% of men of

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the overall European population develop allergies to this metal (Lidén and Norberg, 2005). This is related to the presence of Ni in metallic alloys used to produce various kinds of objects that daily come into contact with the skin creating sensitization and elicitation considered the first steps in the development of ACD. The corrosive power of the human sweat allows the diffusion of metal from the object into the skin. The items largely accountable for ACD are those present on dresses such as buttons, clasps, zippers, clips and belt buckles or jewels as earrings, necklaces, bracelets, pins, watches, *etc.* (Dotterud and Falk, 1994; Ehrlich et al., 2001; Kanerva et al., 1994; Menné, 1994). Taking into account their large diffusion among people, Euro coins containing Ni have been recognized to be potential allergizing objects as well (Seidenari et al., 2005). The capability of Co and Cr in causing ACD is also documented even if its prevalence is lower compared with Ni (Fowler, 1998). These elements are mainly used in occupational fields, *i.e.* building materials, electronic and electroplating industry, glass, ceramic and paint, photograph development and tannery industry, and, as a consequence, the observed ACD cases predominantly referred to people exposed to these metals (Motolese et al., 1993; Fowler, 1998; Barré Hansen et al., 2006). Nevertheless, there are some evidence of skin sensitization due to the exposure to Ni-alloyed jewellery containing Co or to Cr-plated cellular phones (Hindsén et al., 2005; Seishima et al., 2003). With reference to precious metals, the use of Ag, Au and the platinum group elements (PGEs, namely Ir, Pd, Pt and Rh) in jewellery alloys and plating is nowadays frequent (Vilaplana and Romaguera, 1998). Despite these metals in the elemental form are normally stable and safe for the skin, their salts gave positive patch-test reactions in pre-sensitized people (Cristaudo et al., 2005). Gold was responsible for ACD incidence due to its large use in pierced earrings (Ehrlich and Belsito, 2000; Lidén et al., 1998) and the synergy between Au and Hg is also suggested in cases of hypersensitivity (Osawa et al., 1994). A jewel worker which developed an Ag-ACD after continuative handling of this metal (Agarwal and Gawkrödger, 2002) and one case of Pd allergic contact granuloma due to ear piercing (Goossens et al., 2006) are other examples of sensitization caused by metals. Among its various uses, manganese is a metal adopted in dental alloys. In this frame, the continuative contact of the prosthesis with saliva and mucosa posed a serious risk in generating Mn-induced ACD (Pardo et al., 2004). Aluminium is described as a rare sensitizer, but Al-ACD cases have been evidenced after occupational contact in machine construction plant or by hyposensitization therapies or vaccinations with substances containing Al (Akyol et al., 2004; Hindsén,

2005; Peters et al., 1998). As regards Sn, in spite of its wide use in many fields including alloys for imitation jewellery, only rare cases of skin sensitization to metallic Sn have been reported (de Fine Olivarius et al., 1993). Also other metals such as Cd, Pb and V gave sensitization after occupational exposure or percutaneous absorption by cosmetics (Motolese et al., 1993; Sainio et al., 2000). As regards Cu and Zn, they are considered to be a rare cause of ACD. Nevertheless, their presence in intrauterine and dental devices, adornment, jewels and Euro coins was responsible for some cases of Cu- and Zn-ACD (Hostynek and Maibach, 2004; Seidenari et al., 2005; Shimizu et al., 2003; Wöhrle et al., 2001).

In this view, to reduce the diffusion of the Ni-induced ACD, the presence and the release of this metal from objects that come in direct and continuative contact with the skin have been regulated by the Council Directive 94/27/EC. This document reports a limit of 0.05% (*i.e.*, 500 µg/g) for the total Ni content in alloys and a maximum Ni release rate of 0.5 µg/cm²/week in artificial sweat. Recently, the Commission Directive 2004/96/EC restricted the Ni release rate from piercing post assemblies to 0.2 µg/cm²/week for much consumer's protection. For the other metals which can give allergological effects, no legislation has been drawn out to limit their use in jewellery products.

In the light of this background and after more than ten years from the emanation of the Directive 94/27/EC, it is of great interest to assess the Directive's effectiveness in limiting the consumer's contact with this potential allergen. This may be performed by both monitoring the prevalence and the incidence of Ni dermatitis and checking the market for compliance with the Directive requirements. The aims of this study were: i) to compare the frequency of skin sensitization to Ni before and after the Directive's limit; ii) to investigate the metallic composition of the most common alloys for cheap earrings available on the Italian market; iii) to quantify 18 metals released from jewels in artificial sweat. Not only Ni, Cr and Co, but also other new allergens, such as Al, Ag, Au, Cd, Cu, Fe, Ir, Mn, Pb, Pd, Pt, Rh, Sn, V and Zn, were studied.

2. Experimental

2.1. Samples and reagents

A total number of subjects equal to 931 in 1994 and to 867 in 2005 were subjected to patch tests at the San Gallicano Dermatological Institute because of earlobe allergic contact dermatitis. The tests were carried out by the Finn-Chamber (Epitest Ltd, Oy, Tuusula, Finland)

on Scampor system and utilizing allergens of the Hermal-Trolab series (Reinbek, Germany). The readings were evaluated according to the standard criteria of the International Contact Dermatitis Research Group.

Table 1 reports the photos of the ten components used in cheap jewellery selected for this study. All the items were purchased from small shops in Rome and were selected to represent the most frequently sold products and models (*i.e.*, earring wires, clip-on earrings and earring studs) coloured or plated with different materials (*i.e.*, gold, silver and bronze). All the specimens were sold as “Ni-free” products, but this indication was not reported on the label.

Reagents used for total decomposition were HNO₃ (ROMIL Ltd., Cambridge, UK) and HCl (Carlo Erba, Milan, Italy), both at ultrapure-grade. For the leaching test, suprapure-grade NaCl (Merck, Darmstadt, Germany), lactic acid with a purity >98% (Chem Service, West Chester, USA), urea with a purity >98% (ICN Biomed-

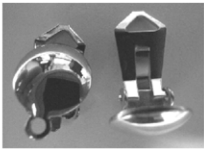
cals, Inc., Aurora, USA) and suprapure-grade NH₃ (Merck, Darmstadt, Germany) were used. High-purity deionized water (EASY-pure, PBI, Milan, Italy) was used for dilution of samples and standards. Single-element standard solutions (SPEX, Edison, NJ, USA) at the concentration of 1 mg/ml were used to prepare calibrants.

2.2. Instrumentation

Analysis of the samples was performed by a scanning electron microscopy (SEM) Philips XL30 equipped with a thin-window EDAX system for X-ray microanalysis by Energy-dispersion spectrometry (EDX). Magnifications from 40× to 2000× and beam energy of 15 KeV were used.

The EDX (0–15 keV) spectrum was acquired to detect the presence of Ag, Al, Au, Cd, Cr, Cu, Fe, Ni, Mn, Pb, Pd, Sn and Zn in the samples. The intensities of the characteristic X-ray lines were converted to the

Table 1
Characteristics of the selected cheap earrings

Sample (no.)		Type	Plating
1		Fish hook earring wire	Au
2		Fish hook earring wire	Ag
3		Fish hook earring wire	Bronze coloured
4		Lever-back earring wire	Au
5		Lever-back earring wire	Ag
6		Clip-on earring	Au
7		Clip-on earring	Ag
8		Stud	Ag
9		Stud	Au
10		Stud	Ag

corresponding atomic concentration by a standardless ZAF correction method.

A Milestone Ethos 900-Mega II microwave (MW) oven with a PTFE-vessel rotor (FKV Milestone, Milan, Italy) was employed for digesting samples. A 720/NE model water-bath (ASAL srl, Florence, Italy) for leaching experiments was adopted.

An Element II Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS, Thermo Finnigan, Bremen, Germany), equipped with Meinhard-type glass nebulizer, water-cooled Scott spray chamber, torch with guard electrode device and nickel interface cones, was used for metal quantification. The SF-ICP-MS measurement parameters were: radiofrequency power, 1200 W; plasma flow, 14.0 l/min; auxiliary flow, 0.90 l/min; sample flow, 0.85 ml/min; mass resolution, 300 m/ Δ m (low resolution, LR) for Ag, Au, Cd, Ir, Pb, Pt and Sn, and 4000 m/ Δ m (medium resolution, MR) for Al, Co, Cr, Cu, Fe, Mn, Ni, Pd, Rh, V and Zn. In SF-ICP-MS quantifications, the standard addition approach for calibration on 5 concentration levels was used in order to keep the matrix-induced variations under control. Due to the very different and inhomogeneous metallic composition of the jewels, it was not possible to find a suitable internal standard (IS) with ionization energy similar to that of the analytes, not occurring naturally in the samples. As an alternative to the use of an IS, a check sample (*i.e.*, the lowest concentration point of the calibration curve) was repeatedly measured during the analytical sequence.

2.3. Sample treatment

The manufactured objects were analyzed without being destroyed by means of non-invasive EDX. Afterwards, some of them were disassembled and, in order to highlight the internal structure, their surface was scraped off before being analyzed.

In the case of acid digestion for the SF-ICP-MS analysis of total metal content, earrings were weighed into PTFE vessels. A mixture of HNO₃ and HCl, 6+3 v/v, was added to each vessel and MW irradiated under the following cycle: 10 min at 250 W; 5 min at 400 W; 5 min at 500 W and 5 min at 600 W. After cooling, samples were quantitatively transferred into polystyrene liners and diluted up to 15 ml with high-purity deionized water. Samples were digested in triplicate and reagent blanks run together with matrices. Both were considered in the final evaluation. For the SF-ICP-MS analysis, samples were further diluted 1:10.

Parts expected to come into contact with the skin were subjected to leaching experiments. A sweat-simulating aqueous solution composed by urea (0.1%), NaCl (0.5%) and lactic acid (0.1%) was used. Ammonia solution (1%) was used to adjust the pH solution at the value of 6.50. Three samples of each kind of earring were soaked in the artificial sweat in the ratio 1:1 (*i.e.*, 1 ml of solution for 1 cm² of the object's surface) and placed in a water-bath at 30 °C for 1 week. Details of the method are reported in the regulation UNI EN 1811 (2000). The resulting solutions were directly SF-ICP-MS analyzed.

Table 2
SF-ICP-MS method parameters

Element	<i>m/z</i>	Abundance (%)	Resolution (m/ Δ m)	Interferences separated with the selected resolution
Ag	109	48.2	300	^a
Al	27	100	4000	¹¹ B ¹⁶ O, ¹⁰ B ¹⁶ OH, ¹³ C ¹⁴ N, ¹² C ¹⁵ N, ¹² C ¹⁴ NH, ⁵⁴ Fe ⁺
Au	197	100	300	^a
Cd	111	12.8	300	^a
Co	59	100	4000	⁴⁰ Ar ¹⁹ F, ⁴³ Ca ¹⁶ O, ⁴¹ K ¹⁸ O, ³⁶ Ar ²³ Na, ⁴² Ca ¹⁶ O ¹ H
Cr	52	83.8	4000	⁴⁰ Ar ¹² C, ³⁶ Ar ¹⁶ O, ³⁸ Ar ¹⁴ N, ³⁵ Cl ¹⁷ O, ³⁷ Cl ¹⁵ N, ³⁵ Cl ¹⁶ O ¹ H
Cu	63	69.2	4000	⁴⁰ Ar ²³ Na, ⁴⁴ Ca ¹⁹ F
Fe	56	91.7	4000	⁴⁰ Ar ¹⁶ O, ⁴⁰ Ca ¹⁶ O, ³⁹ K ¹⁷ O, ⁴⁰ K ¹⁶ O
Ir	193	62.7	300	^a
Mn	55	100	4000	³⁷ Cl ¹⁸ O, ⁴⁰ Ar ¹⁵ N, ³⁹ K ¹⁶ O, ⁴⁰ Ar ¹⁴ N ¹ H
Ni	60	26.1	4000	⁴⁴ Ca ¹⁶ O, ²³ Na ³⁷ Cl, ³⁶ Ar ²⁴ Mg, ¹²⁰ Sn ⁺⁺
Pb	208	52.4	300	^a
Pd	105	27.3	4000	⁴⁰ Ar ⁶⁵ Cu, ⁶⁸ Zn ³⁷ Cl, ⁷⁰ Zn ³⁵ Cl
Pt	195	33.8	300	^a
Rh	103	100	4000	⁴⁰ Ar ⁶³ Cu, ²⁰⁶ Pb ⁺⁺ , ⁶⁸ Zn ³⁵ Cl, ⁶⁶ Zn ³⁷ Cl
V	51	99.8	4000	³⁵ Cl ¹⁶ O, ³⁷ Cl ¹⁴ N, ⁴⁰ Ar ¹¹ B, ³⁶ Ar ¹⁴ N ¹ H
Sn	120	32.6	300	^a
Zn	64	48.6	4000	⁴⁰ Ar ²⁴ Mg, ⁴⁸ Ca ¹⁶ O, ³⁶ Ar ²⁸ Si

^a No relevant interference for the considered matrix.

3. Results and discussion

3.1. Patch tests

In 1994, testing on 931 patients, a percentage of 54.3% resulted to be positive to Ni. In 2005, among the 867 tested subjects, 53.5% of them reacted to Ni. Comparing the data, there wasn't a difference in the frequency of allergy to Ni between subjects sampled in 1994 and 2005. This result evidenced that Ni allergy has not decreased after the introduction of the Ni limit confirming that a high risk for the population in skin sensitization to this metal is still persisting.

3.2. SF-ICP-MS method

The SF-ICP-MS was the technique of election, due to the lower detection limits compared with other techniques, allowing to quantify even those elements, as the PGEs, whose concentration in the matrix was very low. Isotopes and instrumental resolution (*i.e.*, changing from LR, 300 m/ Δm , to MR, 4000 m/ Δm) were carefully selected in order to eliminate spectral interferences and maintain a suitable sensitivity at the same time. Table 2 shows the isotopes and the resolution setting used for the study. Elements, not hampered by any relevant interference, were quantified in the LR resolution and by using their most abundant mass to reach the maximum of sensitivity, except for Ag and Cd. Silver was not quantified at mass 107 (abundance of 51.8%) because it was interfered by $^{40}\text{Ar}^{67}\text{Zn}$ and Cd was not determined at mass 114 (abundance of 28.7%) because it was covered by the isobaric interference of ^{114}Sn . Aluminium, Co, Cr, Cu, Fe, Mn, Ni, Pd, Rh, V and Zn

were quantified at MR to avoid serious interfering species which would lead to false high values. In fact, the addition of several reagents and salts occurring during the sample treatment and the metallic matrix with high contents of Cu, Fe and Zn created not negligible interferences. For example, the formation of CN^+ , ArN^+ , ArNH^+ overlapped the signals of Al, Cr, Mn and V; ClO^+ and ClOH^+ heavily covered the signal of Cr, Mn and V; ZnCl^+ and ArCu^+ interfered with Pd and Rh signals and ClN^+ laid on the masses of V and Cr. Moreover, the high content of Ca, K, Na and Mg in the mixture used for leaching formed several interfering oxides, argides and chlorides posing serious problems for the quantification of Co, Cu, Fe, Mn, Ni and Zn. In this study, by using the MR mode, all these interferences were shifted far from the analytical peak and, thus, unequivocally separated. As for the LR, the most abundant isotopes were selected for each element except for Ni which, at mass 58, was interfered by the isobaric ^{58}Fe , and for Pd, which at mass 106 (the most abundant one), was interfered by ArZn^+ .

The developed SF-ICP-MS method had limits of quantification (LoQs), based on the 10σ criterion, equal to or below 5 ng/g for Ag, Au, Cd, Co, Ir, Pb, Pd, Pt, Rh, Sn and V, and *ca.* 25 ng/g for Al, Cr, Mn and Ni. Copper, Fe and Zn had the highest LoQs (*i.e.*, 100 ng/g), but this was not a problem because of their abundance in the alloys.

3.3. Characterization of jewels by EDX

The fish hook and the lever-back earring wires were all based on the same metallic composition, *i.e.*, a Cu/Zn alloy. Sample no. 2 was manufactured in Fe and it was the earring wire which contained Ni at the highest amount. In

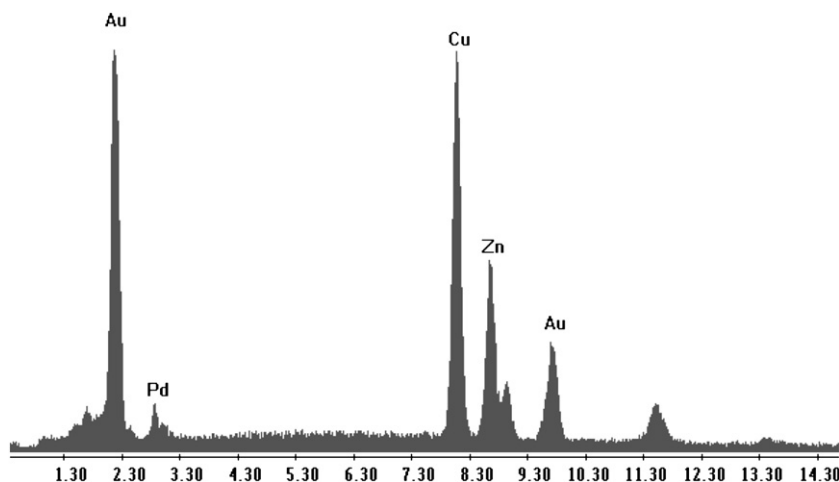


Fig. 1. EDX analysis spectrum of the gold-plated fish hook (no. 1) based on a Cu/Zn alloy.

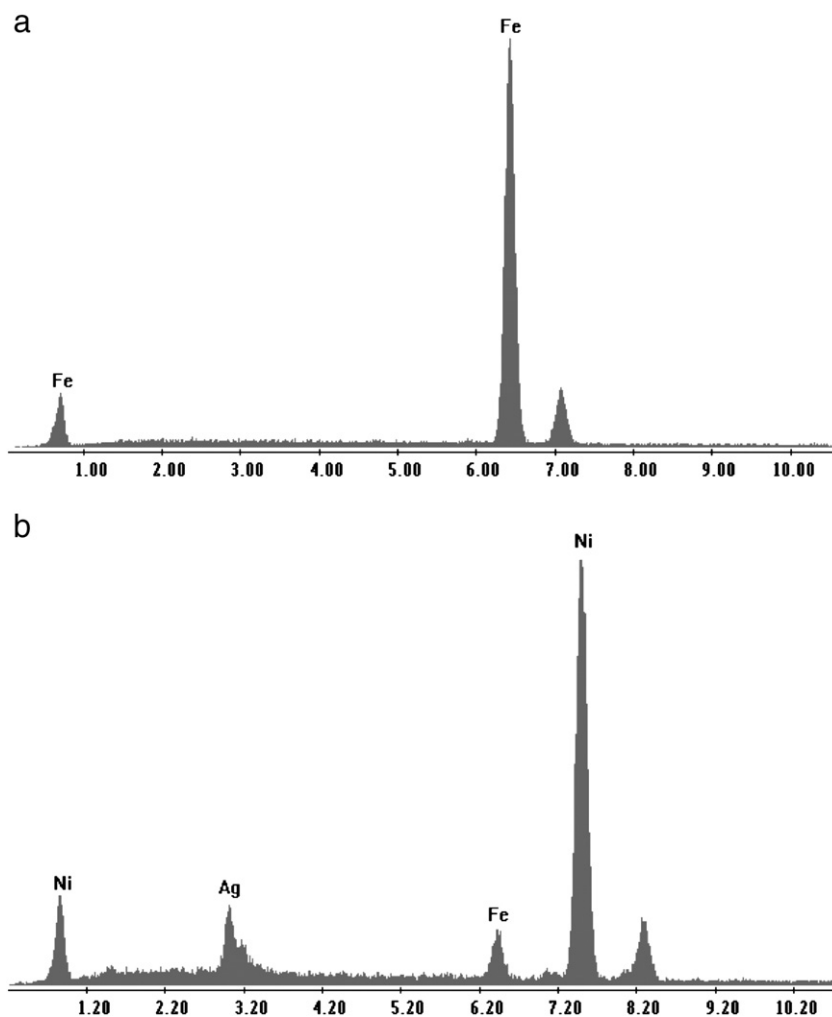


Fig. 2. EDX analysis spectrum of the silver-plated fish hook (no. 2): a) the Fe base; b) the Ni layer plated with Ag.

particular, sample no. 1 had the inner part constituted by Cu and Zn while the surface was uniformly covered by a thin layer of Au with a small percentage of Pd (Fig. 1);

sample no. 2 was made of pure Fe, the surface was uniformly covered by Ni, plated, in its turn, with a thin layer of Ag (Fig. 2a and b); sample no. 3 presented internal

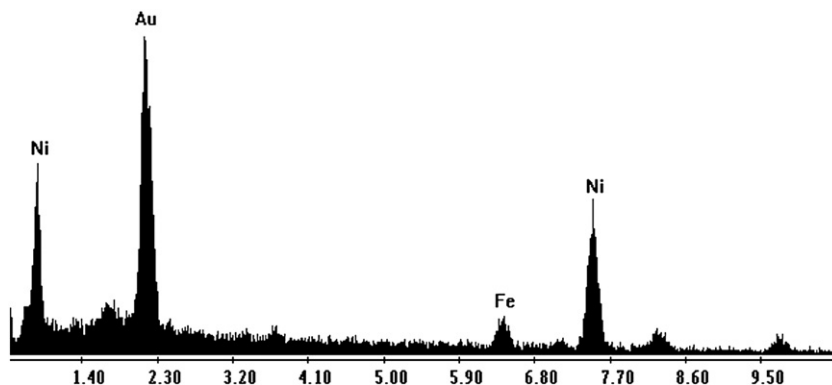


Fig. 3. EDX analysis spectrum of the Ni intermediate layer of the gold-plated clip (no. 6).

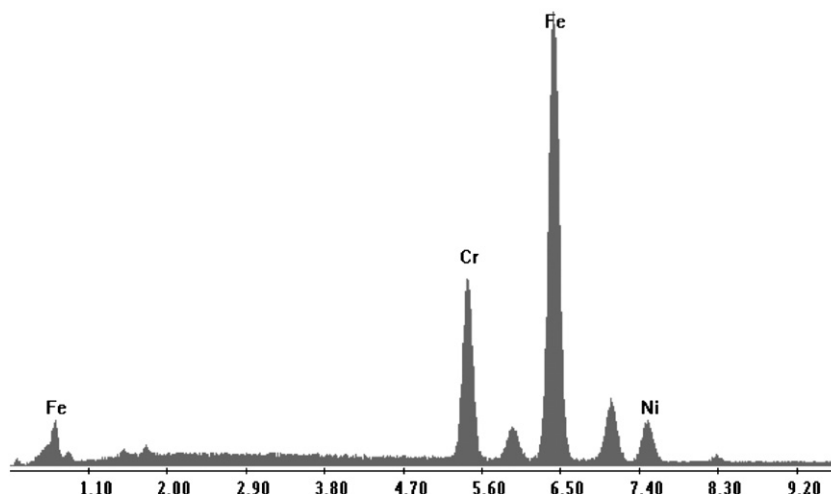


Fig. 4. EDX analysis spectrum of the silver-plated stud (no. 8) based on a steel composition.

and external parts of the object constituted by Cu/Zn; samples no. 4 and 5 internally were a Cu/Zn alloy, covered by a film of Sn; Au (no. 4) and Ag (no. 5) were present as the external layer.

The two clip-on earrings (nos. 6 and 7) had a different metallic structure depending on the components (button or clasp), and both contained high levels of Ni. In clip 6, the button had a core of Fe, an intermediate stratum of Ni, an external thin film of Au (Fig. 3) and the clasp was a Cu/Zn alloy covered by a film of Ni plated with Au. In clip 7, the button had a inner nucleus of Fe covered by a stratum of Ni, in its turn, covered with a thin film of Ag, while the clasp was a Cu/Zn alloy with the Ni on this core.

The different parts of the three studs, *i.e.*, button, stud or support, varied in metallic composition. In sample no. 8, the stud was made up of an alloy of Fe/Cr/Ni (Fig. 4), the button and the support were made of Cu/Zn covered by a layer of Ag. In sample no. 9, the stud was of Fe/Cr/Ni alloy, while the button and the support had Cu/Zn in the inner layer and Au on the surface. In sample no. 10, the stud had a base of Fe/Cr/Ni covered by a layer of Zn, which, in its turn, was covered by a layer of Ag; the button and the support had Cu/Zn in the inner layer and Ag as the external layer.

It is worth noting that the tested objects had a complex structure depending on the different pieces. In general, they presented a core of brass, or Fe, or steel, on which laid a film of precious metal, such as Ag or Au. In some cases, the precious metal plating was not directly deposited on the alloy, but it was applied over an under-layer of Ni. Because coatings of Ag or Au were very thin and cracked, it can be verisimilar to assume that coatings can worn off by use. Thus, Ni-

containing layers are likely to come into contact with the skin.

3.4. Total content and release of nickel by SF-ICP-MS

Table 3 reports Ni total content and Ni release in artificial sweat (method EN1811) from each of the earring components obtained by SF-ICP-MS analysis.

Nickel was present in all the objects analyzed, also in those cases where it was unquantifiable by X-ray analysis and ranged from 0.004% to 0.61%. In five cases, the total Ni exceeded the limit given by the Directive (<0.05%); in particular, not allowed concentrations were observed in one silver-earring wire (no. 2, 0.61%), in two silver-earring studs (no. 8, 0.48%, no. 10, 0.069%) and in the two clips (nos. 6 and 7, mean of 0.24%). These earring components were the same objects containing the highest amounts of Ni in the X-ray analysis.

Table 3

Ni total content (in $\mu\text{g/g}$) and Ni release (in $\mu\text{g/cm}^2/\text{week}$) from cheap jewellery

Jewel (no.)	Total ^a	Release ^b
1	172 $\pm$ 16	0.154 $\pm$ 0.011
2	6066 $\pm$ 355	4.62 $\pm$ 0.25
3	53.9 $\pm$ 2.1	0.194 $\pm$ 0.015
4	42.4 $\pm$ 1.2	0.021 $\pm$ 0.001
5	47.1 $\pm$ 1.5	0.088 $\pm$ 0.005
6	2153 $\pm$ 184	225 $\pm$ 14
7	2763 $\pm$ 200	10.9 $\pm$ 0.3
8	4791 $\pm$ 153	0.030 $\pm$ 0.002
9	396 $\pm$ 24	0.058 $\pm$ 0.003
10	686 $\pm$ 44	0.032 $\pm$ 0.002

^a<0.05% (*i.e.*, <500 $\mu\text{g/g}$) and ^b<0.5 $\mu\text{g/cm}^2/\text{week}$ as limited by the 94/27/EC.

As regards the results of leaching experiments, all the objects released quantifiable Ni concentrations. The amount of Ni released was less than $0.05 \mu\text{g}/\text{cm}^2/\text{week}$ in three cases; between 0.06 and $0.19 \mu\text{g}/\text{cm}^2/\text{week}$ in four cases; two objects released Ni at $4.62 \mu\text{g}/\text{cm}^2/\text{week}$ (no. 2) and $10.9 \mu\text{g}/\text{cm}^2/\text{week}$ (no. 7) and one leached more than $200 \mu\text{g}/\text{cm}^2/\text{week}$ (no. 6). The clips (nos. 6 and 7) were the pieces that released a higher quantity of Ni compared to the other components with the gold-plated clip, which released more Ni than the ones with the silver-coloured clip. Kanerva et al. (1994) observed a value of Ni released from gold-plated earrings, *i.e.*, $142\text{--}165 \mu\text{g}/\text{cm}^2/\text{week}$, similar to that here found and higher than that for silver-earrings ($0.8\text{--}0.9 \mu\text{g}/\text{cm}^2/\text{week}$) (5).

Fig. 5 displays the comparison between the results on Ni (total and released) and the limit levels reported in the Directives 94/27/EC and 2004/96/EC. From the figure emerges that five (nos. 2, 6, 7, 8 and 10) earring components contained a Ni percentage greater than the limit. Except for one case (no. 10), which laid around the limit, four alloys showed Ni contents from 4 to 12-times higher than the limit. Among these five jewels, three (nos. 2, 6 and 7) released Ni above the sensitizing limit of $0.2 \mu\text{g}/\text{cm}^2/\text{week}$ reported in the recent Directive 2004/96/EC, but they were also over the less severe limit of

$0.5 \mu\text{g}/\text{cm}^2/\text{week}$. It is worth noting that, even if some items (*i.e.*, nos. 8 and 10) contained total Ni more than allowed, they released safe Ni concentrations in synthetic sweat. In the objects 8 and 10, Ni was a constituent of the steel alloy and probably for this reason much more stable and less subjected to migration in sweat. Otherwise, when the presence of Ni was more superficial (nos. 2, 6 and 7), it was much more likely for migration to occur.

A previous study conducted in Italy before the introduction of Regulations, reported a mean release of Ni equal to $1024 \mu\text{g}/\text{week}$ for lever-back earring wires and $1075 \mu\text{g}/\text{week}$ for clips but, unfortunately, surface areas were not reported (Santucci et al., 1989). Anyway, these data can be tentatively transformed in $\mu\text{g}/\text{cm}^2/\text{week}$ considering the similarity of the objects sampled in 1989 and those sampled in this study, besides the similarity in the surface areas exposed to sweat. By this approach, the Ni release was *ca.* $700 \mu\text{g}/\text{cm}^2/\text{week}$ for wires and *ca.* $300 \mu\text{g}/\text{cm}^2/\text{week}$ for clips showing a much greater release from jewellery available two decades ago than from those here found, especially for wires.

Present results were similar to those reported by Fischer et al. who found a Ni range of $0.05\text{--}442 \mu\text{g}/\text{cm}^2/\text{week}$ in different earrings (Fischer et al., 1984). The study of Haudrechy et al. (1994) found a release from Ni-plated steel equal to $100 \mu\text{g}/\text{cm}^2/\text{week}$, while Menné

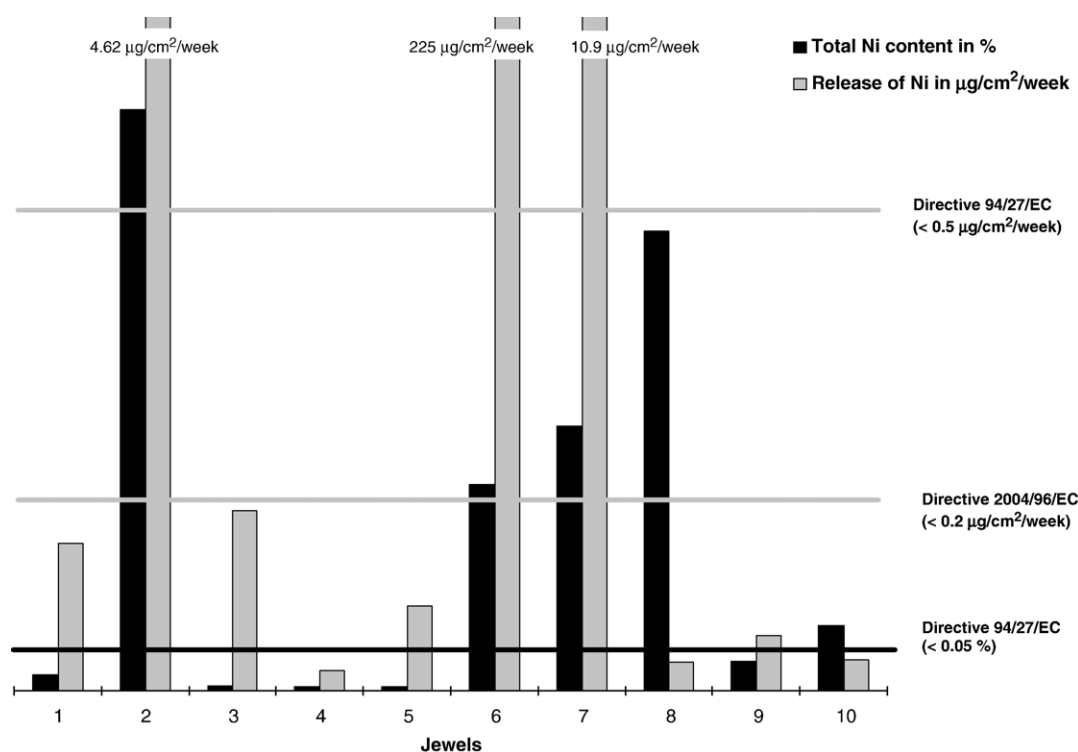


Fig. 5. Data on Ni in earrings vs. the limits reported in the Directives 94/27/EC and 2004/96/EC.

et al. (1987) found Ni value of 20–30 $\mu\text{g}/\text{cm}^2/\text{week}$ from a nickel–silver alloy, of 0.3 $\mu\text{g}/\text{cm}^2/\text{week}$ from a white gold alloy and of 0.5 $\mu\text{g}/\text{cm}^2/\text{week}$ from Ni–Sn alloy.

3.5. Total and release of other metals by SF-ICP-MS

In the selected jewels, the SF-ICP-MS was used to quantify the total content of minor and impurity elements (as Al, Cd, Cr, Co, Mn, Pb, Sn, V and PGEs) complementing the data obtained in the X-ray analysis. Aluminium was practically absent in all the items, only the clip-on earrings (nos. 6 and 7) showed a quantity of Al of *ca.* 100 $\mu\text{g}/\text{g}$. Cadmium and V were present in significant amounts only in the studs (nos. 8–10) (Cd, *ca.* 33 $\mu\text{g}/\text{g}$; V, *ca.* 14 $\mu\text{g}/\text{g}$) and in the earring wire no. 2 (V, 10.4 $\mu\text{g}/\text{g}$). The same trend was observed for Pb, which presented the maximum concentration in studs nos. 9 and 10 (*ca.* 10,000 $\mu\text{g}/\text{g}$) compared with the other earring pieces (<150 $\mu\text{g}/\text{g}$). The studs also presented the highest Cr concentrations, about 8500 $\mu\text{g}/\text{g}$. Small amounts of Cr were observed in the clips (37.5 and 574 $\mu\text{g}/\text{g}$) and in fish hook no. 2 (209 $\mu\text{g}/\text{g}$). Object no. 2 showed the highest concentration of Co (29.7 $\mu\text{g}/\text{g}$) and Mn (2080 $\mu\text{g}/\text{g}$). In all the other jewels Co and Mn were below 20 $\mu\text{g}/\text{g}$ and 600 $\mu\text{g}/\text{g}$, respectively. Tin was present at 4000 $\mu\text{g}/\text{g}$ in the lever-back earring wire (nos. 4 and 5), and at level of 1300 $\mu\text{g}/\text{g}$ in studs nos. 9 and 10. As expected, since the sampling was devoted to cheap

jewellery, PGEs were very low in all the alloys with the following order of abundance: Rh (mean of 8.18 $\mu\text{g}/\text{g}$) > Pd (0.46 $\mu\text{g}/\text{g}$) > Pt (0.014 $\mu\text{g}/\text{g}$) > Ir (<0.005 $\mu\text{g}/\text{g}$). The gold-plated earring wire (no. 1) contained a high concentration of Pd (158 $\mu\text{g}/\text{g}$) (see X-ray analysis, Fig. 1), while wires nos. 2 and 3 showed the highest Pt (*ca.* 0.7 $\mu\text{g}/\text{g}$).

Table 4 shows the release of other metals from the same ten earring components. Copper, Fe and Zn were leached by all the samples. Releases of Cu and Zn were very variable among the different pieces and a common tendency did not emerge (Cu: 0.117–30.9 $\mu\text{g}/\text{cm}^2/\text{week}$; Zn: 0.141–160 $\mu\text{g}/\text{cm}^2/\text{week}$). Object no. 2, which contained the lowest total Cu and Zn levels, showed the smallest release of both elements. The two clips differed in behaviour because the gold-plated one released more Cu and Zn than the silver-plated. Considerable releases of Fe were observed in the two clips (358 and 586 $\mu\text{g}/\text{cm}^2/\text{week}$) while the other objects released less than 0.77 $\mu\text{g}/\text{cm}^2/\text{week}$. Silver-plated objects released Ag at level < 0.08 $\mu\text{g}/\text{cm}^2/\text{week}$. Lead was released from seven objects with the highest release equal to 0.25 $\mu\text{g}/\text{cm}^2/\text{week}$ (no. 2). Releases of other metals, such as Al, Cd, Co, Cr and Sn were observed in the 30%–40% of the items and concentrations of these elements were less than 0.2 $\mu\text{g}/\text{cm}^2/\text{week}$. Manganese ranged 0.72–21.7 $\mu\text{g}/\text{cm}^2/\text{week}$. The greatest releases of Co (0.18 $\mu\text{g}/\text{cm}^2/\text{week}$), Cr (0.25 $\mu\text{g}/\text{cm}^2/\text{week}$) and Mn (21.7 $\mu\text{g}/\text{cm}^2/\text{week}$) were

Table 4
Release of other metals (in $\mu\text{g}/\text{cm}^2/\text{week}$) in ten different earring components

Jewel (no.)	Ag	Al	Cd	Co	Cr	Cu	Fe	Mn	Pb	V	Sn	Zn
1	nr	nr	0.015 (0.001)	nr	nr	8.88 (0.51)	0.033 (0.002)	nr	0.009 (0.001)	nr	nr	103 (9)
2	0.078 (0.002)	0.015 (0.001)	nr	0.181 (0.010)	0.253 (0.014)	0.117 (0.007)	0.320 (0.015)	21.7 (1.1)	0.253 (0.013)	0.015 (0.001)	nr	0.262 (0.011)
3	nr	nr	0.008 (0.001)	0.013 (0.001)	nr	16.7 (0.9)	0.773 (0.029)	nr	0.015 (0.001)	nr	nr	81.3 (3.8)
4	nr	nr	nr	nr	nr	16.4 (1.1)	0.400 (0.014)	nr	nr	nr	nr	22.6 (1.1)
5	nr	nr	nr	nr	nr	1.99 (0.02)	0.173 (0.009)	nr	nr	nr	0.015 (0.001)	160 (12)
6	nr	0.083 (0.006)	nr	0.166 (0.011)	0.035 (0.003)	30.9 (2.2)	586 (36)	1.55 (0.09)	0.017 (0.002)	nr	nr	29.7 (1.9)
7	nr	0.071 (0.002)	nr	0.025 (0.002)	0.019 (0.002)	0.134 (0.008)	358 (22)	0.717 (0.026)	0.010 (0.001)	nr	nr	0.141 (0.009)
8	0.004 (0.001)	nr	nr	nr	nr	3.90 (0.14)	0.290 (0.011)	nr	nr	nr	nr	18.5 (1.3)
9	nr	nr	nr	nr	nr	5.40 (0.29)	0.116 (0.008)	nr	0.006 (0.001)	nr	0.020 (0.002)	41.9 (3.4)
10	0.003 (0.001)	nr	0.011 (0.001)	nr	nr	0.796 (0.041)	0.072 (0.002)	nr	0.056 (0.002)	nr	0.026 (0.003)	36.0 (2.8)

nr: Not released. The release of Au and the PGEs was not observed from any of the objects under study.
The standard deviation is reported in brackets.

observed for object no. 2. The PGEs (Ir, Pt, Pd and Rh) and Au were not leached by any of the tested earrings. These observations are in agreement with Lidén et al. (1998) which found that Au, Rh and Pd ions were not released from gold-containing jewellery alloys, while Cu was always released and Ag and Ni only in few cases.

Considering Table 3 as well, objects nos. 2, 6 and 7, which released the highest quantity of Ni, also leached the highest concentrations of other metals. In fact, object no. 2 presented the highest release of Ag, Co, Cr, Mn, Pb and V, and clips 6 and 7 released the highest Fe concentrations.

4. Conclusions

The frequency of allergy to Ni due to earrings has not decreased after the introduction of the Ni limit; in fact, in 1994 and in 2005, patients positive to Ni patch tests were 54.3% and 53.5%, respectively. The cheap earrings under study were made up of alloys of Cu/Zn or Fe/Cr/Ni, or Fe-based, covered by a film of precious metal, as Ag or Au. In some cases, the precious metal plating was combined with a Ni layer beneath. Because Ag and Au coatings were often thin, the daily use of jewels might worn off the coating exposing the skin to Ni. Five of the 10 earring components analyzed, had a total Ni content >0.05% and, thus, were not in compliance with the Ni Directive 94/27/EC. Three of them released Ni in artificial sweat above the safe allergological limit given by the above mentioned Regulation (*i.e.*, <0.5 µg/cm²/week). Copper, Fe and Zn were released by all kinds of objects, Pb from 70% of the objects and Ag, Al, Cd, Co, Cr, Mn and Sn from *ca.* 30% of the items. Vanadium was released by only one object and Au, Ir, Pd, Pt and Rh were never leached. This study produces the preliminary results for creating a baseline value for the Ni and other potentially sensitizing metals that are on the Italian jewellery market after the introduction of the Commission Directive 2004/96/EC and Council Directive 94/27/EC.

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