

The X-Ray and SF-ICP-MS Analysis of Content and Release of Allergenic Metals from Body Piercing

Beatrice Bocca*, Stefano Caimi, Oreste Senofonte, Francesco Petrucci, Roberta Feliciani, Maria Rosaria Milana, Barbara De Berardis, Luigi Paoletti and Giovanni Forte

Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy

Abstract: Metallic piercing which have lack of resistance to sweat corrosion might be able to release metallic ions in the local tissue producing adverse effects in the human body, including allergic contact dermatitis (ACD). The aim of this study was double: 1) the metallic characterization of piercings and 2) the release of metals (Al, Co, Cr, Cu, Fe, Ir, Mn, Ni, Pd, Pt, Rh, Ti, V and Zn) in artificial sweat to simulate conditions of use. Stainless steel and titanium piercings were sampled, and both the official and non official markets were checked. The X-ray microanalysis by Energy-Dispersion Spectrometry and the Sector Field Inductively Coupled Plasma Mass Spectrometry were the techniques of election for metallic characterization and leaching analysis. The piercings analyzed were alloys of Fe/Cr/Ni or Fe/Mn/Cr. The coloured piercings had a layer of Ti varying from 0.3 to 0.5 μm above the steel core and an external C stratum (0.04 μm). The titanium piercing was pure Ti. Piercings sampled from the official market released less than 0.05 $\mu\text{g}/\text{cm}^2/\text{week}$ of metal and thus, most likely, they are allergologically safe. Piercing purchased from the non official market were more susceptible to sweat corrosion promoting the release of considerable amounts of Cr (2.78 $\mu\text{g}/\text{cm}^2/\text{week}$), Fe (26.95 $\mu\text{g}/\text{cm}^2/\text{week}$), Mn (51.15 $\mu\text{g}/\text{cm}^2/\text{week}$) and Ni (0.157 $\mu\text{g}/\text{cm}^2/\text{week}$). Iridium, Pd, Pt and Rh were not leached by any of the analyzed piercings.

Keywords: Piercings, nickel allergy, metallic characterization, allergenic metals, sweat corrosion, X-ray analysis, SF-ICP-MS, EDX.

1. INTRODUCTION

Piercing practices are steadily growing among young people, and, with them, the concern about the associated allergological risk. Most body piercing jewelry is made of metal, usually stainless steel, Au, Ti, Pt or alloys. Even if stainless steel rarely causes allergic skin reactions some of stainless steel products are not “nickel-free”. Gold itself is often combined with Ni or other metals to make alloys that have improved hardness and durability. Moreover, jewelry with a high karat rating commonly is paired with less expensive studs or earring backs made of Ni and plated with a thin and imperfect layer of precious metals.

Metallic piercing with intense linear irregularities on their surface and which have lack of resistance to sweat corrosion are able to release metallic ions in the local tissue and to generate several types of adverse effects in the human body, including allergic contact dermatitis (ACD) [1]. The ACD is characterized by rash in the skin which is usually very itchy and consists of redness, scaling, fissuring, vesicles, and lichenification. In addition to primary eruptions at the site of contact, secondary eruptions might occur on the flexor surfaces of the arms and elbows [2, 3].

Nickel allergy has been the most common and has a great socio-economic impact. With the aim of providing scientific information necessary for primary prevention, the European Surveillance System on Contact Allergies (ESSCA) linking

dermatological departments from 11 European countries was founded. In the year 2004, altogether 11,643 patients were patch tested and the highest sensitization prevalence (32.2%) for Ni was observed consistently for Italian departments; on the other side of this spectrum, the percentage positive for Ni (9.7%) were lowest for the Danish department [4].

It is estimated that between 10% and 15% of women and 2-5% of men in Europe are nickel-sensitized, so the danger of a customer suffering bad reactions from a non-conforming product is significant. The significant differences in prevalence between females and males correlates with the much higher prevalence of body piercing among women, particularly in European cultures [5]. The 30-40% of nickel-sensitive people develop hand eczema that may be recurrent, chronic and severe, and might affect work ability [5]. Moreover, nickel allergy it can be so severe as to induce asthma [6]. In population studies from Scandinavian countries, the prevalence of nickel allergy among young females with pierced skin has varied from 13% to 20% in the 1980s [7], and in the 1990s it has been reported to be roughly 30% [8]. In Finland, the occurrence of nickel sensitivity in female university students increased from 13% to 39% during the period 1985–1995 [9].

Studies supported that the risk of becoming allergic is higher depending on the number of piercing applied and if the piercing is practiced at age less than 20 years [8]. Sensitivity has even been shown to develop in infants who have their ears pierced within the first few weeks of life [10]. Once an allergy to Ni has been acquired, it generally lasts for life. An individual who became sensitized to Ni, when re-exposed to nickel ions might have an allergic response

*Address correspondence to this author at the Istituto Superiore di Sanità, Viale Regina Elena 299, 00161 Rome, Italy; Fax: (39) 06 4990 2011; E-mail: beatrice.bocca@iss.it

within a matter of hours and at a much lower concentration of Ni than that required for inducing sensitization. Moreover, it has been demonstrated that small residues of Ni and other metals remained in the skin lesions of pierced earlobes long after the studs were removed. Researchers hypothesized that Ni was retained in the tissues for a mean of hundreds of days [11]. The physical persistence of allergen can cause prolonged irritation and various cutaneous manifestations long after a patient stops wearing the nickel-releasing ear piercing.

In addition, there is emerging evidence that other metals, as Ag, Au, Co, Cr, Pt and Pd are sensitizing agents. The ESSCA data revealed percentage of European people allergic to cobalt chloride which varied from 1.1% in Denmark to 17.6% in Italy, and to potassium dichromate from 1.3% in Sheffield (UK) to 9.1% in Liverpool (UK) [4]. In the Swedish population, a total of 44 (4.6%) girls had contact allergy to both Ni and Co, whereas 7 (0.7%) girls had contact allergy to Co [7]. Evidence that ear piercing increases the risk of Au sensitization is that there were significantly more positive reactions to gold chloride in the patients with pierced than in patients without pierced ears [12]. In Portugal, contact allergy to gold sodium thiosulfate (0.78%) was found in 23 patients, all the reactors were women and had their ears pierced with Au earrings [13]. Silver may also cause problems such as localized argyria, this lesion typically has been associated with embedded jewelry. The skin is believed to become discovered from the leaching of Ag with formation of silver salts [6]. Finally, as most patients with strong sensitization to Ni also react to other elements as Pd because of cross-reactivity, piercing posts that do not leach Ni but which contains other elements as Pd cannot be a safe alternative.

There is widespread unanimity among dermatologists that the principal way in which sensitization can be induced appears to be by contact with a high concentration of sweat-soluble Ni from a localized area. In the case of piercing, where the duration of exposure may occur for a the whole life, the chronic exposure to a low concentration of allergenic metal in the alloy might be sufficient to elicit a response. On this base, the European Directive 94/27/EC limited the content of Ni in products where intimate and prolonged skin contact will result in solubilization of Ni at a rate exceeding $0.5 \mu\text{g}/\text{cm}^2/\text{week}$ [14]. It should be noted that the $0.5 \mu\text{g Ni}/\text{cm}^2/\text{week}$ release rate likely would not protect 100% of sensitized people from elicitation of ACD. However, clinical data indicates that the vast majority of sensitized individuals would not experience ACD at this level of Ni release and the vast majority of individuals not previously sensitized require substantially higher concentrations than $0.5 \mu\text{g Ni}/\text{cm}^2/\text{week}$ to be released to the skin for sensitization to occur.

The Directive represented the instrument for the primary and secondary prevention of Ni-ACD and many of the major suppliers have included Ni in their quality control programme and they are trying to follow the regulation. Since some years elapsed from the Directive emanation, one of the main questions is "have had the limitation a real impact in reducing allergies?" Actually, some reports indicates a decrease in the sensitization rate to Ni. Among Danish children

aged 0–18 years, nickel allergy decreased significantly from 24.8% to 9.2% over a 12-year period [15]. In 2002-2003, the Swedish market showed that the 8% only of the tested piercing posts released Ni compared to a percentage of 25% in 1999 [16]. In a study published in 2003, nickel sensitization was found significantly decreased from 36.7% to 25.8% among German women younger than 30 years over a 9-year period [17]. In the USA, where no nickel regulation has been introduced, Ni continues to be responsible for clinical disease among youngsters [18]. In other countries the situation is different. In Italy, in 2005, the percentage of subjects living in Rome allergic to Ni contained in cheap jewellery was the same as that found in 1994 and a part of jewellery market was not yet in compliance with the law standard [19]. Similarly, in Finland, in the years 1995-97 and 2000-02 the patch tests revealed percentages of 20.8% and 21.9% for nickel allergy, thus testifying that the frequency of allergy remained at the same level [20].

It must be stressed out that alloys used for piercing are mostly uncharacterized especially for the content and the release of allergenic metals. For this reason, the aim of this study was double: *i)* to investigate the metallic composition of common piercings available on the Italian market, both the official and non official market; and *ii)* to quantify the metals released from piercings in a solution simulating the human sweat. Aluminium, Co, Cr, Cu, Fe, Ir, Mn, Ni, Pd, Pt, Rh, Ti, V and Zn were studied. To this end, the X-ray microanalysis by Energy-Dispersion Spectrometry (EDX) and the Sector Field Inductively Coupled Plasma Mass Spectrometry (SF-ICP-MS) were the techniques of election for metal quantification.

2. EXPERIMENTAL

2.1. Samples Collection

Three stainless steel (see Fig. 1, nos. 1-3) and two black coloured piercings (see Fig. 2, nos. 4 and 5) used for ears, lips, eyebrow, nipple, and navel were characterised for their metallic content and their release in artificial sweat. One titanium piercing was also analyzed (see Fig. 3). These items were purchased from official shops in Rome and were selected to represent the most frequently sold products and models. Moreover, four piercings, one uncoloured (no. 7), two black coloured (nos. 8 and 9) and one blue coloured (no. 10) (see Fig. 4) were non official products purchased from the street.

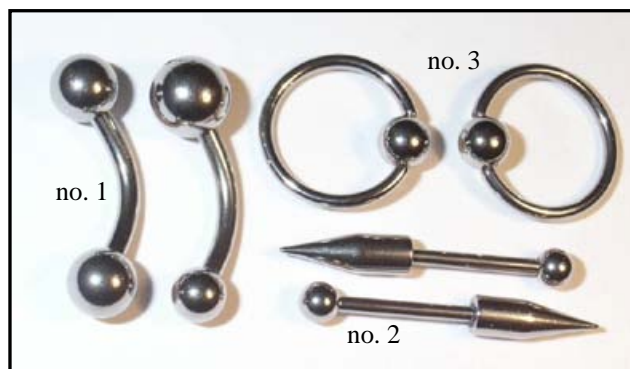


Fig. (1). Stainless steel piercings (nos. 1-3).

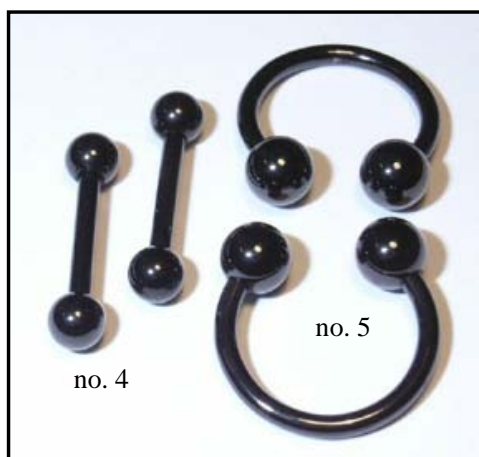


Fig. (2). Carbon/titanium piercings (nos. 4 and 5, both black coloured).

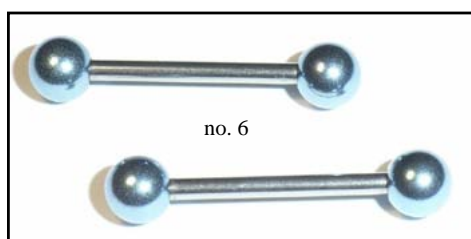


Fig. (3). Titanium piercing (no. 6).

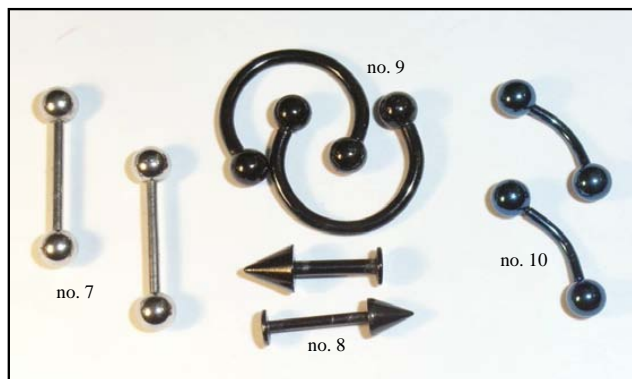


Fig. (4). Stainless steel piercings uncoloured (no. 7), black coloured (nos. 8 and 9) and blue (no. 10).

2.2. Sample Preparation

For the determinations by X-ray, piercings were analyzed without being destroyed. Leaching experiments were performed by soaking piercings in artificial sweat in the ratio 1:1 (i.e., 1 ml of solution for 1 cm² of the object) and placed in a water-bath at 30 °C for 1 week. To do the artificial sweat solution, suprapure-grade NaCl (Merck, Darmstadt, Germany), lactic acid with a purity of 98% (Chem Service, West Chester, USA), urea with a purity of 98% (ICN Biomedicals, Inc., Aurora, USA) and suprapure-grade ammonia water (28-30% as NH₃) from Merck, Darmstadt, Germany were used. The sweat-simulating solution was composed by 0.1% of urea, 0.5% of NaCl and 0.1% of lactic acid (0.1%). The pH of the simulating solution was brought to the pH value of 6.50 with ammonia solution (1%). Details of the method are reported in the regulation “Reference test method for release of nickel from products intended to come into direct and pro-

longed contact with the skin” [21]. The resulting solutions were directly SF-ICP-MS analyzed.

2.3. Instrumentation

A scanning electron microscopy (SEM) Philips XL30 (Phillips, Eindhoven, The Netherlands) equipped with a thin-window EDAX system for X-ray microanalysis by EDX was used to detect the presence of metals in the samples. Magnifications from 40x to 2000x and a beam energy of 15 KeV were utilized. The intensities of the characteristic X-ray lines were converted to the corresponding atomic concentration by a standardless ZAF correction method.

An Element II SF-ICP-MS (Thermo Finnigan, Bremen, Germany), equipped with a Meinhard-type glass nebulizer, a water-cooled Scott spray chamber and a torch with guard electrode device 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, 0.9 mL/min. Two resolution settings were used: the low resolution (LR) at 300 m/Δm for quantifying Pt and Ir, and the medium resolution (MR) at 4000 m/Δm for quantifying Al, Co, Cr, Cu, Fe, Mn, Ni, Pd, Rh, Ti, V and Zn. The standard addition approach for calibration on five concentration levels was used in order to keep the matrix-induced variations under control. Moreover, a check sample (i.e., the lowest concentration point of the calibration curve) was measured frequently during the analytical run to take into account for instrumental drift.

3. RESULTS

3.1. Method Performances

Table 1 shows the isotopes and the resolution setting used for the study. Elements such as Pt and Ir, not hampered by any relevant interference, were quantified in the LR resolution mode and by using their most abundant mass to obtain the maximum of sensitivity. Aluminium, Co, Cr, Cu, Fe, Mn, Ni, Pd, Rh, Ti, V and Zn were quantified at MR mode to avoid severe interferences which would lead to false high values. In fact, the high content of Ca, Cl, K, Na and Mg in the mixture used for sample leaching and the metallic matrix with high contents of Cu, Fe and Zn created not negligible interferences.

In particular, the heaviest interferences were the following: CN⁺ and CNH⁺ on Al; ArNa⁺, KO⁺ and CaO⁺ on Co; ArC⁺, ArO⁺, ArN⁺, ClO⁺ and ClN⁺ on Cr; ArNa⁺ on Cu; ArO⁺, CaO⁺, KO⁺ on Fe; NaCl⁺, ClO⁺, NaCl⁺, ArMg⁺ on Mn; NaCl⁺, ArMg⁺ and CaO⁺ on Ni; ArCu⁺ and ZnCl⁺ on Pd and Rh; NOO⁺ on Ti; ArNH⁺ and ClN⁺ on V⁺. By using the MR mode, all these interferences were shifted far from the analytical peak and, thus, unequivocally separated. Whenever possible the most abundant isotope was selected for each element. Anyway, there were some exceptions: the mass 58 (68.7% of abundance) for Ni was not used because hampered by the isobaric ⁵⁸Fe, the mass 49 for Ti (73.8%) could not be used because of the isobaric interference of ⁴⁹Ca and the mass 106 (27.3%) for Pd was troubled by ArZn⁺.

In Table 2, the figures of merit of the developed SF-ICP-MS method are reported. Repeatability was calculated on 10 replicated measurements of a leaching solution and the resulting average relative standard deviation (SD) was equal to

Table 1. Selection of Isotopes and Mass Resolution

Element	m/z	Abundance (%)	Resolution (m/ Δ m)	Interferences Separated with the Selected Resolution
Al	27	100	4000	$^{11}\text{B}^{16}\text{O}$, $^{10}\text{B}^{16}\text{O}^1\text{H}$, $^{13}\text{C}^{14}\text{N}$, $^{12}\text{C}^{15}\text{N}$, $^{12}\text{C}^{14}\text{NH}$, $^{54}\text{Fe}^{++}$
Co	59	100	4000	$^{40}\text{Ar}^{19}\text{F}$, $^{43}\text{Ca}^{16}\text{O}$, $^{41}\text{K}^{18}\text{O}$, $^{36}\text{Ar}^{23}\text{Na}$, $^{42}\text{Ca}^{16}\text{O}^1\text{H}$
Cr	52	83.8	4000	$^{40}\text{Ar}^{12}\text{C}$, $^{36}\text{Ar}^{16}\text{O}$, $^{38}\text{Ar}^{14}\text{N}$, $^{35}\text{Cl}^{17}\text{O}$, $^{37}\text{Cl}^{15}\text{N}$, $^{35}\text{Cl}^{16}\text{O}^1\text{H}$
Cu	63	69.2	4000	$^{40}\text{Ar}^{23}\text{Na}$, $^{44}\text{Ca}^{19}\text{F}$
Fe	56	91.7	4000	$^{40}\text{Ar}^{16}\text{O}$, $^{40}\text{Ca}^{16}\text{O}$, $^{39}\text{K}^{17}\text{O}$, $^{40}\text{K}^{16}\text{O}$
Ir	193	62.7	300	^a
Mn	55	100	4000	$^{37}\text{Cl}^{18}\text{O}$, $^{40}\text{Ar}^{15}\text{N}$, $^{39}\text{K}^{16}\text{O}$, $^{40}\text{Ar}^{14}\text{N}^1\text{H}$
Ni	60	26.1	4000	$^{44}\text{Ca}^{16}\text{O}$, $^{23}\text{Na}^{37}\text{Cl}$, $^{36}\text{Ar}^{24}\text{Mg}$, $^{120}\text{Sn}^{++}$
Pd	105	27.3	4000	$^{40}\text{Ar}^{65}\text{Cu}$, $^{68}\text{Zn}^{37}\text{Cl}$, $^{70}\text{Zn}^{35}\text{Cl}$
Pt	195	33.8	300	^a
Rh	103	100	4000	$^{40}\text{Ar}^{63}\text{Cu}$, $^{106}\text{Pb}^{++}$, $^{68}\text{Zn}^{35}\text{Cl}$, $^{66}\text{Zn}^{37}\text{Cl}$
Ti	47	7.30	4000	$^{15}\text{N}^{16}\text{O}^{16}\text{O}$, $^{36}\text{Ar}^{11}\text{B}$
V	51	99.8	4000	$^{35}\text{Cl}^{16}\text{O}$, $^{37}\text{Cl}^{14}\text{N}$, $^{40}\text{Ar}^{11}\text{B}$, $^{36}\text{Ar}^{14}\text{N}^1\text{H}$
Zn	64	48.6	4000	$^{40}\text{Ar}^{24}\text{Mg}$, $^{48}\text{Ca}^{16}\text{O}$, $^{36}\text{Ar}^{28}\text{Si}$

^a No relevant interference for the considered matrix.

3.9%. Recovery tests were performed to determine the accuracy of the method. To this end, one leaching solution was added with a multi-element spike which included all the elements to be determined. An average recovery of 97.6% was obtained.

Table 2. SF-ICP-MS Method Performances in Artificial Sweat

Metal	Repeatability (%)	Recovery	
		Spiked ($\mu\text{g/l}$)	Found (%)
Al	3.1	5	95.4
Co	4.2	1	94.3
Cr	2.2	1	92.5
Cu	5.6	5	98.6
Fe	3.0	5	100
Ir	2.9	0.10	90.9
Mn	5.6	1	104
Ni	2.5	1	97.8
Pd	3.6	0.10	98.5
Pt	2.7	0.10	102
Rh	5.4	0.10	94.8
Ti	4.9	1	97.8
V	3.6	1	99.2
Zn	5.4	5	101

3.2. Chemical Characterization

The results indicated that the three kinds of stainless steel piercings (nos. 1-3) were all manufactured in an alloy of

Fe/Cr/Ni (68.5/17.5/14.0); both the body of the object (see Fig. 5) and the lateral spheres had the same metallic composition. The two black piercings (nos. 4 and 5) presented a core of Fe/Cr/Ni (68.5/18.0/13.5) covered by a layer of Ti of ca. 0.5 μm , covered, in its turn, by a very thin layer of C (0.04 μm). Fig. (6) showed the composition of the central part of the piercing no. 4; the spheres were similarly composed. The piercing no. 6 sold as pure Ti was effectively made in 100% Ti (Fig. 7). The piercings purchased over the non official market were alloys of two different types of steel: the body of the object being manufactured in Fe/Cr/Ni (72.5/18/9.5), while its extremities (spherical nuts) were made of Fe/Mn/Cr (71.5/16.5/12.0) (Fig. 8, piercing no. 7). In the black and blue coloured piercings (nos. 8-10), both the body of the item and the lateral spheres were covered by a film of 0.36 μm of Ti (Fig. 9).

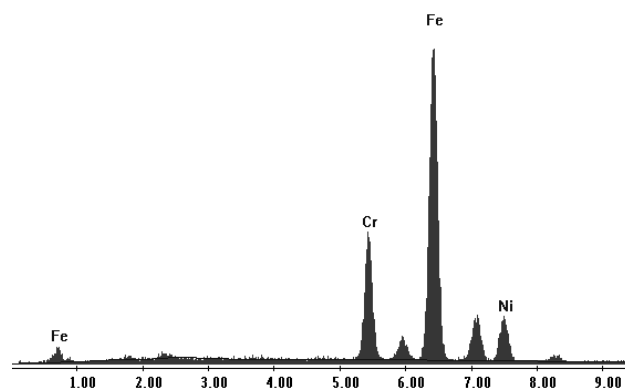


Fig. (5). EDX analysis spectrum of piercing no. 1 based on Fe/Cr/Ni alloy.

3.3. Sweat Corrosion

The results of element determination in the extract of piercing in artificial sweat are presented in Table 3. The

chemical analysis by SF-ICP-MS revealed undetectable concentrations of Ir, Pd, Pt and Rh in the simulating solution. The other metals showed quantifiable concentrations in all the ten piercings; V was released only by 3 out of 10 piercings.

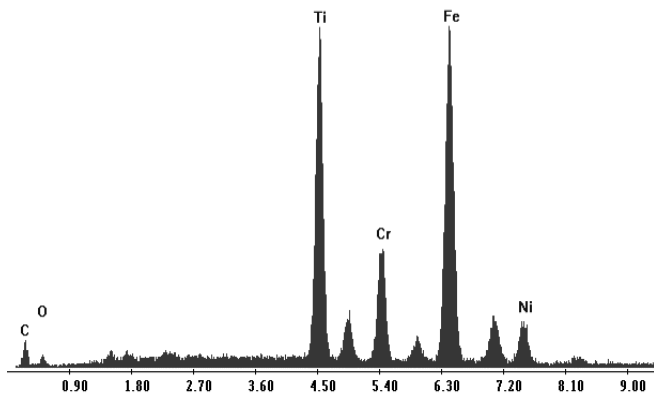


Fig. (6). EDX analysis spectrum of piercing no. 4 based on Fe/Cr/Ni alloy covered by C and Ti layers

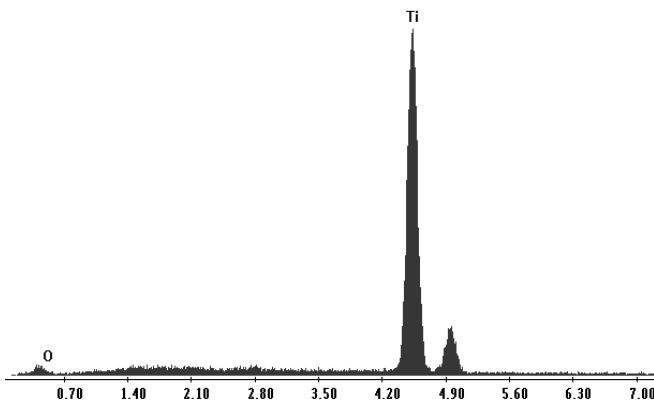


Fig. (7). EDX analysis spectrum of piercing no. 6 based on pure Ti.

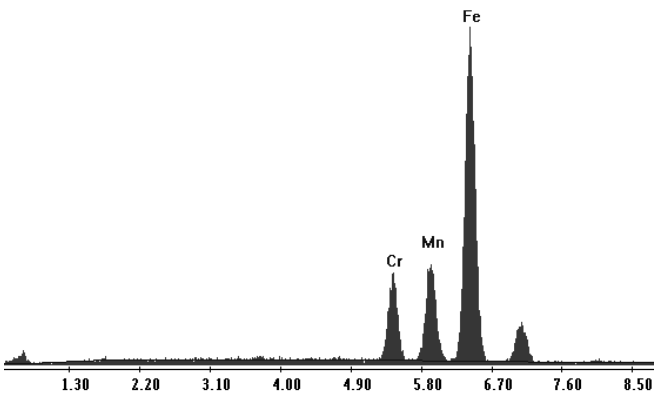


Fig. (8). EDX analysis spectrum of the spherical nuts of piercing no. 7 based on Fe/Cr/Mn alloy.

The group of piercings purchased from shops (nos. 1-6) released median concentrations of metal very low (in $\mu\text{g}/\text{cm}^2/\text{week}$): Al, 0.00635; Co, 0.0003; Cr, 0.00275; Cu, 0.0053; Fe, 0.020; Mn, 0.0057; Ni, 0.012; Ti, 0.023; V, not detected; and Zn, 0.0088. It is worth noting that, even if almost all the piercings contained Cr and Ni as constituents of the stainless steel alloy at percentages of ca. 17% for Cr and ca. 12% for Ni, these ions were not subjected to migration in sweat. These results give evidence that people wearing stain-

less steel piercings are not likely to manifest an allergic response to the alloys. In the extract from Ti piercings, the release of Ti was very low and equal to that found in the stainless steel piercings testifying the safety of this material.

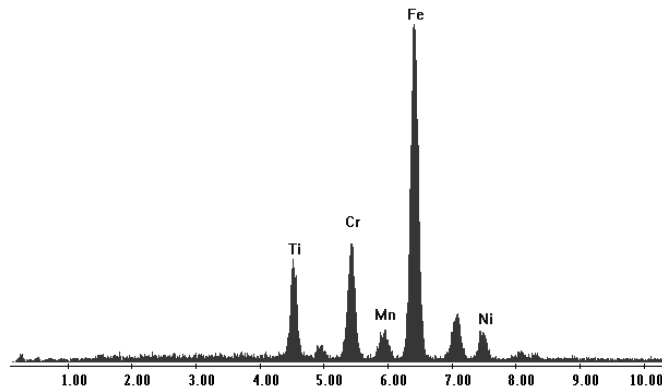


Fig. (9). EDX analysis spectrum of piercing no. 10 based on Fe/Cr/Ni alloy covered by a Ti layer.

Differences between objects sampled in official shops and those available on the non official market were observed. Non official products (nos. 7-10) showed a lack of resistance to corrosion because, firstly, during the leaching experiments a rust colouration of the sweat solution was noticed, and secondly, release rates of some metals were significant. As regards Co and Cr, they were leached as traces ($< 0.003 \mu\text{g}/\text{cm}^2/\text{week}$) from piercings purchased in shops, but from 0.017 to $0.056 \mu\text{g}/\text{cm}^2/\text{week}$ (Co) and from 0.5 to $3.11 \mu\text{g}/\text{cm}^2/\text{week}$ (Cr) in items coming from the non official market. Iron showed a 1000-times higher release in non official than in official products (26.95 vs $0.020 \mu\text{g}/\text{cm}^2/\text{week}$), and another metal released much more by non official products was Mn with a median release of $51.15 \mu\text{g}/\text{cm}^2/\text{week}$ in non official items vs $0.0057 \mu\text{g}/\text{cm}^2/\text{week}$ in official items. Similarly, the released quantity of Cu from non official objects ($0.0765 \mu\text{g}/\text{cm}^2/\text{week}$) was ca. 10-fold higher than that from official ones. On the contrary, the releases of Al, Ti, V and Zn were quite similar between official and non official products.

Similar trend was observed for Ni. The amount of Ni released was less than $0.05 \mu\text{g}/\text{cm}^2/\text{week}$ in all the piercings purchased from official shops and, for this reason, the materials sampled in regular shops can be considered allergologically safe. On the contrary, Ni was between $0.087 \mu\text{g}/\text{cm}^2/\text{week}$ and $0.988 \mu\text{g}/\text{cm}^2/\text{week}$ in the four piercings acquired on the non official market. In particular, two piercings released Ni at $0.988 \mu\text{g}/\text{cm}^2/\text{week}$ (no. 8) and $0.194 \mu\text{g}/\text{cm}^2/\text{week}$ (no. 10). In accordance with European laws, pierced parts of the human body must release less than $0.5 \mu\text{g}/\text{cm}^2/\text{week}$ of Ni [14]. From the comparison, it emerges that the no. 8 released a Ni amount greater than the sensitizing limit of $0.5 \mu\text{g}/\text{cm}^2/\text{week}$, and the no. 10 laid around the sensitizing limit of $0.2 \mu\text{g}/\text{cm}^2/\text{week}$ reported in the recent and more restrictive Directive 2004/96/EC [22]. For these two materials, the risk of skin sensitization cannot be excluded.

Other papers reported that body piercings kept in synthetic sweat released metallic ions, but the previously published data seemed to be much higher than the present findings. For example, Fischer *et al.* (1984) found a Ni release

Table 3. Release of Elements (in $\mu\text{g}/\text{cm}^2/\text{Week}$) in Ten Different Piercings

Piercing	Al	Co	Cr	Cu	Fe
Fig. (1), no. 1	0.0035 \pm 0.0003	0.00045 \pm 0.00002	0.0053 \pm 0.0003	0.0077 \pm 0.0005	0.029 \pm 0.002
Fig. (1), no. 2	0.016 \pm 0.001	0.00063 \pm 0.00003	0.0041 \pm 0.0002	0.013 \pm 0.001	0.051 \pm 0.003
Fig. (1), no. 3	0.022 \pm 0.001	0.00044 \pm 0.00002	0.0040 \pm 0.0002	0.0013 \pm 0.0001	0.098 \pm 0.004
Fig. (2), no. 4	0.0047 \pm 0.0002	0.00016 \pm 0.00002	0.00034 \pm 0.00003	0.0029 \pm 0.0001	0.0084 \pm 0.0005
Fig. (2), no. 5	0.0038 \pm 0.0003	0.00010 \pm 0.00001	0.00038 \pm 0.00002	0.0029 \pm 0.0002	0.011 \pm 0.001
Fig. (3), no. 6	0.0080 \pm 0.0007	0.00010 \pm 0.00001	0.0015 \pm 0.0001	0.021 \pm 0.001	0.0010 \pm 0.0001
Fig. (4), no. 7	0.0046 \pm 0.0003	0.037 \pm 0.003	2.45 \pm 0.14	0.060 \pm 0.003	30.0 \pm 1.8
Fig. (4), no. 8	0.104 \pm 0.034	0.017 \pm 0.002	0.510 \pm 0.019	0.119 \pm 0.007	1.72 \pm 0.11
Fig. (4), no. 9	0.030 \pm 0.002	0.056 \pm 0.002	11.6 \pm 0.6	0.093 \pm 0.004	84.5 \pm 3.7
Fig. (4), no. 10	0.00016 \pm 0.00002	0.035 \pm 0.002	3.11 \pm 0.22	0.019 \pm 0.002	23.9 \pm 2.0

Piercing	Mn	Ni	Ti	V	Zn
Fig. (1), no. 1	0.0042 \pm 0.0003	0.016 \pm 0.001	0.001 \pm 0.0001	nr	0.0076 \pm 0.0005
Fig. (1), no. 2	0.068 \pm 0.003	0.014 \pm 0.001	0.002 \pm 0.0001	nr	0.010 \pm 0.001
Fig. (1), no. 3	0.0072 \pm 0.0005	0.010 \pm 0.001	0.002 \pm 0.0002	nr	0.0054 \pm 0.0003
Fig. (2), no. 4	0.028 \pm 0.002	0.024 \pm 0.002	0.048 \pm 0.002	nr	0.020 \pm 0.001
Fig. (2), no. 5	0.00090 \pm 0.00005	0.0011 \pm 0.0001	0.044 \pm 0.003	nr	0.010 \pm 0.001
Fig. (3), no. 6	0.0014 \pm 0.0001	0.0023 \pm 0.0001	0.054 \pm 0.003	nr	0.0023 \pm 0.0002
Fig. (4), no. 7	50.8 \pm 4.1	0.087 \pm 0.007	nr	0.0038 \pm 0.0002	0.0033 \pm 0.0002
Fig. (4), no. 8	0.553 \pm 0.022	0.988 \pm 0.024	0.057 \pm 0.002	nr	0.124 \pm 0.008
Fig. (4), no. 9	84.3 \pm 3.7	0.119 \pm 0.008	0.023 \pm 0.002	0.019 \pm 0.002	0.020 \pm 0.002
Fig. (4), no. 10	51.5 \pm 1.9	0.194 \pm 0.011	0.003 \pm 0.0002	0.0063 \pm 0.0003	0.0079 \pm 0.0003

nr: not released. The release of Ir, Pd, Pt, and Rh was not observed from any of the objects under study.

range of 0.05-442 $\mu\text{g}/\text{cm}^2/\text{week}$ in different ear piercings [23]. 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 Mennè *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 [24, 25]. Kanerva *et al.* (1994) observed a value of Ni released from gold-plated earrings, i.e., 142-165 $\mu\text{g}/\text{cm}^2/\text{week}$, and higher than that for silver-earrings (0.8-0.9 $\mu\text{g}/\text{cm}^2/\text{week}$) [26]. More similar results were found by Summer *et al.*, who reported releases from stainless steel in synthetic sweat of Ni and Cr equal to 0.30 and 0.38 $\mu\text{g}/\text{cm}^2/2$ days, respectively [27]. In another study stainless steel alloys released small amounts of Ni in sweat, i.e. less than 0.05 $\mu\text{g}/\text{cm}^2/\text{week}$ and thus the items were considered safe for most Ni-sensitized individuals [15].

Even if the concentrations of allergenic metals as Co, Cr, and Ni we found in stainless and titanium piercings were relatively low, it should be considered that the metal fragments derived from piercings can remain in a skin lesion for a long time even after the removal of the accessories. It is acknowledged that the retention time of Ni in the tissues may be of the order of 100s day [11] and that the small residue of Ni causes irritative inflammatory reactions and other medical problems including various cutaneous reactions like for instance the ACD [28]. It should be also taken into account that the ACD, once developed, tends to persist for several

months. Kobayashi *et al.* reported a case of a woman with lymphocytomatous lesions induced by gold earrings; the lesions grew and persisted for 20 years, although the patients had removed the earrings in the lobe [29]. Another case of granulomatous reaction due to a titanium alloy was discovered in a woman who had her lobe pierced ca. 10 years earlier [30]. Recent legislation in Europe will lead to the replacement of Ni interliners with nonallergenic interliners [31]. McDonagh *et al.* stated that jewellery suppliers should be encouraged to provide Ni-free earrings to reduce the frequency of nickel induced hypersensitivity [32].

CONCLUSIONS

The phenomenon of piercing is so widespread that its observation and understanding is a challenge that stimulates researchers, doctors, parents and teachers. Consequently, it is undoubtedly the importance of efforts in collecting data to create a common base of knowledge about this emerging social and health problem in order to obtain an overview of the dangers and adopt prevention programs. Corrosion of metallic piercings can be critical because it can introduce additional ions into the body and induce localised adverse effects, among which particular concern has to be devoted to ACD. This study revealed that metallic piercings subjected to sweat corrosion presented a lack of resistance only when the items were purchased from the non official market. In fact, metals such as Co, Cr, Fe, Mn and Ni were leached in

significant amounts from the non official products. On the contrary, data showed that piercings sampled from official shops revealed a good resistance to sweat corrosion and thus are likely to be safe for consumers. Hopefully, more work should be done to standardize the metal content in piercings and, in general, in the so-called fashion jewellery including clinically relevant recommendations.

ABBREVIATIONS

ACD	= Allergic contact dermatitis
EDX	= X-ray energy-dispersion spectrometry
ESSCA	= The European Surveillance System on Contact Allergies
LR	= Low resolution
MR	= Medium resolution
SD	= Standard deviation
SEM	= Scanning electron microscopy
SF-ICP-MS	= Sector field inductively coupled plasma mass spectrometry
ZAF	= Matrix corrections in reference to the three components of matrix effects: atomic number (Z), absorption (A) and fluorescence (F)

REFERENCES

- [1] Azevedo, C.R.F. Characterization of metallic piercings. *Eng. Fail. Anal. J.*, **2003**, *10*, 255.
- [2] Mortz, C.G.; Andersen, K.E. Allergic contact dermatitis in children and adolescents. *Contact Dermatitis*, **1999**, *41*, 121.
- [3] Belsito, D.V. Allergic contact dermatitis. In *Fitzpatrick's Dermatology in General Medicine*, Freedberg, I.M.; Eisen, A.Z.; Wolff, K.; Austen, K.F.; Goldsmith, L.A.; Katz, S.I.; Fitzpatrick, T.B. Eds.; McGraw-Hill: New York, **1999**, pp. 1447-61.
- [4] The ESSCA Writing Group. The European Surveillance System of Contact Allergies (ESSCA): results of patch testing the standard series, 2004. *J. Eur. Acad. Dermatol. Venereol.*, **2008**, *22*, 174.
- [5] Lidén, C.; Bruze, M.; Menné, T. Metals. In *Textbook of Contact Dermatitis*, Rycroft, R.G.; Menné, T.; Frosch, P.J.; Lepoitertin, J.-P., Eds.; Springer: Berlin, **2001**, pp. 935-50.
- [6] Koenig, L.M.; Carnes, M.J. Body piercing. Medical concerns with cutting-edge fashion. *Gen. Intern. Med.*, **1999**, *14*, 379.
- [7] Larsson-Stymne, B.; Widstrom, L. Ear piercing—a cause of nickel allergy in schoolgirls? *Contact Dermatitis*, **1985**, *13*, 289.
- [8] Dotterud, L.; Falk, E. Metal allergy in north Norwegian school-children and its relationship with ear piercing and atopy. *Contact Dermatitis*, **1994**, *31*, 308.
- [9] Mattila, L.; Kilpeläinen, M.; Terho, E.O.; Koskenvuo, M.; Helenius, H.; Kalimo, K. Prevalence of nickel allergy among Finnish university students in 1995. *Contact Dermatitis*, **2001**, *44*, 218.
- [10] Fisher, A.A. Nickel dermatitis in children. *Cutis*, **1991**, *47*, 19.
- [11] Suzuki, H. Nickel and gold in skin lesions of pierced earlobes with contact dermatitis. A study using scanning electron microscopy and x-ray microanalysis. *Arch. Dermatol. Res.*, **1998**, *290*, 523.
- [12] Nakada, T.; Iijima, M.; Nakayama, H.; Maibach, H.I. Role of ear piercing in metal allergic contact dermatitis. *Contact Dermatitis*, **1997**, *36*, 233.
- [13] Silva, R.; Pereira, F.; Bordalo, O.; Silva, E.; Barros, A.; Gonçalo, M.; Correia, T.; Pessoa, G.; Baptista, A.; Pecegueiro, M. Contact allergy to gold sodium thiosulfate. A comparative study. *Contact Dermatitis*, **1997**, *37*, 78.
- [14] Council Directive 94/27/EC of 30 June **1994**. *Official Journal*, L 188, 22/07/1994, 1.
- [15] Jensen, C.S.; Lisby, S.; Baadsgaard, O.; Vølund, A.; Menné, T. Decrease in nickel sensitization in a Danish schoolgirl population with ears pierced after implementation of a nickel-exposure regulation. *Br. J. Dermatol.*, **2002**, *146*, 636.
- [16] Lidén, C.; Norberg, K. Nickel on the Swedish market. Follow-up after implementation of the Nickel Directive. *Contact Dermatitis*, **2005**, *52*, 29.
- [17] Schnuch, A.; Uter, W. Decrease in nickel allergy in Germany and regulatory interventions. *Contact Dermatitis*, **2003**, *49*, 107.
- [18] Nguyen, S.H.; Dang, T.P.; Macpherson, C.; Maibach, H.; Maibach, H.I. Prevalence of patch test results from 1970 to 2002 in a multi-centre population in North America (NACDG). *Contact Dermatitis*, **2008**, *58*, 101.
- [19] Bocca, B.; Forte, G.; Senofonte, O.; Violante, N.; Paoletti, L.; De Berardis, B.; Petrucci, F.; Cristaudo, A. A pilot study on the content and the release of Ni and other allergenic metals from cheap earrings available on the Italian market. *Sci. Total Environ.*, **2007**, *388*, 24.
- [20] Hasan, T.; Rantanen, T.; Alanko, K.; Harvima, R.J.; Jolanki, R.; Kalimo, K.; Lahti, A.; Lammintausta, K.; Lauerma, A.I.; Laukkanen, A.; Luukkaala, T.; Riekkki, R.; Turjanmaa, K.; Varjonen, E.; Vuorela, A.M. Patch test reactions to cosmetic allergens in 1995–1997 and 2000–2002 in Finland – a multicentre study. *Contact Dermatitis*, **2005**, *53*, 40.
- [21] UNI EN 1811:2000. Reference test method for release of nickel from products intended to come into direct and prolonged contact with the skin (Italian version). Ente Nazionale Italiano di Unificazione: Milan, Italy, **2000**.
- [22] Commission Directive 2004/96/EC of 27 September **2004**. *Official Journal*, L 301, 51.
- [23] Fischer, T.; Fregert, S.; Gruvberger, B.; Rystedt, I. Nickel release from ear piercing kits and earrings. *Contact Dermatitis*, **1984**, *10*, 39.
- [24] Haudrechy, P.; Fossereau, J.; Mantout, B.; Baroux, B. Nickel release from nickel-plated metals and stainless steels. *Contact Dermatitis*, **1994**, *31*, 249.
- [25] Menné, T.; Brandrup, F.; Thestrup-Pedersen, K.; Veien, N.K.; Andersen, J.R.; Yding, F.; Valeur, G. Patch test reactivity to nickel alloys. *Contact Dermatitis*, **1987**, *16*, 255.
- [26] Kanerva, L.; Sipiläinen-Malm, T.; Estlander, T.; Zitting, A.; Jolanki, R.; Tarvainen, K. Nickel release from metals, and a case report of allergic contact dermatitis from stainless steel. *Contact Dermatitis*, **1994**, *31*, 299.
- [27] Summer, B.; Fink, U.; Zeller, R.; Rueff, F.; Maier, S.; Roeder, G.; Thomas, P. Patch test reactivity to a cobalt-chromium-molybdenum alloy and stainless steel in metal-allergic patients in correlation to the metal ion release. *Contact Dermatitis*, **2007**, *57*, 35.
- [28] Hendricks, W.M. Complications of ear piercing: treatment and prevention. *Cutis*, **1991**, *48*, 386.
- [29] Kobayashi, Y.; Nanko, H.; Nakamura, J.; Mizoguchi, M. Lymphocytoma cutis induced by gold pierced earrings. *J. Am. Acad. Dermatol.*, **1992**, *27*, 457.
- [30] High, W.A.; Ayers, R.A.; Adams, J.R.; Chang, A.; Fitzpatrick, J.E. Granulomatous reaction to titanium alloy: an unusual reaction to ear piercing. *J. Am. Acad. Dermatol.*, **2006**, *55*, 716.
- [31] Lidén, C.; Menné, T.; Burrows, D. Nickel-containing alloys and platings and their ability to cause dermatitis. *Br. J. Dermatol.*, **1996**, *134*, 193.
- [32] McDonagh, A.J.; Wright, A.L.; Cork, M.J.; Gawkrödger, D.J. Nickel sensitivity: the influence of ear piercing and atopy. *Br. J. Dermatol.*, **1992**, *126*, 16.