Scholarly Research Exchange

SRX Chemistry • Volume 2010 • Article ID 769070 • doi:10.3814/2010/769070

Research Article

Nickel Release from Piercing Jewellery

Miloslav Pouzar, Miroslav Schmidt, Anna Krejčová, and Tomáš Černohorský

Institute of Environmental and Chemical Engineering, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic

Correspondence should be addressed to Miloslav Pouzar, milan.pouzar@upce.cz

Received 2 December 2009; Revised 29 December 2009; Accepted 14 January 2010

The migration of nickel was studied for a set of twelve new units of piercing jewellery and eleven ones used for longer than one year. First, the surface of the samples was analysed using ED XRF and then samples were submerged into the artificial sweat solution for 168 hours at 30°C. The resulting solutions were then analysed using ICP OES. A significant migration of nickel was found for four samples used, whereas only one of them was considered to exceed the migration limit given by ČSN EN 1811 +A1. Regrettably, no connection between elemental composition of particular jewellery sample measured by ED XRF and corresponding Ni release to the artificial sweat was observed.

1. Introduction

Nickel has long been known as a major skin allergen. Heightened exposure to Ni is among the most frequent causes of contact dermatitis. Allergic skin reactions caused by nickel are much more prevalent with women than with men (men 3%, women 17%). The use of earrings and piercing jewellery made from improper material releasing, when in contact with sweat, this element, to the skin, is among the primary risk factors that lead to an allergy. The difference in the frequency of using jewellery in the male and female population also explains the marked difference in the prevalence of the allergy in question [1].

In an attempt to reduce the occurrence of allergic contact dermatitis caused by nickel, the European Parliament and EU Council passed in 1994 Directive 94/27/EC specifying the maximum permissible concentration of Ni in objects that are worn in pierced ears and in other pierced parts of the human body. According to this directive, the mass concentration of Ni in a homogenous part of the product will not exceed 0.05%. For products designed for direct and long-term contact with the skin (earrings, necklaces, bracelets, etc.) the rate of release of Ni will not exceed $0.5\,\mu g \cdot cm^2$ per week. A more recent measure passed by the Commission, Directive 2004/96/EC, in an attempt at more effective protection of EU citizens and taking into consideration new findings on the toxic properties of nickel, sets a migration limit of $0.2\,\mu g \cdot cm^2$ per week. This new limit also applies for earring posts inserted into the pierced ear or into other pierced parts of the human body. In the USA this has currently led to a professional debate on the appropriateness of introducing similar limits [2].

Several works have recently been published that focus on monitoring the content of Ni in jewellery and on assessing the particular migration limit. Kim et al. [3] analysed the Ni content in a set of 9 pairs of earrings, 2 belt buckles, and 2 buttons. The leaching rate of Ni to the artificial sweat solution was also determined for these samples. In another part of the work the authors used a patch test to try to verify the appropriateness of the aforementioned European limits for the Korean population. Since some of the monitored individuals showed greater sensitivity to Ni than that shown in comparable studies within the European population, the authors recommended the passing of a stricter migration limit for the Korean population. The influence of the introduction of Regulation 2004/96/EC to prevent contact between consumers and the products that excessively release Ni and cause allergic contact dermatitis was studied in the work of the Italian authors Bocca et al. [4]. The content of a set of ten earrings was analysed in a pilot study, whereas the Ni concentration in the individual samples ranged from 0.004 mass % to 0.6 mass %. With five of the samples the Ni

content exceeded the 0.05% limit. Of these five samples, three exceeded the permissible migration limit of Ni 0.2 μg/cm^2 per week. A dimethylglyoxime (DMG) test was used to identify earrings releasing a health-risk amount of Ni in the study of Thyssen and Maibach [5]. A total of 277 samples of earrings purchased from 34 different shops in San Francisco were tested, whereas 85 samples (30.7%) showed a positive reaction. No correlation between the price and the health risk of the jewellery was recorded. According to Thyssen et al., a considerable positive influence of the introduction of a norm, which regulates the total content of Ni in jewellery as well as its released percentage when in contact with the skin, on the prevalence of skin allergies (especially among women [6]) was apparent in Denmark. The last study of Thyssen et al. was focused on problems of Ni release from inexpensive jewellery and hair clips. DMG testing revealed that 78 of 354 pieces of jewellery and accessory randomly purchased from 36 stores in Copenhagen, Denmark released an excessive amount of nickel [7].

ED XRF spectrometry is cheap, fast, and nondestructive method of elemental analysis well established in the area of jewellery production and merchandise. This method is used especially for material control and authentication. The objective of this work was to evaluate the possibility of additional use of ED XRF data for the assessing of jewellery health risk connected with Ni migration. The results of the ED XRF analysis of two groups of samples (new jewellery and jewellery used for over one year) were used in the work. Ni leaching into the solution of artificial sweat was used for these samples in accordance with norm ČSN EN 1811 +A1.

2. Experimental Part

2.1. Analysis of Surface Composition of Samples. A set of twelve new hitherto unused items of piercing jewellery was borrowed from a jewellery shop in Zlín. A set of eleven items of piercing jewellery used regularly for over a year was borrowed from students of the Faculty of Chemical Technology, University of Pardubice. The Elva X energy-dispersive X-ray fluorescence spectrometer (Elvatech Ltd., Kiev, Ukraine) equipped with a Pd X-ray and thermoelectric cooler Si-pin detector PF 550 (MOXTEC, USA) was used for a quantitative analysis of the surface of piercing jewellery. In all cases a working voltage of 40 kV was set on the X-ray. The current was optimised for each sample (measuring point) so that the total recorded intensity of radiation emitted by the sample was in the range of 6,000–6,500 impulses. The integration period used was 150 s. An assessment of the measured spectra was made using the Elva 2.7. spectrometer software. The concentration of the different elements was calculated by using combined calibration/noncalibration methods of fundamental parameters described in detail in the work [8]. Three independent measurements were performed at each of the three selected measuring points at each jewellery sample. The average compositions of the surfaces of material-homogeneous parts of samples that were measured using ED XRF spectrometry are included in Table 1. Schematic sketches of samples with an indication of points at which the ED XRF analysis was made are included in Table 2.

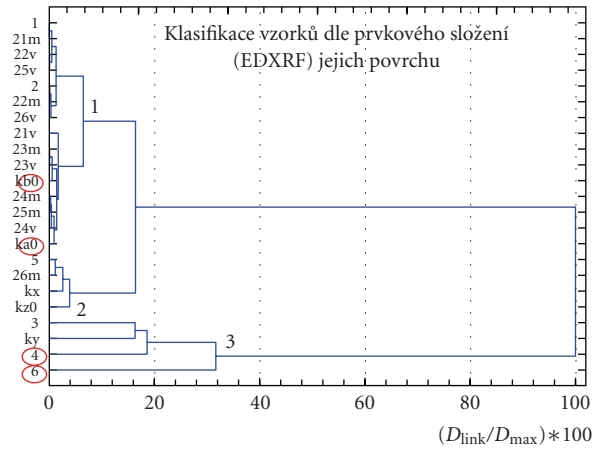


Figure 1: Dendogram of the surface composition of the analysed samples, classification of samples according to the element composition (EDXRF) of their surface.

2.2. Ni Leaching to the Artificial Sweat Solution. The piercing samples were first washed in the solution of common dish soap (JAR-lemon), dried and next leached in the artificial sweat solution prepared in accordance with ČSN EN 1811 +A1. The solution contained 0.1 mass % urea, 0.5 mass % NaCl, and 0.1 mass % lactic acid. Ammonium hydroxide (1 mass %) was used for pH adjusting to the value of 6.5. The PET test tubes contained 7–10 mL of the artificial sweat solution so that the jewellery was always completely submerged. Although in ČSN EN +A1 there is only prescribed use of 1 mL of the artificial sweat for each 1 cm^2 of the sample, this amount in the case of the jewellery we analysed did not allow for complete submersion and so the ensuing analysis of such an amount of solution via ICP OES was unfeasible in our conditions. In similar cases ČSN EN 1811 +A1 recommends the simultaneous soaking of a greater number of jewellery items of a given type, but this was not possible under the conditions of the experiment that we conducted. The soaking of samples was conducted in a water bath at a temperature of 30°C for a period of one week (168 hours). A blank sample was also prepared for each type of test tube. The concentration of leached Ni was measured using the ICP OES spectrometer (Integra XL) (GBC Scientific Equipment Pty Ltd., Australia). The standard solution $1,000 \pm 0.002$ g·l^{-1} (Analytica Co. Ltd., Prague) and Milli Q+ demineralised water (Millipore, USA) were used to prepare the calibration standards Ni 10–25–50–75–100–200 μg·l^{-1}. The detection limit calculated as triple the standard deviation of the sum at the background correction was 5 μg·l^{-1}. Size of soaked sample area and corresponding Ni mass leached to the artificial sweat for each sample are presented in Table 2.

Table 1: Surface composition of the samples measured by ED XRF.

Sample	Measuring points	Fe (mass%)	Cr (mass%)	Ni (mass%)	Mo (mass%)	Cu (mass%)	Mn (mass%)
1	a, b, c	65.19	16.44	14.89	2.13	0.73	0.62
2	a, b	67.06	15.23	13.99	2.22	0.86	0.64
3	a,b	7.60	2.65	2.35	0.00	87.40	0.00
4	a	58.62	13.75	12.49	2.08	12.88	0.18
	b,c	4.25	0.00	8.06	2.30	85.39	0.00
5	a	73.32	16.78	6.18	0.18	1.10	2.44
	b	70.67	15.21	1.53	0.01	2.90	9.68
6	a	0.00	0.00	100	0.00	0.00	0.00
	b	0.00	0.00	70.31	0.00	20.35	0.00
ka	ka0	67.58	17.12	12.27	0.26	0.75	2.02
kb	kb0	68.39	16.23	10.45	0.18	3.01	1.74
kx	kx0	72.73	13.11	0.48	0.04	2.95	10.69
ky	ky0	0.37	0.00	24.87	0.00	45.05	0.00
kz	kz0	64.91	17.12	1.04	0.53	1.94	14.45
21m	21m0, 21mk0	65.14	16.35	14.98	2.08	0.80	0.65
21v	21v0, 21vk0	70.51	16.86	9.33	0.09	1.84	1.37
22m	21m0, 21mk0	67.31	15.44	13.90	1.95	0.64	0.76
22v	22v0, 22vk0	65.94	16.27	14.89	2.02	0.53	0.36
23m	23m0, 23mk0	67.38	16.15	11.06	0.18	3.74	1.50
23v	23v0, 23vk0	67.07	16.17	11.13	0.17	3.91	1.55
24m	23m0, 23mk0	66.93	16.09	12.64	0.47	2.63	1.25
24v	24v0, 24vk0	67.50	15.74	12.43	1.18	1.92	1.23
25m	25m0, 25mk0	66.93	15.57	12.17	0.94	3.23	1.16
25v	25v0, 25vk0	66.19	16.11	14.88	1.90	0.53	0.40
26m	26m0, 26mk0	70.10	14.68	7.15	0.43	1.98	5.66
26v	26v0, 26vk0	66.44	15.43	14.51	2.15	0.55	0.92

In sample 6 (measuring point b) 9.34% Zn was determined and in sample ky 28.68% Zn, 1.6% Pb, and 0.43% Sn were determined.

3. Results and Discussion

Using the Statistica program's cluster analysis (version 6.0, StatSoft), the studied samples were classified into groups according to the details of the surface composition. The input data (symbols) were the contents of the elements (Fe, Cr, Ni, Mo, Cu, Mn, Zn, Pb, and Sn) determined using ED XRF. The cluster analysis was done using Ward's Method employing the Euclidean distance. The resulting dendogram displayed in Figure 1 shows that based on surface layer composition the analysed jewellery can be divided into three groups. The first group has all unworn jewellery 21 through 25m and 21 through 26v as well as worn samples 1, 2, ka, and kb. The second group has unworn jewellery 26m and worn samples 5, ky, and kz. The data in Table 1 show that the samples in groups 1 and 2 differ particularly in Mn content. The third group consists of material worn samples 3, 4, 6, and ky. However, none of these obtained groups represent samples that would show either only a low or only a high share of migrating Ni.

As apparent from the data included in Table 2, 22 out of the 26 analysed samples safely comply with the Ni migration limit 0.2 $\mu g \cdot cm^{-2}$ per week, required by norm ČSN EN 1811 +A1 for earring posts inserted into pierced ears or other parts of the human body. A greater amount of Ni was leached from samples ka, kb, 4, and 6. All these samples were obtained from University of Pardubice students.

The ka and kb samples do not show significant statistical difference in their surface composition from other samples, included during a discrimination analysis in group 1, that comply to the norm. It is therefore impossible to predict from the sample surface composition determined by ED XRF whether the Ni from the sample will be released in an amount that exceeds the limit or not. The intended goal of our further work, which is to consist of the creation of a database of ED XRF spectra of various materials by which (in applying advanced statistical methods) it would be possible to quickly and cheaply estimate the possible health risk that a piece of measured jewellery represents, seems to be unfeasible in light of these results. A test by submersion in the artificial sweat is apparently necessary for this given purpose.

These samples (ka and kb) represent parts of the piercing jewellery that are not directly inserted into pierced parts of the human body, therefore, in accordance with ČSN EN 1811 +A1, it is necessary to leach only the part of the surface that comes into direct contact with the human body. In effort to save time, we decided to leach all the samples. The subsequent more detailed analysis of samples

Table 2: Amount of Ni leached to the artificial sweat solution.

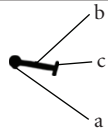
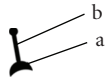
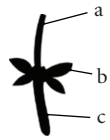
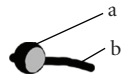
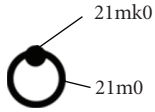
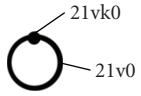
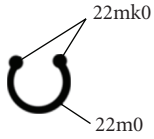
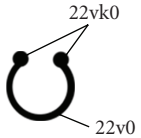
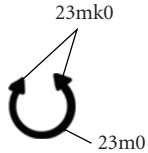
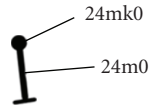
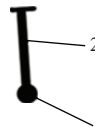
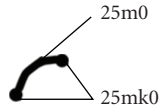
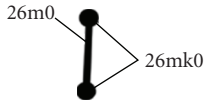
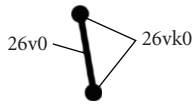
Sample		Surface area (cm^2)	Worn	Released nickel ($\mu g \cdot cm^{-2}$ per week)	Number of groups appointed by discrimination analysis
1		0.25	Yes	X	1
2		0.56	Yes	0.02	1
3		0.21	Yes	0.06	3
4		5.66	Yes	0.61	3
5		2.02	Yes	0.01	2
6		1.66	Yes	2.14	3
ka		0.79	Yes	0.71	1
kb		0.79	Yes	0.34	1
kx		0.79	Yes	X	2
ky		0.79	Yes	X	3
kz		0.79	Yes	X	2
21m		1.50	No	0.01	1
21v		1.61	No	0.01	1
22m		0.92	No	0.04	1
22v		1.82	No	0.01	1
23m		1.34	No	0.01	1

Table 2: Continued.

Sample		Surface area (cm^2)	Worn	Released nickel ($\mu g \cdot cm^{-2}$ per week)	Number of groups appointed by discrimination analysis
23v		1.49	No	0.01	1
24m		0.61	No	0.02	1
24v		1.00	No	0.03	1
25m		0.72	No	0.07	1
25v		1.15	No	0.03	1
26m		2.44	No	0.01	2
26v		2.27	No	0.01	1

X: concentration of Ni in the artificial sweat was below the ICP OES limit of detection 5 $\mu g \cdot l^{-1}$.

breaking the limit in accordance with ČSN EN 1811 +A1 was supposed. But for ka and kb it was not necessary to perform a new analysis. ED XRF results demonstrated material homogeneity of the analysed pieces of jewellery. So, it was possible to suppose a uniform Ni release from the whole sample surface. Maximal part of jewellery coming into direct contact with the skin was estimated on 1/4 of the whole surface. Moreover, the ČSN EN 1811 +A1 advises application of conversion factor 0,4 for samples with Ni release near the limit to overcome the particular laboratory differences. Surface corrections of Ni release for ka and kb samples together with the conversion factor application would give us results safely below the release limit.

Sample 4 consists of an earring post, which is inserted into a pierced part of the body, and an earring jewel, a small part of which may come into contact with the skin. The high amount of Ni released to the artificial sweat solution shows the possible health risk of this jewel. However, further testing separately determining the leaching rate of Ni from the earring post and from the earring jewel would be needed for a more detailed assessment of the sample compliance with ČSN EN 1811 +A1.

Sample 6 also consists of two parts. The part coming into contact with the skin is coated with a layer of pure Ni, the earring post designed to be inserted into the pierced part of the body has a surface layer made up of 70% Ni, 20% Cu, and 10% Zn. Even if all the Ni concentrations ascertained during the leaching test were released from the part of the jewel that is not inserted directly into the pierced part of the body, it can be assumed that this sample would not comply with norm ČSN EN 1811 +A1.

4. Conclusion

The process described in norm ČSN EN 1811 +A1 was used to assess the health risk presented by the release of Ni from piercing jewellery. Of the 26 analysed pieces of jewellery, 22 easily fell within the prescribed migration limit for Ni of 0.2 $\mu g \cdot cm^{-2}$ per week. A greater leaching rate was ascertained for two other samples, but since these were for parts of the jewellery that were not inserted directly into pierced parts of the body, the less strict limit of 0.5 $\mu g \cdot cm^{-2}$ per week could be applied. These samples also easily fell within

this limit. One sample demonstrably fell outside the norm limits and another sample required more detailed testing regarding the leaching rate limit. All four samples for which a higher Ni leaching rate was ascertained came from University of Pardubice students; the samples were regularly used for more than one year. The ED XRF analysis of the surface of samples did not provide information that could be used for an accurate prediction of the Ni leaching rate from piercing rings.

Acknowledgment

This work was carried out thanks to the financial support of the MSM 0021627502 project.

References

[1] J. P. Thyssen, A. Linneberg, T. Menné, and J. D. Johansen, "The epidemiology of contact allergy in the general population—prevalence and main findings," *Contact Dermatitis*, vol. 57, no. 5, pp. 287–299, 2007.

[2] L. K. Lu, E. M. Warshaw, and C. A. Dunnick, "Prevention of Nickel allergy: the case for regulation?" *Dermatologic Clinics*, vol. 27, no. 2, pp. 155–161, 2009.

[3] Y. Y. Kim, M. Y. Kim, Y. M. Park, H. O. Kim, C. S. Koh, and H. K. Lee, "Evaluating the nickel content in metal alloys and the threshold for nickel-induced allergic contact dermatitis," *Journal of Korean Medical Science*, vol. 23, no. 2, pp. 315–319, 2008.

[4] B. Bocca, G. Forte, O. Senofonte, et al., "A pilot study on the content and the release of Ni and other allergenic metals from cheap earrings available on the Italian market," *Science of the Total Environment*, vol. 388, no. 1–3, pp. 24–34, 2007.

[5] J. P. Thyssen and H. I. Maibach, "Nickel release from earrings purchased in the United States: the San Francisco earring study," *Journal of the American Academy of Dermatology*, vol. 58, no. 6, pp. 1000–1005, 2008.

[6] J. P. Thyssen, J. D. Johansen, T. Menné, N. H. Nielsen, and A. Linneberg, "Nickel allergy in danish women before and after nickel regulation," *New England Journal of Medicine*, vol. 360, no. 21, pp. 2259–2260, 2009.

[7] J. P. Thyssen, T. Menné, and J. D. Johansen, "Nickel release from inexpensive jewelry and hair clasps purchased in an EU country—are consumers sufficiently protected from nickel exposure?" *Science of the Total Environment*, vol. 407, no. 20, pp. 5315–5318, 2009.

[8] T. Černohorský, M. Pouzar, and K. Jakubec, "ED XRF analysis of precious metallic alloys with the use of combined FP method," *Talanta*, vol. 69, no. 3, pp. 538–541, 2006.