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Article

Nondestructive Determination of Allergenic and Toxic Elements in Jewelry: a Comparison of Benchtop and Portable Energy Dispersive X-Ray Fluorescence Spectrometers

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A fluorescência de raios X (XRF) é uma técnica bem estabelecida na caracterização de ligas metálicas e, atualmente, aparelhos portáteis começam a se tornar populares. O objetivo desse estudo foi analisar colares, brincos, pulseiras, anéis e *piercings* com espectrômetros de XRF portátil e de bancada, verificando se o método permite a classificação de joias com relação às exigências das normas. Além disso, comparar e checar a viabilidade de análises de campo com o equipamento portátil em apenas 5 s de irradiação. No total, 117 peças foram analisadas, ultrapassando 450 medidas. Os elementos Ni e Pb foram encontrados em uma série de amostras com concentrações superiores àquelas recomendadas, mesmo naquelas consideradas livres de Ni e Pb. Assim, foi possível determinar teores de elementos nobres e alergênicos com adequada detectabilidade, baixos desvios e boa concordância entre os equipamentos empregados, sem etapas de pré-tratamento das amostras e sem geração de resíduos.

X-ray fluorescence (XRF) is a widespread technique for alloy characterization and nowadays portable instruments are becoming popular. The objective of this study was to analyze necklaces, earrings, bracelets, rings and piercings by portable and benchtop XRF equipments, in order to verify if the presented methodology allows characterization of these objects, determining whether they meet – or not – current legislations regarding the concentrations of metals. Also to compare the equipments and check the feasibility of field measurements with portable equipments in just 5 s of analysis. In total 117 pieces were analyzed, surpassing 450 measurements. Nickel and Pb were found over the established limit in several samples, even on those attested as Ni- and Pb-free. It was possible to verify contents of noble or allergenic metals, with adequate detectability, low deviation and good agreement between both equipments employed, without sample treatment steps and without residue generation.

Keywords: jewelry, contact dermatitis, toxic elements, allergenic elements, X-ray fluorescence

Introduction

Contact dermatitis is a skin inflammation induced by exposure to an external sensitizing agent. In severe cases, it is characterized by redness and itchy blistering. It is the most common skin disease, causing large socioeconomic impact due to sick leave and job changes.[1]

This allergy, triggered by frequent or constant contact of the allergenic with the skin, may be caused by metals such as Al, Au, Co, Cr, Cu and Ni. The toxicity is associated with the metal ions and the process of irritation starts with the corrosion of the pure metal or its alloy. In the skin, corrosion may be favored by the presence of sweat, which also has an important role in the ion diffusion, enhancing the sensitizing effect.[2]

A large number of contact dermatitis cases are related to Ni, since it is present in a variety of metal alloys found in everyday life, such as white gold or stainless steel.[3] Studies have shown that in the period from July 1998 to December 2000, 16.2% of patients tested showed positive allergic reactions to this metal; moreover, allergy to Ni is associated with all ages, being especially common in childhood and adolescence.[4] Common sources of exposure to these age groups are belt buckles, metal buttons on clothing, jewelry and eyeglass frames.[5] Among the jewelry, ear piercings represent the major source of exposure and, because they

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are more commonly used by women, the incidence among them is up to 20 times higher than among men.[5,6]

To minimize the problem, the European Community created in 1976 a resolution which established maximum values of Ni in products with direct and prolonged contact with skin, such as earrings, necklaces, bracelets, rings, buttons and zippers (Directive 76/769/EEC).[7] This directive stated initially that the products should have a content of less than 0.05% of Ni. More recently, after the implementation of Directive 2004/96/EC, the rate of migration of the metal and not just its total content has been considered. Thus, it was allowed a maximum rate of migration of 0.5 µg cm^{-2} week^{-1} for products with direct and prolonged contact with skin and 0.2 µg cm^{-2} week^{-1} for those who are inserted into the body.[7,8]

Similar concern is found in ASTM rules, considering the material quality used in human body implants, such as stainless steel alloys, for example. These steels must have very well controlled mechanical properties and the knowledge of their composition is of vital importance, since these characteristics depend on the levels of metals present. In the case of the 316 alloy family, the presence of Cr and Mo has a direct influence on the corrosion resistance, thus avoiding the undesirable migration of elements to the body.[9,10]

There are different methods for metal quantification in metallic alloys. The methodology presented in this study is energy dispersive X-ray fluorescence (EDXRF), now a widespread technique due to its ability to identify and quantify inorganic species in a fast, simple, non-destructive and inexpensive way. Moreover, it is applicable to a wide concentration range, has appropriate analytical accuracy and precision, and requires minimal and sometimes no sample preparation.[11]

The larger resolution of near X-ray energies provided by EDXRF is due to the emergence of Si(Li), Ge(Li) and hyper pure germanium (HPGe) semiconductor detectors. The disadvantages of these detectors are the high cost and the necessity to operate at cryogenic temperatures. Over the past 10 years, however, portable EDXRF devices were made possible by new cooling technologies, such as the Peltier effect, allowing smaller, lighter detectors that are able to operate at room temperature. This scenario suggests that portable EDXRF seems to be ideal for non-destructive analyses in the field.[12,13]

Although X-ray fluorescence (XRF) has been used in the laboratory for decades, field portable XRF (FPXRF) proved to be a highly promising technique in recent years, becoming increasingly accepted and nowadays operating at the forefront of the area in most varied applications.[14,15] FPXRF presents a very favorable cost-benefit ratio for field measurements of environmental and archaeological samples, quality control and others. It also offers advantages when compared to conventional methods of analysis.[16,17]

Metal alloy analysis by XRF is a common application of the technique. Specifically for jewelry analysis, XRF is often used for quality control and authentication of pieces, with benchtop equipments being commonly used.[18-20] On the other hand, portable equipments are also used, albeit in a much smaller number of papers;[21] for example, portable devices are associated with analyses of cultural heritage pieces, due to the non-destructive nature of the technique and the possibility of performing analyses without removing, for example, valuable items from their exhibition places.[22-24]

The objective of this study was to analyze jewelry (necklaces, earrings, bracelets, rings and piercings) by portable and benchtop EDXRF equipments, in order to verify if the presented methodology allows characterization of these objects, determining whether they meet – or not – current legislations regarding the concentrations of metals and to compare the equipments and check the feasibility of field measurements with portable equipments.

Experimental

Sampling

In this study, jewelry and costume jewelry purchased in Brazil and Spain were analyzed. The set consists of necklaces, bracelets, earrings and rings. Most of the samples carried indications of their origins, like India, Mexico, Philippines; samples whose origins were not identified were assumed to be Brazilian. Samples purchased in Spain have Indian and Chinese origins and bring the indication that they are Ni- and Pb-free. Ten pieces of various piercings (ear reamers, navel piercings, ear and eyebrow) were also analyzed, totalizing 17 irradiation points. These piercings were acquired at the popular market of Campinas, with all the pieces coming from China.

The pieces were analyzed without any pre-treatment, being simply cleaned with tissue paper, classified and analyzed directly, with most of the points that could vary in composition being sampled: a typical case is that of a necklace composed of chain, its clasp and a pendant.

Measurement conditions

For irradiation, two energy dispersive X-ray spectrometers were used: a Shimadzu EDX700 and a portable Innov-X Alpha6500. Measurement conditions are displayed at Table 1. The criteria for the irradiation time definition in the portable equipment was the peak to background ratio greater than 3, considering the deviations, for the elements of interest. It was tested 20 s, 10 s and 5 s. As a handheld equipment was used, the smallest time was considered, due to problems with measurement geometry.

Table 1. X-ray fluorescence spectrometer operational conditions

Equipment	Shimadzu EDX700	Innov-X Alpha 6500
X-ray tube target	Rh	Ta
High voltage applied / keV	50	40
Current / µA	Variable	20.5
Filter	No filter	Cu (250 µm)
Atmosphere	Air	Air
Detector dead time / %	25	–
Resolution / keV	0.02	0.22
Irradiation time / s	100	5

Measurements

In the portable equipment, 52 bracelets, 28 necklaces, 21 earrings and 6 rings were analyzed, totaling 400 measurements in different parts of each piece. For the benchtop equipment, 52 bracelets and 28 necklaces were analyzed. Rings and earrings were not analyzed in the benchtop equipment due to geometry constraints.

Most samples were analyzed in manual mode in the portable equipment. So it was possible to analyze regions with less favorable geometry. It would not be possible to measure these samples in the benchtop system. However, in some cases the samples were placed in the specific support of the equipment.

All measurements were performed in triplicate for each sampled point, with average intensities being subsequently calculated. Quantification of detected elements was performed by routines provided with the equipments' own software, and in both cases calculations were based on the fundamental parameters (FP) method.[25]

Detection limit calculations for the portable equipment were obtained with standard metallic alloy with Ag, Au, Cu, Ni and Pb in different concentrations (UPA Technology Inc. Thickness Standard Ag-Cu 10132-3, Au-Cu-Ni 10132-1 and Sn-Pb-8 11048, USA). For recovery calculations, certified steel metallic alloys C4340, 316 and 416 (KR5100 and KR5101, Metal Samples Company, USA), were used. The concentration values were determined in triplicate for the presence of Cr, Cu, Fe, Mn, Mo and Ni, elements commonly found in jewelry. All measurements were performed under the same operating conditions for each equipment, as described in the measurement conditions section.

Limits of detection (LOD) calculations

Typically, softwares employed in FP quantification do not provide limits of detection (LOD) for the analyzed metals. The limits were therefore calculated by analytical curve construction and the use of background net area as an estimate of the standard deviation of the blank. FP is a method with great ability to resolve interference from inter-element effects, provided that samples are not complex – which is the case of metal alloys. The basic principle is to establish a relation between the intensity of an emission line with its concentration. However, it is necessary to have prior knowledge of physical constants, elemental sensitivities, geometric factor, detector efficiency values and the mass absorption coefficient for each element, in addition to the energy range of interest. Thus, it is necessary to obtain an analytical curve similar to those provided by the Beer-Lambert law ($A = \varepsilon LC$) for radiation absorption, as well as its linear attenuation coefficient.

To circumvent this problem, certified metal standards were irradiated and calibration curves for Ni, Ag, Au and Pb constructed employing the concentration values provided by the FP method, calculated by the equipment software, and the Kα peak areas of the elements. Estimation of background area and standard deviation for the blank were obtained with WinQxas 1.30 software from the International Atomic Energy Agency.[26]

Results and Discussion

Limits of detection and recovery

Limits of detection were calculated according to IUPAC indications, using $LOD = (3.3\ \sigma/s)$, where σ is the standard deviation and s is the angular coefficient of the analytical curve.[27] Limit comparisons are presented in Figure 1.

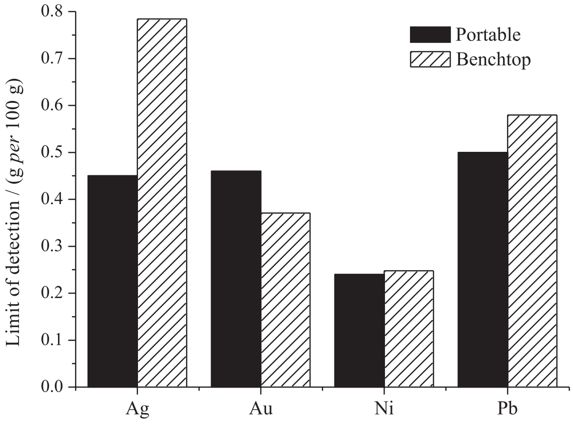

Figure 1. LOD comparison for Ag, Au, Ni and Pb from metallic alloy standard samples.

A case with a large variation is that for the Ag LOD, where the portable equipment, considering the Lα and Lβ lines of Ag, has a better efficiency. It must be noted that the values for LOD are adequate for analysis of jewelry and costume jewelry samples. In the specific case of Ni, the values of 0.2 g *per* 100 g for both equipments are larger than the maximum value of 0.05 g *per* 100 g recommended by the European Community. However, as the concentrations of most samples were superior to the LOD values, this indicates that there is no compromise in the quality of analysis. In the case that the determined concentration falls below the LOD, there will be a range where nothing can be stated about the sample quality.

For Ni the maximum concentration level established in ASTM F138-08 and F139-08 rules is 13 to 15 g *per* 100 g.[9,10] The LOD values for both portable and benchtop equipment was 0.2 g *per* 100 g, since these materials present compatible use with jewelry. In this case, the LOD values are suitable for the compliance verification with the norms and the equipments may be used without any problem. Furthermore, the numbers for Au and Ag, which exhibit high economic value, are lower than those typically present in jewelry samples, which entitles the use of the scanning technique in these types of material composition.

In recovery calculations where the irradiation conditions are closer to ideal, that is, without geometry problems, the contents are adequate regarding the metals present in the samples. These values are displayed in Table 2.

Considering the values for Ni, the most important element in this study due to the above mentioned allergenic problems, for both the C4340 and 316 alloys a great accuracy with certified values is observed with both the equipments. The only case in which this trend is not met is with the 416 alloy, since the concentration of the metal (0.43 g *per* 100 g) is significantly lower than the others and very close to the LOD (0.2 g *per* 100 g). This indicates that not only irregular geometry may hamper analysis, but also concentrations very close to the LOD increase the quantification difficulties.

In LOD estimation, samples were composed of only 3 elements (Au, Cu, and Ni), and are less complex than those

Table 2. Average recovery standard reference materials for C4340, 316 and 416 steel alloys (n = 3)

Element	Certificate / (g *per* 100 g)	Benchtop		Portable	
		Measured / (g *per* 100 g)	Recovery / %	Measured / (g *per* 100 g)	Recovery / %
Steel C4340					
Cr	0.82	0.91 ± 0.01	111	0.9 ± 0.2	106
Cu	0.15	0.13 ± 0.02	83	–	–
Fe	95.59	96.4 ± 0.1	101	96.6 ± 0.4	101
Mn	0.72	0.69 ± 0.03	96	0.7 ± 0.1	90
Mo	0.25	0.28 ± 0.01	112	0.24 ± 0.01	96
Ni	1.72	1.56 ± 0.03	91	1.6 ± 0.3	94
Steel 316					
Cr	16.55	17.6 ± 0.2	106	17.3 ± 0.7	104
Cu	0.19	–	–	–	–
Fe	68.723	67.4 ± 0.7	98	68.5 ± 0.6	100
Mn	1.74	1.8 ± 0.2	103	1.3 ± 0.2	75
Mo	2.1	2.48 ± 0.06	119	2.15 ± 0.05	102
Ni	10.48	10.6 ± 0.4	101	10.5 ± 0.5	100
Steel 416					
Cr	12.45	13.23 ± 0.08	106	12.2 ± 0.1	98
Cu	0.19	0.145 ± 0.009	76	–	–
Fe	85.036	85.2 ± 0.1	100	86.9 ± 0.2	102
Mn	0.9	0.99 ± 0.03	110	0.90 ± 0.07	100
Mo	0.07	0.099 ± 0.06	143	0.073 ± 0.006	100
Ni	0.43	0.26 ± 0.02	60	–	–

Table 3. Concentration range for all analyzed jewelry samples in the benchtop and portable XRF equipment

Element	Benchtop / (g *per* 100 g)			Portable / (g *per* 100 g)		
	Min.	Average	Max.	Min.	Average	Max.
Ag	0.157 ± 0.004	26	98.7 ± 0.1	0.53 ± 0.04	38	100 ± 1
Au	0.07 ± 0.01	12	39 ± 2	1.8 ± 0.3	6.0	17 ± 1
Br	0.8 ± 0.5	7.6	25 ± 7	–	–	–
Ca	0.12 ± 0.08	2.9	10.7 ± 0.8	–	–	–
Cd	0.16 ± 0.02	1.1	2.3 ± 0.1	–	–	–
Cr	0.009 ± 0.005	4.4	19.5 ± 0.4	15.4 ± 0.3	–	–
Cu	0.20 ± 0.03	53	99.7 ± 0.3	1.7 ± 0.3	49	100 ± 1
Fe	0.08 ± 0.01	12	71.5 ± 0.3	0.17 ± 0.06	22	100 ± 28
Mn	0.027 ± 0.006	0.4	1.55 ± 0.04	–	–	–
Ni	0.02 ± 0.01	32	98.3 ± 0.1	0.82 ± 0.08	23	86.3 ± 0.8
Pb	0.015 ± 0.005	4.6	24 ± 2	0.3 ± 0.1	10	48.1 ± 0.9
Pt	0.14 ± 0.02	0.2	0.17 ± 0.02	–	–	–
Sb	0.18 ± 0.02	16	73 ± 6	0.695 ± 0.007	2.5	6.8 ± 0.2
Sn	0.1070 ± 0.0003	18	97 ± 1	0.5 ± 0.2	18	49.3 ± 0.6
Ti	–	–	–	0.9 ± 0.3	12	90 ± 9
Zn	0.11 ± 0.01	9.4	40.6 ± 0.3	1.0 ± 0.2	16	66 ± 1

of steel, consisting of 6 metals (Cr, Cu, Fe, Mn, Mo and Ni). Besides the number of species, their concentrations also differ. This situation is a very good example of the interelemental effect in XRF and PF quantification, and the considerations apply only to the set of samples originally used in the calculation of LOD.

Since more than 450 measurements were performed, Table 3 presents the minimum, average and maximum values obtained for each element in all the jewelry samples. Detailed concentration values for the elements detected by both devices in all samples are presented in Tables S1 to S6 in the Supplementary Information (SI).

Figure 2 presents, as example, the spectra from portable and benchtop equipment of sample C20. The concentration of the quantified elements are, (in g *per* 100 g), Ag (1.38 ± 0.07), Cd (1.2 ± 0.1), Cu (41 ± 2), Ni (26 ± 2), Pb (1.00 ± 0.02) and Sn (29.0 ± 0.7) for the benchtop equipment and Ag (0.85 ± 0.02), Cu (35 ± 1), Ni (24 ± 2), Pb (1.1 ± 0.3) and Sn (38.9 ± 0.3) for the portable one. The scattering peaks from the X-ray tube targets are very small compared to the metallic element peaks that are in high concentration.

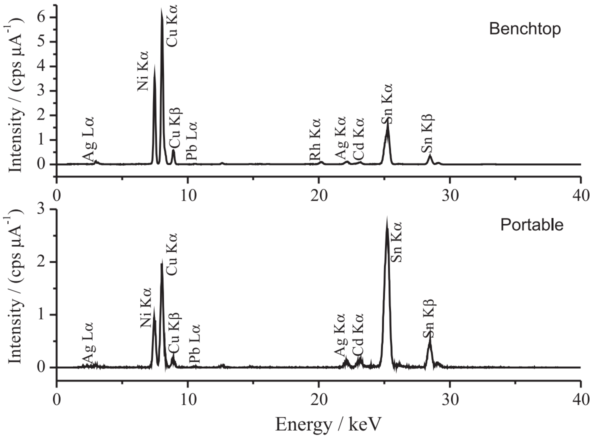

Figure 2. Spectra from the portable and benchtop equipments of sample C20.

Ni and Pb investigation

Metal quantification was performed in 26 necklaces, and in several of them there was agreement among the elements and concentrations obtained in both devices. A good example is sample C07 (Figure S1a), where Ni was quantified at a 5 g *per* 100 g level in both equipments.

Besides Ni, levels of Cu and Fe were determined to be in agreement with each other, which, in this case, is explained by the favorable geometry of the samples. Favorable geometry is understood as the absence of significant surface imperfections and pronounced changes in the angles and surface roughness, which would generate a very large variation in the piece angulations or in the distance between the optimum position of the X-ray beam incidence and the real measurement position. Changes in these parameters would cause different scattering and an increase in deviations for the same sample. For sample C07, Ni levels are higher than that established by the 94/27/EC directive, which allows 0.05% for products with direct and long skin contact, as jewelry. The packaging of this sample indicates that the product is Ni-free.

Another example of coincidence between the sample measurements is sample C20 (Figure S1b), where pendant Ni and Pb contents are found at 24 ± 2 and 1.1 ± 0.2 g *per* 100 g for the portable, 26 ± 2 and 1.00 ± 0.02 g *per* 100 g for the benchtop equipments, respectively. This piece is flat and smooth, thus reducing the geometry effect and favoring minor deviations between the measurements. For the same piece, when the chains are analyzed, the results do not follow the same trend observed previously, since the measurement region is narrow, rugged and cylindrical. These characteristics lead to incidence of X-rays with different angles and distances in each measurement. This is reflected in the Ni values, which differ by 53% between equipments (21 ± 1 to 45 ± 2 g *per* 100 g for portable and benchtop, respectively). Again, these values are above the limits established by regulatory agencies.

The same situation occurs with bracelets, such as sample P06, where Ni concentrations (0.78 ± 0.02 and 0.93 ± 0.08 g *per* 100 g for benchtop and portable equipments, respectively) and Pb (4.2 ± 0.1 and 7.1 ± 0.4 g *per* 100 g) show relative agreement. This correlation is again due to the piece's favorable geometry (Figure S1c), which displays smooth and relatively flat regions.

However, this trend is not always observed and values may differ. Sample C13 is an example of this behavior (Figure S1d). In this sample, Ni values present considerable variance (Table 4), probably due to geometric sample characteristics. A spherical shape makes irradiation under the same conditions difficult, especially for a handheld portable equipment, and this explains the poor correlation between the values.

Table 4. Comparison between C1 sample Ni concentrations

Irradiation region	Benchtop / (g *per* 100 g)	Portable / (g *per* 100 g)
Smaller sphere	–	10 ± 1
Medium sphere	14 ± 1	–
Bigger sphere	4.3 ± 0.7	1.2 ± 0.2
Chain	10.8 ± 0.3	5.4 ± 0.5

Despite this lack of agreement, all values are higher than those indicated in the EC norms, which is 0.05%, showing that the technique allows evaluation of the jewelry quality.

In bracelet P19 (Figure S1e), Ni values were 7.0 ± 0.2 and 4.4 ± 0.3 g *per* 100 g for the benchtop and portable equipments, respectively, corresponding to a variation of 58% compared to the lowest value. Again, these concentrations are higher than the limit of 0.05%, constituting a sample out of specifications. Nevertheless, there is agreement for Cu (53 g *per* 100 g) and Ag (39 g *per* 100 g) in the bracelet, due to its high concentration.

Regarding piercings (Figure S1f), Fe (0.27 to 74.7 g *per* 100 g), Cr (12.5 to 19.4 g *per* 100 g), Mn (1.3 to 16.5 g *per* 100 g), Ni (0.4 to 69.5 g *per* 100 g), Cu (0.3 to 45.2 g *per* 100 g) and Mo (0.03 to 2.8 g *per* 100 g) were found in all samples. The critical case, for the reasons already explained, is Ni, whose content was higher than 0.05% (the maximum recommended by the EC) in 80% of the pieces, which would be sufficient to induce allergic processes in predisposed individuals. Even more alarming was the indication of 1.8% of Pb in one of these samples. A graph compares the values for Ni detected by both equipments (Figure 3).

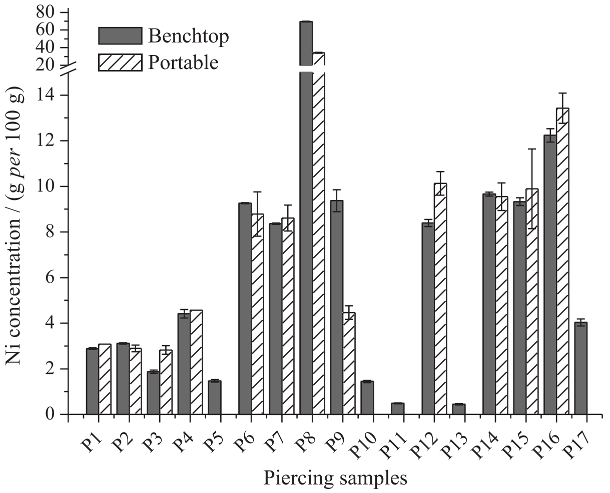

Figure 3. Comparison between Ni values in piercing samples for benchtop and portable equipments.

When it comes to the precision of the measurements, a trend in almost all of the determinations is that standard deviation values in the portable equipment are larger than those displayed by the benchtop equipment. For bracelet P06, for example, standard deviations for Ni were 0.2 and 0.8% for benchtop and portable equipments, respectively, and for Pb, 1 and 2%. This trend is due to the difficulty in positioning the portable equipment in handheld mode, where little modifications in position and angulations are associated with noise in the spectrum. In addition, measurements with smaller irradiation times are subject to larger deviations because the signal to noise ratio is decreased.

Nevertheless, the technique has adequate capacity for detection and quantification of the various elements present in the samples, with the advantage of non-destructive analysis, preserving the integrity of the piece after its irradiation. The measurement time is very low – 5 s for the portable and 100 s for the benchtop systems. When compared to traditional analysis by wet sample preparation, which employs steps that require time such as sample digestion, standard preparation, disposal and treatment of waste, these 100 s are negligible. For XRF, there is no need for using concentrated acids, avoiding exposure of the analyst to a considerable risk. In addition, the use of gases such as acetylene, in the case of FAAS, or argon, in the case of ICP OES, which raises the analysis cost, is not necessary. Another very interesting factor for the use of the portable equipment is the possibility of field analyses, making it a suitable tool for quality control and material compliance verification with applicable governmental laws and regulations.

Precious metals

XRF is indicated not only for situations of suspected contamination of jewelry or compliance verification, but also for quantification of metals that have high economical value, such as Ag and Au. In some samples, these metals could be quantified, with the results being in agreement between equipments: such was the situation, for example, for necklace C16 (Figure S2a).

For this sample, 75.2 and 81 g *per* 100 g of Ag were determined by the benchtop and portable equipments, respectively. The difference in the values is due to geometry reasons. This behavior is even more pronounced for Ni, with a content of 21.1 g *per* 100 g on the benchtop and 13 g *per* 100 g on the portable equipment, which still indicates a real capacity to cause allergic reactions in people with sensitivity to the metal.

Sample C27 presented 3.4 and 5.7 g *per* 100 g of Au in the chain by the benchtop and portable equipments, respectively, and 4 and 6 g *per* 100 g in the medallion. The variation could be attributed to the geometry, but in the case of the medallion, there is an influence of the polymeric material that fills the piece, indicated by the 2.2 g *per* 100 g of Br. This probably occurs due to the irradiation of the metal layer and the polymeric material, leading to diverse concentrations (Figure S2b).

Regarding bracelets, Ag was detected in sample P15 (Figure S2c) (93.7 and 96 g *per* 100 g for benchtop and portable equipments, respectively), while Au (39 and 43 g *per* 100 g for benchtop and portable equipments, respectively) was observed in sample P21 (Figure S2d). In both cases, the standard deviation is relatively small, around 2%.

Sample P36 presented 41 and 40 g *per* 100 g levels of Ag for benchtop and portable equipments, respectively. Ni levels of 15 and 12 g *per* 100 g for benchtop and portable equipments, respectively, were detected, showing that jewelry or trinkets with higher prices are not always a suitable alternative for people with a history of Ni allergy (Figure S2e).

Evaluation of corrosion resistance of piercings' metallic alloy

Unlike traditional jewelry or trinkets, piercings remain in direct and constant contact with the skin. This lengthened contact time of the metallic material with sweat may cause corrosion, and thus migration of metals to the body.[2] Therefore, corrosion is an important matter to be addressed regarding metallic alloy quality. An example of this concern is indicated in ASTM F138-08 and F139-08[9,10] and ISO 5832-1[28] norms. In this case, Cr and Mo concentrations, calculated through equation 1, must exceed 26%.

$$\%\text{Cr} + 3.3\%\ \text{Mo} \geq 26 \qquad (1)$$

When this is not observed, localized corrosion may take place through a superficial pitting that vertically reaches the inner part of the piece. Stainless steels are subject to this type of corrosion and the addition of Cr and especially Mo can prevent fraying, justifying its concentration control.[29] Chromium and Mo concentrations can easily be determined by the proposed method, and experimental values calculated by equation 1 for the studied piercing samples (Figure S1f) are between 13 and 20, in disagreement with the norms.

Conclusions

The jewelry, costume jewelry and piercing studies provided one of the best work situations for XRF with the FP method, since inter-element effects are less pronounced due to the low complexity of the samples. Thus, it was possible to verify contents of noble or allergenic metals, with adequate detectability, low deviation and good agreement with the determined values. Besides these advantages, the fact that the samples are not destroyed during analysis is very advantageous due to the economic value of some samples. With regards to the levels found for Ni, there is obvious concern, since most of the samples have concentrations that are sufficient to trigger allergic processes in prone people. This would indicate the need for greater attention by healthcare government agencies.

Supplementary Information

Supplementary information (Figures S1-S2, Tables S1-S6) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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