CONFORMITY ASSESSMENT OF TOXIC METALS IN JEWELRY IN SOUTH OF BRAZIL

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Abstract

Chemical exposure beyond legal limits can be harmful to the human body. Several cases of death caused by toxic metal exposure had already been reported all over the world. Among those, infection by jewelry is a common threat. The awareness in this subject was brought up in the early 2000's, and since then, several countries began to create standards and legislations in order to lower the people's exposure to it. In Brazil, the limit concentration of toxic elements, such as lead, cadmium, chrome and other toxic metal was defined in January of 2019, to have a maximum concentration between 0.01% and 0.03%. This legislation, however, could not stand without verification. The purpose of this research is to evaluate, by X-Ray spectrophotometer and by Inductively Coupled Plasma Optical Emission Spectrometry, the concentration of toxic metals in jewelry commercialized in Brazil and the compliance of the concentrations with the legislation. The result showed that approximately 90% of the 48 samples analyzed did not meet the requirements of maximum limits allowed. Not only this means that the general population is at a constant risk, but also that the conformity assessment procedures should be evaluated carefully by the government.

Keywords: Toxical metals, conformity assessment, jewelry.

1. Introduction

The elevated concentration of toxic metal in jewelry can become a national public health issue. In 2013, a loading of 16 tons of jewelry was apprehended by the Brazilian Revenue Service, due to suspected tax fraud. For purposes of tax fraud verification, 24 samples from this load were taken for chemical analysis. It was found that 14 of these samples had over 30% of cadmium [Anvisa, 2018; Portal G1, 2013]. In Brazil, until then, there was no legislation for the maximum concentration of cadmium nor lead in jewelry. In contrast, in the USA, cadmium's maximum limit is 0.03%, and in Europe, since 2011, its limit is 0.01% [Anvisa, 2018; Portal G1, 2013].

Cadmium's concentration found in jewelry in Brazil, apprehended in the harbor of Rio de Janeiro, was almost four thousand times the maximum limit allowed in Europe. Nowadays, Brazil imports around 11 tons of jewelry per year, which could contain a sort of toxic elements [Anvisa, 2018; Portal G1, 2013].

In 2016, it was published a new legislation by Inmetro, due to denunciation, unfair competition and the existence of low-quality products. This ordinance prohibits, in Brazil, the commercialization of jewelry that have concentration of cadmium and lead equal or over 0.01% and 0.03%, respectively [Ferreira et al., 2016; Inmetro, 2018a].It establishes maximum limits for lead and cadmium in jewelry for adults and child. Some of these items are hair decoration, bracelets, necklaces, rings, piercings, watches, cufflinks, earrings, and others. Moreover, it sets a maximum of 36 months to producers to fit in its rules, having the maturity for the January of 2019. For merchants, the maturity is extended to 60 months to have their products to fit in the ordinance's establishments. In other words, the maturity is to the January of 2021 [Inmetro, 2018a]. By the beginning of this year, the ordinance started to be obligated. However, it wasn't noticeable any kind market surveillance regarding these aspects.

Due to the globalization and through the commerce, chemical level in some countries influenced regulatory practices in other nations [Negev et al., 2018b]. National patterns generate potential barriers to the international commerce, and the regimentations are gradually more independents. Without a consistent international regulation approach of toxic elements in jewelry, big countries that import and export great amounts of it tend to influence different markets beyond its jurisdiction.

Initially, the regulation for jewelry in different countries became restrictive for lead. In the case of cadmium, its regulations became stricter, and its use in the production of Ni-Cd batteries decreased. That happened because it's being replaced for less environmental damaging products [Ferreira et al., 2016].

Lead became an element with restricted levels since it's a cumulative toxin to the human body. Its exposure can provoke neurological, cardiovascular and renal damage [Negev et al., 2018a;Rehan et al., 2018]. However, it's used to enhance the painting to jewelry, and to act as an anticorrosive agent [Hillyer et al, 2014;Schuh, 2012;Cui et al., 2015].

It's replacement, cadmium, also has stabilizing properties, paint enhancement and can act as a corrosive agent [Hillyer et al, 2014]. Nevertheless, can induce to cancer, digestive dysfunction and respiratory problems [Hillyer et al, 2014; Schuh, 2012; Cui et al., 2015].

In regard of Pb and Cd, the contamination from other metals had less visibility. Some of those metals are arsenic (As), antimony (Sb), chrome (Cr) and nickel (Ni).

Children are the ones that are the most affected, since the hematoencephalic barrier isn't fully developed. Therefore, noxious chemical substances can enter the neural system easily [Negev et al., 2018b]. Due to the rapid growth and development occurring during childhood, the neural, endocrine and reproducible systems, damage done to them can have profound impacts throughout life [Negev et al., 2018b; Ferreira et al., 2016]. Thus, children have longer time to develop these diseases triggered by early exposure [Negev et al., 2018b; Ferreira et al., 2016;Guney and Zagury, 2012].

By children being exposed to little and constant levels of metals through air, water and soil, and addition exposure from other sources increases the risk of carcinogenic diseases [Ferreira et al., 2016; Guney and Zagury, 2012]. The mouth and the skin contact creates these extra risks [Ferreira et al., 2016; Guney and Zagury, 2012]. Furthermore, in cases of fully ingestion and acute toxicity, the chronic toxicity by metals can be observed after repeated exposures [Negev et al., 2018b].

In 2007, after the death of a children in Minnesota, in the USA, by lead poisoning due to ingestion of contaminated jewelry, it became clear the jewelry dangerous [Weidenhamer, 2007a]. So, researchers were looking to determinate the connection between low cost imported jewelry and the lead contamination. A total of 139 jewelry items were analyses by atomic absorption spectrometry [Weidenhamer, 2007a]. Almost half of those tested samples (42.6%) exceeded 80% lead in mass composition. Accordingly to a research made in the USA, regarding the human exposure to chemical substances, American's urine analyses shown recent and cumulative exposure to a variety of chemical elements, such as arsenic, cadmium and lead [Ferreira et al., 2016; Guney and Zagury, 2012]. This study made clear that low cost jewelry represent harm to human health [Weidenhamer, 2007a].

In the same year, said researchers, while evaluating great quantities of lead in jewelry imported from China. By doing so, they were investigating if the electronic scrap with high levels of lead, exported to the United States, were being recycled and used to make jewelry [Weidenhamer, 2007b; Ferreira et al., 2016]. To do so, the content of lead, tin and copper was tested by atomic absorption spectrometry. These, sixteen samples had over 20% to 80% of lead in mass composition [Weidenhamer, 2007b]. The combination composition of copper, tin and lead of these samples varies from 93.5% to 100%, suggesting that those are, in fact, a material that is weld based. Those results are consistent with the hypothesis that weld is the base of electronic circuit recycled being used to produce some of the jewelry imported with high lead concentration sold in the USA[Weidenhamer, 2007b,Ferreira et al., 2016].

In 2010, wristbands had a recall, due to high levels of cadmium. It happened in the United States, even though there was no regulation for it [Negev et al., 2018a]. In the state of Virginia, in 2014, an evaluation comparing jewelry sample gathered in low priced popular retails that had been made in China [Hillyer et al., 2014]. The elements that were analyzed were lead, cadmium and arsenic [Hillyer et al., 2014]. These samples were cut and crushed, after being digested in nitric acid. After this, they were analyzed by atomic absorption spectrometry (AAS) and by atomic absorption with graphite furnace (AAS-GF) [Hillyer et al., 2014]. The following limits were considered, based in ASTM F2999 [ASTM, 2014], that are 25 mg.kg^{-1} for arsenic, 75 mg.kg^{-1} for cadmium and 90 mg.kg^{-1} for lead [Hillyer et al., 2014,ASTM, 2014]. From the 46 samples from popular retails, 35% reproved in arsenic, 5% in cadmium and 10% in lead [Hillyer et al., 2014]. In regard of the 46 samples from department stores, 20% reproved in arsenic, 5% in lead and none in cadmium [Hillyer et al., 2014]. The study indicates that the type of store from which a person can acquire these jewelries is a significant factor in the levels of toxic elements found and in the public exposure [Hillyer et al., 2014; Ferreira et al., 2016]. Another point made was that jewelry made from metal are way more dangerous than those made from polymeric material [Hillyer et al., 2014]. Recent research exposes the emerging problem of heavy metal contamination of costume jewelry at retail stores or in the USA.

This situation isn't exclusive to the USA. In 2015, 45 children's products samples were analyzed, being 10 jewelry [Cui et al., 2015]. All the jewelry was collected in a local Chinese market, having the following elements analyzed: arsenic, cadmium, antimony, chromium, nickel and lead [Cui et al., 2015]. Having the limits obtained compared with those stablished in the European Union, all the samples were approved in antimony and arsenic [Cui et al., 2015]. In chrome evaluation, one sample showed almost twice the stablished limit [Cui et al., 2015]. For nickel, 7 of 10 were over the limit. For cadmium, two samples were over the limit, one of those being six times higher. For lead, three samples had concentration over the limit stablished, one of those having exceeded 67 times de limit [Cui et al., 2015]. In summary, all the samples reproved in, at least, one evaluated element [Cui et al., 2015].

In 2017, 22 samples of children's wear jewelry were gathered and analyzed from local market and imported from Israel. They were dismantled in 83 homogeneous pieces, and analyzed in x-ray fluorescence spectrometry (XRF), due to high levels of metal. The analytes were lead, cadmium and nickel[Negev et al., 2018a]. Until then, Israel didn't have a maximum regulation limit for these metals [Negev et al., 2018a]. Thus, taking the European

Union maximum concentration level, 75% of the samples would be over the stablished limit for cadmium, and 51% would reprove in lead [Negev et al., 2018a].

In 2016, 9 pieces of jewelry were acquired and tested from local market in Juiz de Fora, Brazil. The analyzes were performed by differential pulse voltammetry (DPV) and by atomic absorption spectrometry (AAS) [Ferreira et al., 2016].Of the 9 necklaces tested, 3 were above the limits allowed under the national regulations in both cadmium and lead [Ferreira et al., 2016, Inmetro, 2018a].

Nowadays, the most common technique for determination of metal content in jewelry is based on atomic absorption spectrophotometry, due to its high sensitivity and high selectivity [Ferreira et al., 2016].However, methods based on atomic absorption spectrometry have some drawbacks, such as monoelement and slow detection, mainly in heating and cooling steps [Ferreira et al., 2016].Differential pulse voltammetry (DPV) has also been used to detect lead and cadmium in low cost jewelry [Ferreira et al., 2016].The advantages of the DPV method over conventional methods include simplicity, low reagent consumption and simultaneous detection [Ferreira et al., 2016].

Another technique used is the XRF spectrometry, a technique capable of identifying and quantifying elements in a fast, simple, non-destructive and low-cost manner [Da-Col et al., 2014; Negev et al., 2018a; IEC, 2013c;Inmetro, 2018a;ASTM, 2010].In addition, it is applicable to a wide concentration range, has adequate analytical precision at high limits and does not require sample preparation in homogeneous parts [Da-Col et al., 2014; Negev et al., 2018a; IEC, 2013c;Inmetro, 2018a;ASTM, 2010].However, according to normative documents, the imprecision of this method for metal alloys may be ± 25% and the inaccuracy may be ± 10% [IEC, 2013c].For this reason, the use of this technique, with the addition of ones that are more precise is indicated [Da-Col et al., 2014; Negev et al., 2018a; IEC, 2013c].

Among the available analytical techniques to quantify the elements present in this type of sample, inductively coupled plasma optical emission spectrometry (ICP-OES) is a multi-element technique that combines qualities such as relatively low detection limits, simultaneous and accurate determination capabilities, in a short time interval and of wide concentration [Larrea-Marín et al., 2010; Rehan et al., 2018].

Despite the evident advantages of ICP-OES, it presents certain limitations due to spectral and non-spectral interference originating from concomitant elements that may coexist with the analyte in the sample [Larrea-Marín et al., 2010; Rehan et al., 2018; Gazulla et al., 2018]. Spectral interferences are commonly corrected using the software provided with the ICP-OES equipment systems available [Larrea-Marín et al., 2010]. Nevertheless, non-spectral interferences, also called matrix effects, require the development of specific tests, for which a high degree of specialization is required [Larrea-Marín et al., 2010; Rehan et al., 2018; Gazulla et al., 2018].

Therefore, it is necessary to provide an optimized and validated method for ICP-OES, which allows to define the analytical requirements and to confirm that the method has sufficient capacity of performance and with has consistency, regarding the requirements for its application [Larrea-Marín et al., 2010; Rehan et al., 2018; Gazulla et al., 2018].

The main goal of this research is to evaluate the concentration of toxic metals (cadmium and lead) in jewelry in the South of Brazil. The research also presents the method validation

for the evaluation of toxic metals using ICP-OES. In this study, several types of jewelry that were already used by students of one private university were selected to evaluate their exposure, in the city of Porto Alegre, Brazil. In addition, other types of costume jewelry were purchased in the local market for an assessment of the level of toxic elements.

2. Methodandmaterials
2.1 Samples

Forty-eight samples were evaluated. Of these, twenty-four were used by students at a local university. The others twenty-four were obtained in the local market of Porto Alegre, Brazil. During the selection, lower priced samples were preferred, since previous studies reported that these may contain higher levels of metal, mainly due to the recycling of contaminated materials or to the lack of regulation for raw materials [Weidenhamer et al., 2007a; Cui et al., 2015; Ferreira et al., 2016]. Among the samples, there were bracelets, earrings and rings, all made of metal and gold-colored.

2.2 Equipment

A pre-analysis of the samples with x-ray fluorescence spectrophotometer (XRF, Delta brand, Innov X model) was carried out to evaluate the boundaries of metals [IEC, 2013c].For the more precise elemental analysis, an inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific Model ICAP 6200, dual-view) was used, equipped with a concentric glass nebulizer and a cyclonic nebulizer chamber. Plasma was used with axial view, and the analytical parameters of the ICP-OES instrument are summarized in Table 1.

Table 1 – ICP-OES Instrumental Analytical Parameters.

AnalyticalParameters:	
RF Power (W)	1150
Plasma gasflow rate ($*10^{-5}$ m³.s^{-1})	25.0
Auxilliary gas flow rate ($*10^{-5}$ m³.s^{-1})	0.83
Nebulizer gas flow rate ($*10^{-5}$ m³.s^{-1})	0.83
Replicates	5
Wavelengths (nm)	Pb (220.3) ; Cd (214.4)

For grinding the samples, a cutting mill (Rescht, model SM200) was used. Towards the digestion of the samples, a microwave digester (Berghof, Speedwave model) was used. The digestion details is presented in Table 2.

Table 2 –Microwave Digester Program.

Step	Temperature (°K)	Pressure (kPa)	Time (s)	Power (%)
1	433	4000	900	90
2	498	4000	1500	90
3	473	4000	600	90
4	373	4000	600	90
5	323	4000	60	0

2.3 Reagents

For the XRF analysis, the following certificate reference materials (CRM) were used: IRMM EC BCR 360, with levels of (59.5 ± 0.6) mg.kg^{-1} for cadmium m and (73.9 ± 1.4) mg.kg^{-1} for lead. For the CRM IRMM ERM EB 325, which is a zinc alloy, a concentration of (94.7 ± 2.5) mg.kg^{-1}was used for cadmium and (142 ± 9) mg.kg^{-1} for lead.

In the analyzes by ICP-OES the following CRM were used; for lead: NIST 3128 $(9,995 \pm 14)$ mg.kg^{-1}, batch: 101026 and Accustandard ICP-29N-1 $(1,012.0 \pm 2.4)$ mg.kg^{-1}, batch: 213065079; for cadmium: NIST 3108 $(10,007 \pm 27)$ mg.kg^{-1}, batch: 130116 and Accustandard ICP-08N-1 $(1,012.0 \pm 2.4)$ mg.kg^{-1}, batch: 213065079.

2.4 Sample Preparation

Initially, the samples were disassembled, and the present gemstones were removed. After, they were cut into small pieces using cutting pliers, without contaminants. The product of the cutting step was crushed to particles smaller than or equal to 1mm [IEC, 2013b]. Before the acid digestion, a previous XRF analysis was performed, to evaluate the metals concentration levels [IEC, 2013c].

Using the previously mentioned parameters, an aliquot of approximately 0.5g of each sample was digested with 8 mL of HNO$_3$ (reagent grade, Merck 65%) in the microwave digester, in duplicate. The digested solution was filtered with 0.45 μm nitrocellulose filter and then after that filed at 100 ml with Milli-Q water (Milipore, Ultrapure Direct-Q), before measuring the concentration of metals. Due to the high concentration level of metals, some samples were diluted during the analysis.

2.5 Method Validation

The method validation process, based on the ICP-OES technique, was performed according to the literature guidelines [Larrea-Marín et al., 2010;Eurachem, 2014;Directive, 2004; Rehan et al., 2018;Gazulla et al., 2018]. Table 3 shows the summarize of results about the method validation.

Table 3 – Method Validation Details.

Validation items	*Details*
Selectivity	The selectivity of a method relates to the extent to which the analytical determination can be used to determine specific parameters in matrices without significant interferences from other components of similar characteristics [Eurachem, 2014;Inmetro, 2018b;Schuh, 2012]. The analytical curves were compared to the inclination with and without the matrix. To evaluate the matrix interference, solutions containing zinc and copper were used in high concentrations (in ultra-pure water). According to the literature [Negev et al., 2018a; Hillyer et al, 2014; Weidenhamer et al., 2007b; Guney and Zagury, 2012] and to the previous analyzes by XRF, Zn and Cu were the predominant elements in the evaluated samples. Five different concentrations were analyzed along the working range. The 3 curves were prepared within the same concentrations. The slopes of the curves, obtained from the linear regression, did not differ significantly for both cadmium and lead (*p*-value >0.05). It was observed the existence of parallelism between the results of the 3 curves.The curve's residues variability was evaluated by the ANOVA. There was no significant difference between the results (p>0,05). Therefore, there was no matrix influence in the results.
Limit of quantification	The Limit of Quantification (LOQ) is the smallest amount of analyte in the sample that can be detected during the analysis and quantified with accuracy and precision [Eurachem, 2014;Inmetro, 2018b;Gazulla et al., 2018]. The LOQ was evaluated by estimating the blank sample standard deviation, multiplying by a factor of 10. The cadmium LOQ was $0.021mg.L^{-1}$ and the lead was $0.013mg.L^{-1}$.
Working range	The linearity of the analytical procedure is the ability to produce results that are directly proportional to the element of concentration in the sample, at a given concentration range [Eurachem, 2014].For the quantification of lead, the working range used was from 2.0 to 20 ppm. The points of the curve were 2.0; 5.0; 10; 15; 20 ppm. The curve for cadmium analysis was 5.0 to 25 $mg.L^{-1}$, considering concentrations of 5.0; 10; 15; 20; 25 ppm. The correlation coefficients obtained evidenced the linearity of the method in the established concentration range for lead and cadmium (r> 0.99). Before the simple linear regression, it was verified that there is an absence of outliers for each level of concentration, through the Grubbs test [Eurachem, 2014; Inmetro, 2018b]. In addition, the PDF was, which presented a random distribution of the results around zero - which also shows the linearity of the method [Eurachem, 2014; Inmetro, 2018b].

Trueness	Trueness is the degree of agreement between the result of a measurement and a true value of the measurand [Eurachem, 2014; Inmetro, 2018b; Gazulla et al., 2018]. For this evaluation, additional solutions were prepared with concentrations in the range of the calibration curve, using a different CRM . The results were evaluated based on the recovery rate of the analyte. The recovery obtained was between 99% and 106% for both analytes.
Precision	Precision expresses the dispersion between independent measurements [Eurachem, 2014; Inmetro, 2018b]. Two items were considered for this evaluation: repeatability and intermediate precision. The measurement repeatability condition can be expressed quantitatively in terms of the characteristic of the dispersion of the results, considering the same measuring, in the same measurement characteristics [Eurachem, 2014; Inmetro, 2018b]. The repeatability of each concentration of the analytical curve and the evaluation of the recovery of the method were evaluated. The repeatability was satisfactory, and the Relative Standard Deviation was less than 15% (RSD <15%) [Eurachem, 2014; Inmetro, 2018b].For the intermediate precision, the executor of the test was changed and also the days that the test were performed. There were no significant differences.(ANOVA indicated a *p*-value higher than 0.05).
Measurement uncertainty	To estimate the uncertainty of measurement, the main sources identified that were used are the calibration curve, the repeatability, the trueness and the CRM. The combination of variables was performed according to Eurachem Guide [Eurachem, 2014]. The uncertainty of the cadmium test was 9% and the lead test was 11%.

3. Results and discussions

Initially a XRF screening of the samples was performed. Screening methods provide a convenient approach to assess the presence or quantity of a given substance in samples. Screening may used qualitative or semi-quantitative methods. In some cases, a quantitative method may be used for screening purposes if the target substance is difficult to analyze directly or has a high cost involved [IEC, 2013a ;IEC, 2013c].

XRF analysis is the technical commonly associated with screening tests [IEC, 2013a]. As indicated in the literature, XRF analysis has high uncertainty for the evaluated elements (may be ± 25% or more, depending on the sample matrix) [IEC, 2013a]. For this reason, when the maximum allowable limit of any element is indicated on the test equipment, and a sample has concentrations close to this level or has high background noise, the equipment indicates that the result is "inconclusive" and additional analytical methods need to be used to definitively quantify the presence of controlled substances [IEC, 2013a].

In this research, the total concentrations of Pb and Cd in 48 jewelry were evaluated initially by XRF and then by ICP-OES. The concentrations of lead and cadmium were compared with the Brazilian legislation [Inmetro, 2018a].

3.1 X-ray fluorescence spectrometry (XRF)

The LOQ for this method depends on several factors, such as the material used, the target element, the mode of application and the testing time [Turner et al., 2016;Negev et al., 2018a; IEC, 2013c].For quantified target elements, an LOQ of 80 mg.kg^{-1}was determined for cadmium, and a 50 mg.kg^{-1}for lead. In the lead analysis by XRF, 23% of the samples were above the limits of Brazilian legislation [Inmetro, 2018a], considering a total of 8 used samples and 3 new ones of 48 analyzed jewelry. For cadmium, this percentage rose to 60%, considering 13 samples of used jewelry and 16 of new ones. An inconclusive result was obtained in 42% of the lead analyzes and in 19% of the cadmium results. The data are summarized in the Figure 1 and 2.

Figure 1 – Lead evaluation by XRF.
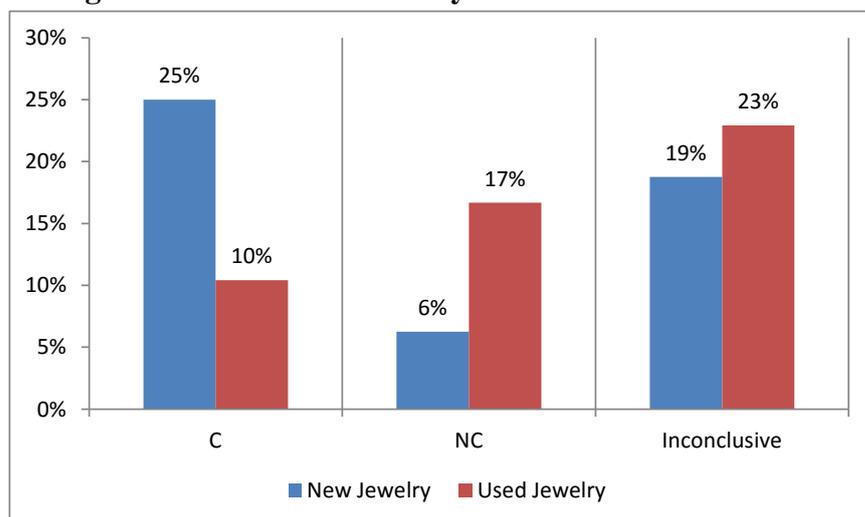
Figure 2 – Cadmium evaluation by XRF.
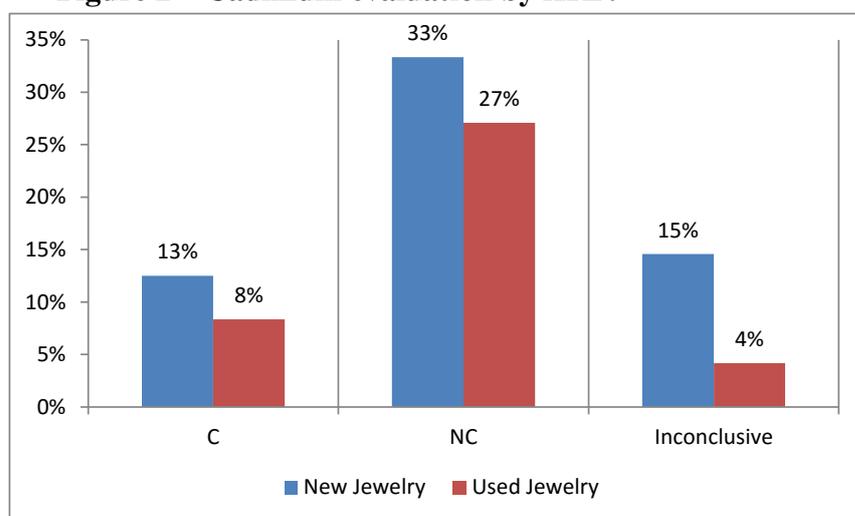
Lead analysis using portable semi-quantitative equipment, such as XRF, would indicate that 58% of the samples had results that could be assessed under national legislation and classified as compliant or non-compliant. For cadmium analysis this number rises to 81%. This shows us that XRF screening is a simple, low cost, non-destructive and fast technique that can be used by regulatory agencies in the process of screening import products in ports, aeroports or national factories to identify possible irregularities.

3.2. Analysis by inductively coupled plasma optical emission spectrometry (ICP-OES):

Lead analysis using ICP-OES method indicated that 27% of samples were above de maximum acceptable limit. Among these, 8 were used jewelry and 5 were new ones. In addition, one of those used samples had the concentration of 24% of lead, which represents an extremely alarming result. Considering the comparison between new and used samples, a total of 33% and 21% failed, respectively. Table 4 presents the frequency and the range for lead and cadmium results(new and used samples).

Table 4 – Concentration of lead and cadmium found in new and used samples.

Lead Concentratio	% newsample	% usedsample	Cadmiumconcentration	% new sample	% usedsample
< 0.001	42	8	< 0.0014	21	0
$0.001 \leq [Pb]$	38	59	$0.0014 \leq [Cd] < 0.01$	8	21
$0.03 \leq [Pb] <$	12	8	$0.01 \leq [Cd] < 1.0$	46	38
$1.0 \leq [Pb] <$	8	21	$1.0 \leq [Cd] < 10$	17	38
< 10	0	4	< 10	8	4

The total percentage of lead non-conformities was 27% in the 48 analyzed samples. Moreover, extremely high percentage values were found in the used samples (for example, one sample had 24.9% of lead mass in the jewelry). For cadmium, the results were most alarming: a total of 75% of all the samples were above the limits allowed by the Brazilian legislation [Inmetro, 2018a].Of these, 19 were used jewelry and 17 were new ones. Among the analyzed samples, 3 presented values above 10% of cadmium in its composition. These results are thousand times above the allowed limit. The number of reprobation, considering new and used samples, does not differ significantly for cadmium.

For Lead, the median concentration of new samples was lower than the used samples, according to data presented in Table 5. A higher% of non-conforming samples was also observed in the used samples (33%).For cadmium, the percentage of nonconformities was 75% in the 48 samples tested (71% in new and 79% in used samples). The median of cadmium concentration was 0.085% in new samples and 0.051% in used ones (Table 5).

Table 5 – Lead and Cadmium tests statistics

Statistics	Lead: New SamplesConcentration	Lead: UsedSamples Concentration	Cadmium: New SamplesConcentration	Cadmium: UsedSamples Concentration
Mean (Concentration)	0.18 %	2.22 %	1.36 %	2.22%
Median (Concentration)	0.009%	0.014 %	0.085%	0.051 %
Minimum (Concentration)	< LOQ (0.013mg.L^{-1})	< LOQ (0.013mg.L^{-1})	< LOQ (0.021mg.L^{-1})	0.0014%
Maximum (Concentration)	1.75 %	24.95 %	11.85%	12.56 %
% Abovethe legal limit	21%	33%	71%	79%

When analyzing all samples, only 10% were approved towards the two metals (lead and cadmium), considering the legal limits in Brazil. In addition, 25% of the samples had the results of lead and cadmium above the maximum allowed [Inmetro, 2018a].

The Brazilian jewelry regulation only indicates that conformity assessment must be performed in the ISO / IEC 17025 accredited laboratories, but does not inform the periodicity of the assessment. In addition, there is no Certification Body involved in this process. There is no guarantee that a suitable sampling process will be taken by the manufacturer at the time of material collection for testing in an accredited laboratory. This law should also be reevaluated to become more effective and standardized like other conformity assessment programs that present suitable results in Brazil.

4. Conclusion

The concentration of the toxic metals tested in this research, considering used and new jewelry traded in Brazil, is still significantly above the legal limit, even with a new legislation being launched. The main goal of the research was to assess the concentration of toxic metals (cadmium and lead) in jewelry in the South of Brazil. The results indicated that the percentage of used and new jewelry samples that do not comply with the legislation remains around 90% (results that did not meet one or two of the requirements of maximum limits allowed for lead and/or cadmium).We also presented details of the method validation considering the ICP-OES technique to quantify the toxic metals in jewelry, which was suitable for the research purpose.

This type of conformity assessment should receive special attention from national regulatory parties. In addition, not only the conformity assessment should happen, but also the dissemination of the importance of this control, since this type of contamination represents an immediate danger to public health. For future researches, we intend to make a new round of tests after one year of the legislation being fully demanded.

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