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Full Length Article

X-ray photoelectron spectroscopy on 1-peso and 2-pesos of the Argentine Republic

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ABSTRACT

Relative concentrations of nickel and copper at the surface of the ring and centre parts of 1-peso and 2-pesos Argentine coins have been studied by means of X-ray photoemission spectroscopy (XPS). It has been observed Ni-enrichment at the surface of the ring (silvery) part of a 1-peso, minted in 1994, whereas the XPS data reveals lack of nickel at the surface of the centre (silvery) part of a 2-pesos, minted in 2016. This discrepancy is explained by analyzing the XPS peaks of oxygen and carbon, and is suggested to be related to the contamination layer on the surface of the coins. The XPS analysis of the golden parts of the coins, namely the centre part of the 1-peso and the ring part of the 2-pesos coins were inconclusive, due to the small amount of the Ni (nominally %2) used in those parts. The possible oxidations states of the metals at the surface of the untreated and treated coins with the artificial human sweat were also identified.

1. Introduction

Due to the physicochemical properties of the nickel, and its silvery bright finish, this metal is used in different daily objects, such as jewelry, buttons, belt buckles, and door handles and so on. It has also been used heavily to mint coins all over the world, since it has some advantages in comparison to the other silvery metals, such as price, color, density, and the ease of minting. However, the community of contact dermatologists has been alarmed that eczema related to Ni allergy has been on rise due to usage of these coins. It has been estimated that around 10-30% of women and 1-3% of men suffer of Nickel allergy [1]. The difference between the prevalence of nickel allergy in men and women is explained by the fact that the women are using more objects containing nickel than the men do [2]. The American Contact Dermatitis Society, in 2008 named the nickel as the Ällergen of the Yeardue to abundant cases of contact allergy with nickel [3].

The problem with the nickel release from the Ni-containing coins is not new. To our knowledge nickel release from silver/nickel alloy of Swedish coins were reported for the first time in 1974 [4]. In this reference, the authors reported not only the Ni release from the coins that contain nickel, but also inform the Ni contamination on the other coins (not containing Ni) and even on the bank notes. Nevertheless, a serious debate over the Ni release of the coins and its health hazardous was triggered after circulation of euro coins in all twelve EU countries, in January 2002, and by publication of a brief communication in the journal Nature [5] in September 2002. The authors, in this reference, report a release of 240 to 320 times more nickel than it is allowed under the European Union Nickel Directive [6]. This phenomenon is explained by the fact that the coins central part and the ring part contain different amounts of nickel, copper and zinc, (see Table 1). This fact encourages galvanic corrosion process during prolonged exposure to human sweat. This was confirmed by submerging a one Euro coin and a Swiss one-franc coin, which contains 25% nickel and 75% copper, in artificial human sweat for 36 hrs: The 1- euro coin was visibly corroded, whereas a Swiss 1-franc coin was not.

Medical aspects of the Ni release from the coins, containing Ni, from different currencies have been heavily studied [8], and the references therein. However to our knowledge, there has been only one study which XPS as the main technique was used to investigate the metallic composition on the surface of the Euro coins [9]. The authors, in this reference, present XPS studies of the central and the ring part of two Dutch 1-euro coins. The results from the untreated coins, directly off the normal circulation, are compared with the polished and oxidized bulk alloy surfaces. They report significant nickel enrichment on the surface of both the ring and the centre parts of the untreated coins. The coins used in that study was

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Table 1
Metallic concentrations of euro coins [7].

Coin	Composition
1 euro-ring (golden) part	1-layer: Cu 75, Zn 20, Ni 5
1 euro-central (silvery) part	3-layers: Cu 75, Ni 25//Ni 100//Cu 75, Ni 25
1 euro-ring (golden) part	1-layer: Cu 75, Zn 20, Ni 5
1 euro-central (silvery) part	3-layers: Cu 75, Ni 25//Ni 100//Cu 75, Ni 25

Table 2
Atomic concentration of Ni, Cu and Zn metals measured by XPS on the ring and centre part of two Dutch 1-euro coins (A and B), reference [9].

	Ring			centre	
	Ni	Cu	Zn	Ni	Cu
Bulk (official composition)	5.4	75.1	19.5	26.5	73.5
Untreated surface (A)	9	58	33	55	45
Untreated surface (B)	10	65	25	42	58

minted in 1999. The paper was published in 2004, so we estimate that the coins had been in circulation for almost to 5 years. Table 2 below summarizes their results from reference [9].

Nevertheless, we believe that a much more detailed XPS studies of the Ni-containing coins is needed in order to present a comprehensive view of the Ni segregation from the alloy used to mint the coins. In the present work, we have used XPS to study Argentine 1- and 2- pesos coins. The main components of these coins, similar to euro coins, are copper and nickel, with an exception that in the Argentine coins, zinc is replaced by aluminum in comparison to the euro coins, see Table 3. High resolution XPS spectra were collected from the untreated coins and treated coins with the artificial sweat. The possible corrosion products of the alloys were identified.

The official atomic concentration of the metals used to mint Argentine coins as published by the Central Bank of Argentina (CBA) are listed in Table 3. Nevertheless, we have also measured the actual composition of a 1-peso coin using Arc-Spark Optical Emission Spectroscopy (Arc-Spark OEM) technique. We followed the standard operation procedure of ASTM E415-99a: Standard Test Method for Optical Emission Vacuum Spectrometric Analysis of Carbon and Low-Alloy Metals. The uncertainty in our measurement was estimated to be 0.1%. The results are also given below in Table 3. There are some small discrepancies between the official information and our measurements. We have no knowledge of the process and the accuracy of preparing the alloys to mint the coins, and our inquiries from the (CBA) are unanswered. Therefore, we cannot comment on these discrepancies, except that, similar to Argentine coins, the values of the official composition of the euro coins reported in ref. [9] are also different than those, published by the European Central Bank (ECB), see Table 1 in comparison to the Table 2.

2. Experimental method

A 1-peso coin from 1994 and a 2-pesos coin from 2016, without any *ex situ* cleaning or pretreatment with the artificial human sweat, along with the standard samples of pure copper and nickel were introduced to the XPS chamber. XPS analysis was carried out in a PHI 5000 VersaProbeII. The base pressure in the chamber was in the range of 10^{-7} - 10^{-8} Pa. A monochromatic aluminum Kα X-ray source (100μ, 25W, 15 kV) was used to probe the samples. An Argon-etched, polished fine grained silver sample was used earlier to measure resolution of the system. The Full Width at Half Maximum (FWHM) of the $3d_{5/2}$ peak of the silver sample was measured to be 0.49 eV. All the Survey scans were collected under the following conditions; Energy Range: 0-1100 eV, the Pass Energy (PE): 187.85 eV, the step size: 0.8 eV, and the time per step was 50 ms. For the high resolution scans the PE was set to be 23.5 eV and the step size changed to 0.1 eV. Spectra were analyzed using CasaXPS software version 2.3.18.

3. Experimental results

In order to eliminate any ambiguities in the identification of the metals (Ni, Cu) and their relevant states of oxidations on the surface of the coins, XPS spectra under the same experimental conditions were collected from Cu- and Ni-standard samples. The XPS spectra collected from the standard samples are particularly essential to analise XPS spectra from the metallic alloys of copper and nickel used to mint the coins. The $2p_{3/2}$ XPS peak of the $Cu^{(0)}$, $Cu^{(I)}$ oxide, $Cu^{(II)}$ oxide, and $Cu^{(II)}$ hydroxide are reported in a narrow range of binding energy of (932.6 -934.6) eV [10]. The 2p region of the XPS spectra of Ni and Ni oxides is rich in features. This can make the chemical quantification of Ni and its oxides, based on the position of the XPS peak, more demanding. The spectra consist of asymmetric peaks, shake-up satellites, and high intrinsic background. The peak fitting process of the samples containing Ni is potentially complex due to multiplet splitting of the Ni $2p_{3/2}$ XPS peak of $Ni^{(0)}$, $Ni^{(I)}$ oxide, and $Ni^{(II)}$ oxide [11].

The standard samples were etched for 10 min by 2 KeV Ar^+ ions, in order to remove the native oxide or hydroxide and carbon from the surface. The raster size was set to be 2×2 mm. The Ni $2p_{3/2}$ XPS spectrum collected from a Ni 99.98% sheet of 0.5 mm, provided by Sigma-Aldridge, is shown in Fig. 1. Two satellite peaks and their binding energy above the main peak of $Ni^{(0)}$ at (852.5 ± 0.1) eV are indicated in the graph. The position of the binding energy of the main line and the additional satellites above the main emission line are in good agreement with the reported values in reference [11], within the uncertainty of our measurements. These satellite structures are suggested to be associated to the energy losses corresponding to the surface and bulk plasmons [11], in contrast to the previous study, where it is suggested that they are related to the holes in the final state of $c3d^9 4s^2$ (c is a core hole) [12].

Fig. 2 shows the photoemission spectrum of Cu $2p_{3/2}$ collected from a Cu 99.98% foil of 0.5 mm, provided by Sigma-Aldridge, in the range of 928-938 eV. A single Gaussian (70%)-Lorentzian (30%) peak defined as GL(30) in CasaXPS is fitted at binding energy of (932.59 ± 0.05) eV with a FWHM of 1.3 eV. This was expected, as we routinely calibrate the energy analyzer based on the values of the binding energies for Cu $2p_{3/2}$ and Au $2p_{3/2}$ peaks, namely 932.62 eV and 83.96 eV, respectively, as recommended by ISO standard procedure.

Table 3
Official metallic concentration (in % weight) of Argentine coins published by the CBA, and measured by Arc-Spark OEM.

Coins	Color	Composition
\$1-peso[a]	Silvery (ext. part) / Golden (central part)	Cu 75, Ni 25 / Cu 92, Al 6, Ni 2
\$2-pesos[a]	Golden (ext. part) / Silvery (central part)	Cu 92, Al 6, Ni 2 / Cu 75, Ni 25
\$1-peso[b]	Silvery (ext. part) / Golden (central part)	Cu 76.1, Ni 23.9 / Cu 90.9, Al 7.5, Ni 1.6

[a] According to the official information the Central Bank of Argentina (CBA).
[b] Measured by Arc-Spark OEM, the uncertainty estimated to be 0.1%.