

A comprehensive study of nickel levels in everyday items in Brazil

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Abstract

Background: Nickel is a ubiquitous element used in many everyday items. In recent decades nickel has become a leading allergen, which has become a public health problem.

Objective: To evaluate frequently used nickel products in Brazil. We investigated if these objects release nickel that is capable of inducing sensitization or cause clinical manifestations in terms of allergic contact dermatitis (ACD).

Methods: Dimethylglyoxime (DMG) spot tests assessed nickel release from several common utensils used in everyday life in São Paulo and Rio de Janeiro, Brazil.

Results: We tested 46 coins (two denominations) and 90 common utensils. Approximately 91.1% produced nickel-positive results using the DMG spot test.

Conclusions: The DMG limit of detection was 1.67 ppm of nickel. We observed that many objects in our test series released nickel above the DMG test limit. This observation suggests that nickel-sensitive individuals may be exposed to nickel, representing a public health issue.

KEYWORDS

allergens, consumer product safety, dimethylglyoxime test, nickel allergy, nickel exposure, nickel release, nickel screening test

1 | INTRODUCTION

Globally, nickel is the most common allergen.¹ It predominantly affects 13.4%–29.5% of women in the general population.² The prevalence of nickel sensitivity is 17.5% in North America,^{3,4} 43.16% in India,⁵ and 8%–19% in Europe, decades after the implementation of restrictive nickel regulations.¹

In São Paulo, Brazil, from 1995 to 2015, Duarte et al.⁶ recorded a 31.6% nickel allergy prevalence in adult patients of both sexes. Occupational dermatology services in Brazil reported a significant association of hand eczema with contact dermatitis which severely affected occupational activity.⁷

Nickel allergy impacts the quality of life of many individuals, including the rehabilitation of workers in other types of work or function and eventually leading to worker incapacity, thereby incorporating significant health burden on individuals and the economy.^{8–10} The

relationship between hand eczema and nickel allergy remains controversial.^{10–15} Interestingly, nickel has been associated with hand eczema in several studies,^{1,16,17} including in non-occupational hand eczema.^{17–19}

In a European multicenter study,²⁰ nickel was the most common contact allergen for both occupational (17.4%) and non-occupational dermatitis (17.8%) in hand eczema patients.

Nickel is considered a clinically relevant allergen and avoidance is the most effective way to prevent allergic contact dermatitis (ACD).¹⁷ Hence, allergen education and recommendations for alternative products should be adopted to prevent ACD.^{10,11} Nowadays, nickel contributes to more than 3000 alloys and is found in more than 300 000 products. Nickel contamination from handling coins is an important issue because many are produced using a cupronickel alloy because of its high resistance to corrosion.^{8,15,22,23,30,31}

A few studies in Brazil have analyzed nickel release from cell phones,²⁴ imported guitar strings²⁵ and from keys.²⁶ The aim of

this study was to extend this knowledge and assess whether Brazilian consumers are exposed to nickel through contact with everyday objects. In identifying these exposure levels, this study will help dermatologists distinguish possible sources of nickel ACD manifestations.

2 | MATERIALS AND METHODS

This study was conducted between November 2018 and February 2019. Selected items included metallic objects (90 utensils and 46 Brazilian coins) common in everyday life.

2.1 | Materials

Commonly-used metallic utensils were purchased in São Paulo and Rio de Janeiro, Brazil. We pre-defined all sampled specimens of musical strings that were produced in Brazil with nickel for guitar and cavaquinho, and all brands of cuticle pliers available on the market. The other items were randomly sampled, avoiding brand repetition. Table 1 shows the objects tested by category, origin, and nickel presence as reported by the manufacturer.

Circulating 1 Real and 50 cent coins collected in markets or donated by individuals were evaluated according to the year of coinage and handling conditions. To maintain the actual handling conditions, we tested coins as received without cleaning. Only one coin, the R\$1.00, coined to celebrate the 25 years of the Real Plan a national economic plan, with monetary devaluation and an exchange of currency for the current "Real", was a non-circulating sample because it had just been issued. Only original products were purchased from specialty stores, and cuticle pliers were purchased from hawkers. The surfaces of the pliers were cleaned and washed in water and neutral soap to remove oil and grease. In fact, most of the pliers purchased in Brazil come into contact with the hands of consumers that are smeared with oil or grease and are, therefore, washed before use. Only these products were subjected to the pre-cleaning treatment.

A 0.1% solution of dimethylglyoxime (DMG) was prepared²⁷ and stored at 4°C until use. Analytical-grade reagent from Sigma-Aldrich (Darmstadt, Germany) was diluted in deionized water to prepare 96% ethanol and 10% ammonium hydroxide solutions. The artificial sweat used in this study contained 0.3% sodium chloride (Sigma-Aldrich), 0.2% urea (Synth, Zola Predosa, Italy), 0.2% lactic acid (Synth, Zola Predosa, Italy) and 0.1% sodium sulfate (Sigma-Aldrich). The solution was prepared from analytical-grade reagents in deionized water, and the pH was adjusted to 4.5 with ammonium hydroxide solution, which is considered the lowest pH in physiological sweat.²⁸⁻³⁰ Nickel for a dilution series was prepared from a nickel single-element standard at 1000 µg/mL in 2% HNO₃ (Atomic Absorption Standards, Perkin Elmer, Waltham, Massachusetts).

2.2 | The DMG test

A cotton-bud containing two drops of DMG and two drops of ammonium solution was rubbed on each test article for 40 s in the touchable part of the tested article. A pink colour reaction indicated a positive result. Sampling yielding unclear reactions, (i.e. non-pink), was repeated. If the reaction was again doubtful it was scored as negative.²⁷

Immersion in artificial sweat at room temperature was used to simulate the natural wear and tear caused by manipulation. In cases of a negative DMG test result, the musical strings and cuticle pliers were immersed in artificial sweat for 24 h and 1 week, respectively, and the DMG test was performed after surface cleaning and drying.

To assess the lowest nickel concentration visually observable by this methodology (i.e. its detection limit), we used a nickel dilution series (Table 2). Fifty microliters of reagent mixture, DMG, and ammonium hydroxide (1/1, v/v) were added to 10 µL of nickel standard solution containing different nickel concentrations on swabs against a white background. The swabs (cotton sticks) were randomly placed out of order, and 22 individuals were invited to evaluate the test by indicating the clearest shade of pink visible. This procedure was repeated after reagent storage of 8 months at 4°C or -20°C). This experiment was performed to verify the stability of the nickel standard solutions and to ascertain the degree of variation resulting from the observer's visual acuity.

3 | RESULTS

All categories of tested objects showed some positive DMG test result. In fact, 83 out of the 90 (91.1%) objects tested showed some nickel release, including three items labelled as aluminum by the producer. The result of the DMG test for the coins varied according to the coinage date. Nickel release data for each utensil are shown in Table 1.

Three US brands (3/3) and three Brazilian brands of guitar strings (3/5) with steel cores and nickel-plated wounds showed a strong pink reaction to the DMG test, even before artificial sweat immersion. For two guitar strings (2/5) from the same Brazilian manufacturer, one had a dual metallic layer and the other cheaper one showed a weakly positive DMG test, before and after 24 h immersion in artificial sweat. All cavaquinho strings contained nickel, as indicated by the manufacturer, however, the DMG test was negative for one (1/4) Brazilian brand.

One Brazilian brand offers two product lines of cuticle pliers. One product manufactured in Brazil (iron-nickel steel) was positive for the DMG test. However, the second professional product (from Pakistan) was weakly positive for the DMG test after 1 week of immersion in artificial sweat. Two negative DMG tests were recorded for the most expensive pliers, one imported from Pakistan and one from Germany.

The lowest nickel concentration observed by all participants was established as 1.67 ppm using the DMG spot test (Table 2). This concentration was used to differentiate positive (nickel >1.67 ppm) and negative

TABLE 1 DMG test results and nickel presence reported by the manufacturers

Items	n	Origin	Presence of nickel according the producer?	Positive test n (%)		
				Immersion in artificial sweat		
				No	24 h	1 week
Musical instruments						
Strings						
Guitar	5	BRA	Ni round wound	7 (87.5)	8 (100)	
	3	USA				
Cavaquinho	4	BRA	Ni round wound	4 (80)	4 (80)	
	1	USA				
Berimbau	1	Unknown	Unknown	Negative	Negative	
Triangle and sticks	2	Unknown	Chrome-plated steel	2 (100)		
		Unknown	Unknown	2 (100)		
Personal care tools						
Eyebrow tweezers						
	10	Unknown	1 Stainless steel	15 (100)		
	3	China	14 Unknown			
	2	Pakistan				
Nail clippers	5	China	Ni-plated steel	8 (100)		
	3	Unknown	Chrome-plated steel			
Cuticle plier	1	BRA	Ni-plated carbon steel	2 (22.2)	2(22.2)	7(77.8)
	3	China	Stainless steel			
	4	Pakistan	Unknown			
	1	Germany				
Hand sewing materials						
Sewing pins						
	5	China	Ni	7 (100)		
	2	Unknown	Unknown			
Hand sewing needles	9	China	Ni-plated steel	12 (100)		
	3	Unknown	Unknown			
Crochet hooks	1	BRA	Ni-plated steel	14 (77.8) ^a		
	11	China	Unknown			
	1	Japan	Unknown			
	3	Bra	Aluminum			
	1	China	Aluminum			
	1	Japan	Aluminum			
Thread bobbin	8	China	Unknown	8 (100)		
Coins						
50 cents	1998/2000/2001 ^b		Copper-nickel	Positive		
50 cents	2002–2019 ^b		Stainless Steel	Negative		
1 Real	1998/1999 ^b		Copper-nickel, alpacca	Positive		
1 Real	2002–2018 ^b		Stainless steel and bronze	Negative		
1 Real	Commemorative coinage, 2019 ^b		Stainless steel and bronze	Negative		

Abbreviations: BRA, Brazil, USA, United States of America.

^aThe 3 Brazilian crochet hooks labelled as aluminum tested positive for nickel release by DMG spot test.^bYear of coinage.

TABLE 2 Nickel dilution series to check visual limit of the used DMG test

Ni (ppm)	Ni (μg) ^a	Visualization % (n/n total)
16.67	1.0000	100 (22/22)
8.33	0.5000	100 (22/22)
1.67	0.1000	100 (22/22)
0.83	0.0500	72 (16/22)
0.17	0.0100	32 (07/22)
0.08	0.0050	4,5 (01/22)
0.04	0.0025	0 (0/22)
0.02	0.00125	0 (0/22)
0	0	0 (0/22)

^aNi quantity in 60 μL .

(nickel <1.67 ppm) results. After 8 months of reagent storage at 4°C or –20°C, the pink color was still visible at this limit concentration.

4 | DISCUSSION

DMG colourimetric reactions are a rapid, efficient and cheap method to detect free nickel on sample surfaces and non-destructible assay. It is estimated as clinically relevant for use as a screening test.³¹

The strength of this study includes representative sampling. Samples include top selling brands, all available brands for Brazilian strings (for guitar and cavaquinho) and for cuticle pliers. To the best of our knowledge, this is the first study to test nickel release from some of these products. The results of this and a few other Brazilian studies^{24–26} represent the initial efforts to identify sources of exposure to nickel in Brazil. Importantly, these objects exemplify cultural aspects of Brazilian life. The percussion instrument the Berimbau is essential for Capoeira (a Brazilian martial art) and the triangle, fundamental for the Brazilian rhythm called Forró. Furthermore, manicuring with cuticle pliers is done by removing the entire cuticle, which may promote contact between the unprotected nail region and nickel. However, our samples may not be representative of the entire country because they were collected only from the two largest cities in Brazil.

There are several obstacles to assessing accurately the prevalence of hand eczema in developing countries such as Brazil, including the difficulty for patients to access specialized public services and a possible high number of underreported cases.^{20,32–35} The decreasing statistical association between nickel allergy and HE may reflect the decline in nickel exposure for general population after EU Nickel Directive implementation. It is expected a greater association between nickel allergy and HE where these restrictions do not exist. Therefore, this study is unique as it highlights the exposure spectrum for nickel contact in everyday Brazilian life.

Ali³⁶ and Hamann³⁷ reported the absence of nickel release in Brazilian coins, regardless of their coinage date, after spot testing and X-ray fluorescence spectrometry analysis of their nickel and cobalt content. However, the data collected from the present study is not consistent with those of Ali³⁶ and Hamann,³⁷ regarding coins released between 1998 and

2001. This discrepancy may be because most Brazilian coins (in terms of quantity used) were made of stainless steel and bronze after 2009.

Currently, there are 106 different Real coins circulating in Brazil, among them the R\$0.50 and R\$1.00 coins minted in cupronickel from 1998 to 2001 and from 1998 to 1999, respectively. From 2002 onwards, Brazil discontinued the production of copper-nickel coins, exclusively for economic reasons. As time progressed, it became much less possible to find cupronickel coins, which decreased the relevance of nickel ACD resulting from coin handling.

Nickel-release, combined with the repetitive mechanical trauma of finger pressure when playing a guitar can cause noticeable lesions in nickel-sensitized individuals. According to Crépy³⁸ and Kraft et al³⁹, the most common sensitizing agents in musicians is nickel.

One cavaquinho string produced a negative DMG test, although the packaging stated the string had a tinned carbon steel core and was wrapped in nickel plating. It is important to note that the carbon steel of the core string is abundant in iron and zinc, which acts as a cathodic coating protection, possibly decreasing nickel ion release. Rezić et al^{40,41} have shown an increase in the release of nickel under acidic conditions from musical strings treated with artificial sweat of different compositions.

From a dermatological perspective, musical performance imposes several stress factors such as pressure, friction, the number of contacts and frequency of repetition, heat, and electrochemical issues. These factors support chronic mechanical irritation and maceration, in addition to allergic or irritant contact dermatitis. Despite these issues, there is shortage of studies reporting causal links between ACD and exposure to nickel via guitar strings.^{28,42,43}

Among Danish patients with nickel dermatitis patients, hand dermatitis was described in 83.3% of seamstresses and tailors.²¹ A Chinese epidemiological study⁴⁴ in 529 textile workers reported high risks of occupational ACD. In sewing and iron workers, nickel was the most prevalent allergenic agent (32.4%). Additionally, one seamstress who was allergic to nickel, with eczema refractory to treatment in the fingertips of both hands, had her condition improved after the suspension of manipulation of needles that tested positive for nickel release by the DMG test.⁴⁵

The positivity in DMG test of needles found in this study (100%) is identical to that reported in Sweden.⁴⁶ As the European Union restricts the nickel release from nickel-containing items, the evaluated items may have originated from countries outside of Europe. All needles found in the Brazilian market were produced in China. The market offers alternatives to nickel-plated crochet needles, such as using bamboo for thicker and aluminum for thinner yarns. Nevertheless, we found needles labelled as aluminum that tested as nickel by the DMG test, which reveals a labelling failure and a lack of surveillance by the Brazilian Health Authorities.

The origin of the items studied (see Table 1) are an example of the availability of these objects in the two largest consumer markets in Brazil (São Paulo and Rio de Janeiro). Some cheaper products are usually sold without packaging, with no indication of origin or composition. With the exception of guitar and cavaquinho strings, we had great difficulty in finding nickel-coated or steel care tools products made in Brazil. We note that Brazilian products seem to be secondary to imports from China (a major steel producer) and Pakistan.

Interestingly, we did not find Brazilian norms or quality standards and technical specifications applied to importing these products.

The contribution of short and frequent contact to the total nickel load on the skin is not yet fully understood.⁴⁷ However, this brief contact may not be harmless since the friction present in use of these items plays an important role in nickel exposure, in addition to the frequency.

While there is no restrictive legislation on nickel release for nickel-containing devices and instruments marketed in Brazil, it is imperative that the consumer is informed on the precise composition of the product, and composition verification as stated on the packaging. Individuals with positive nickel contact tests should be encouraged to replace nickel-plated materials, or they should use gloves when there is no alternative. Nickel barrier creams are not available on the Brazilian market.

The moderate sensitivity of the DMG test was not a limitation in this study. Nevertheless, it is important to know the assay limitations in order to take necessary precautions in minimising false-positive and false-negative results. Technically, it was important to maintain the reaction medium as slightly alkaline to prevent nickel-dimethylglyoxime complex decomposition in an acidic medium, or the reddish brown DMG complex produced⁴⁸ with ferrous ion. Since numerous iron objects are nickel plated or silver plated, care should be taken to avoid false-positive results, since small spots of rust on a silvered object could, eventually, give a false-positive or a doubtful result. Cobalt (Co^{2+}) ions form a soluble complex with DMG, generating a yellowish brown colour. Cobalt coexists with nickel in several alloys and materials^{8,32} which often leads to false-negative results if Co^{2+} availability depletes the DMG⁴⁸, which can occur for jewelry. However, the DMG reaction with the nickel cation Ni^{2+} is quite selective.

5 | CONCLUSIONS

Nickel release was detected in 91.1% of all items (82/90) tested. The greater proportion of Brazilian stainless-steel coins in comparison with the cupronickel ones in circulation has decreased the incidence of allergic reactions due to coin manipulation in Brazil. As in other countries, Brazil discontinued the manufacture of nickel alloy coins for economic reasons, not for health issues. Even so, it is important that coin composition minimizes allergenic ion release.

This study shows that several routinely used nickel-plated objects release enough nickel to generate a positive DMG test. Critically, and depending on the conditions and frequency of use, this may represent an important exposure source of this allergen. Although there are no restrictive regulations for nickel levels in Brazil, it is essential that consumers are aware of the composition of objects and utensils, as a preventive measure to avoid sensitization and elicitation.

Further research is needed to study the actual skin exposure to nickel in conjunction with other metals (co-sensitization), especially those that are allergenic such as cobalt and chromium, to deepen the knowledge of metal allergy risks.

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AUTHOR CONTRIBUTIONS

Thelma Pavesi: Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; resources; supervision; validation; visualization; writing-original draft; writing-review and editing. **Josino Moreira:** Conceptualization; data curation; formal analysis; funding acquisition; investigation; methodology; resources; supervision; validation; visualization; writing-original draft; writing-review and editing.

CONFLICT OF INTERESTS

The authors declare no conflicts of interest.

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