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**DETERMINAÇÃO DE ELEMENTOS BIOACESSÍVEIS EM TATUAGENS  
ADESIVAS TEMPORÁRIAS USADAS POR CRIANÇAS E ADULTOS**

Uberlândia  
Minas Gerais – Brasil  
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Trabalho de Conclusão de Curso apresentado ao  
Instituto de Ciências Agrárias,  
da Universidade Federal de Uberlândia,  
para obtenção do título de  
Bacharel em Engenharia Ambiental.

Orientador: Prof. Dr. Rodrigo Alejandro Abarza Muñoz

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## SUMÁRIO

<b>AGRADECIMENTOS</b> .....	2
<b>RESUMO</b> .....	4
<b>ABSTRACT</b> .....	5
<b>PREFÁCIO</b> .....	6
<b>GRAPHICAL ABSTRACT</b> .....	7
<b>1.INTRODUÇÃO (Introduction)</b> .....	8
1.1 A brief history of tattooing.....	8
1.2 Types of tattoos.....	11
1.3 Temporary press-on tattoo.....	12
<b>2.OBJETIVOS (Objectives)</b> .....	14
2.1 JUSTIFICATIVA (Justification).....	14
2.2 Possible adverse effects of tattoos.....	17
2.2.1 Dermatitis.....	17
2.2.2 Ink deposition.....	18
2.2.3 Metals in tattoo inks.....	19
<b>3.METODOLOGIA (Material and Methods)</b> .....	20
3.1 Bioaccessibility of elements in temporary tattoos and HCl extraction.....	23
3.2. Instrumentation.....	24
<b>4.RESULTADOS E DISCUSSÕES (Results and Discussion)</b> .....	25
4.1 Elementary determination in tattoo samples.....	26
<b>5.CONCLUSÕES (Conclusions)</b> .....	34
<b>6.REFERÊNCIAS BIBLIOGRÁFICAS</b> .....	36

## RESUMO

A presença de elementos bioacessíveis e potencialmente tóxicos em cinco marcas diferentes de tatuagens temporárias (embaladas junto com chicletes) destinadas ao público infantil e três marcas de produtos utilizados pelo público jovem e adulto foram analisadas de acordo com a norma de segurança de brinquedos previstas pela Associação Brasileira de Normas Técnicas (ABNT) e pela Organização Internacional de Padronização (*International Organization for Standardization* - ISO). Empregou-se a extração com HCl 0,07 mol L<sup>-1</sup> e as determinações em um espectrômetro de massa com plasma indutivamente acoplado (ICP-MS). Frações bioacessível de bário, cobre e estrôncio foram encontradas na faixa de concentração entre 2,00–11,1 µg g<sup>-1</sup>; 0,0364–0,875 µg g<sup>-1</sup> e 0,155–9,9 µg g<sup>-1</sup>, respectivamente. Chumbo bioacessível (2,6 ± 0,1 µg g<sup>-1</sup> – 4,36 ± 0,06 µg g<sup>-1</sup>) e boro bioacessível (2,14 ± 0,07 – 3,54 ± 0,07 µg g<sup>-1</sup>) foram encontrados em duas amostras, enquanto o cromo bioacessível (0,403 ± 0,004 µg g<sup>-1</sup>) em uma amostra destinada a crianças. O alumínio bioacessível foi encontrado em seis amostras, principalmente em produtos usados por crianças. Outros elementos cuja bioacessibilidade foi avaliada foram Mo e Cd cujas concentrações se situaram abaixo do limite de detecção, além de V (0,148 ± 0,003 µg g<sup>-1</sup>) e o alérgeno Co (variou entre 0,003 – 1,756 µg g<sup>-1</sup>). Todas as amostras atenderam aos altos limites permitidos pela norma nacional de segurança de brinquedos, porém, cromo, chumbo, cobalto e bário apresentaram níveis de bioacessibilidade superiores aos valores permitidos por norma aplicada a cosméticos (RDC n° 83 da ANVISA). Portanto, estas tatuagens não poderiam ser aplicadas diretamente na pele.

**Palavras-chave:** Brinquedos, tatuagens adesivas temporárias, metais pesados, bioacessibilidade, ICP-MS.

## ABSTRACT

The presence of bioaccessible potentially-toxic elements in five different brands of temporary tattoos (packaged with bubble gums) aimed at children and three product brands used by young and adult audiences were analyzed in accordance with the Brazilian and International Organization for Standardization toys safety standard. It was employed the extraction with  $0.07 \text{ mol L}^{-1}$  HCl and the determinations using inductively-coupled plasma mass spectrometer (ICP-MS). Bioaccessible barium, copper and strontium were found in the concentration range between  $2.00\text{--}11.1 \mu\text{g g}^{-1}$ ,  $0.0364\text{--}0.875 \mu\text{g g}^{-1}$ ,  $0.155\text{--}9.9 \mu\text{g g}^{-1}$ , respectively. Bioaccessible lead ( $2.6 \pm 0.1 \mu\text{g g}^{-1}$  –  $4.36 \pm 0.06 \mu\text{g g}^{-1}$ ) and boron ( $2.14 \pm 0.07$  –  $3.54 \pm 0.07 \mu\text{g g}^{-1}$ ) were found in two samples whereas chromium ( $0.403 \pm 0.004 \mu\text{g g}^{-1}$ ) in a sample aimed at children. Bioaccessible aluminum was found in six samples, mostly at products used by children. Other elements whose bioaccessibility was evaluated were Mo (< LOD), Cd (< LOD), V ( $0.148 \pm 0.003 \mu\text{g g}^{-1}$ ) and the allergen Co (ranged between  $0.003$  –  $1.756 \mu\text{g g}^{-1}$ ). All samples met the high limits permitted by the national toy safety standard, however, chromium, lead, cobalt and barium presented higher bioaccessibility levels than allowed values for cosmetics (RDC n° 83 of the National Health Surveillance Agency, ANVISA) and thus should be prohibited in products applied directly to the skin.

**Keywords:** Toys, temporary adhesive tattoos, heavy metal, bioaccessibility, ICP-MS.

## PREFÁCIO

Este trabalho de conclusão de curso tem como título em português “*Determinação de elementos bioacessíveis em tatuagens adesivas temporárias usadas por crianças e adultos*”; entretanto como visa uma publicação em uma revista indexada internacionalmente foi redigido diretamente na língua inglesa, e terá como título e autores:

**Determination of total and bioaccessible elements in temporary adhesive tattoos  
used by children and adults**

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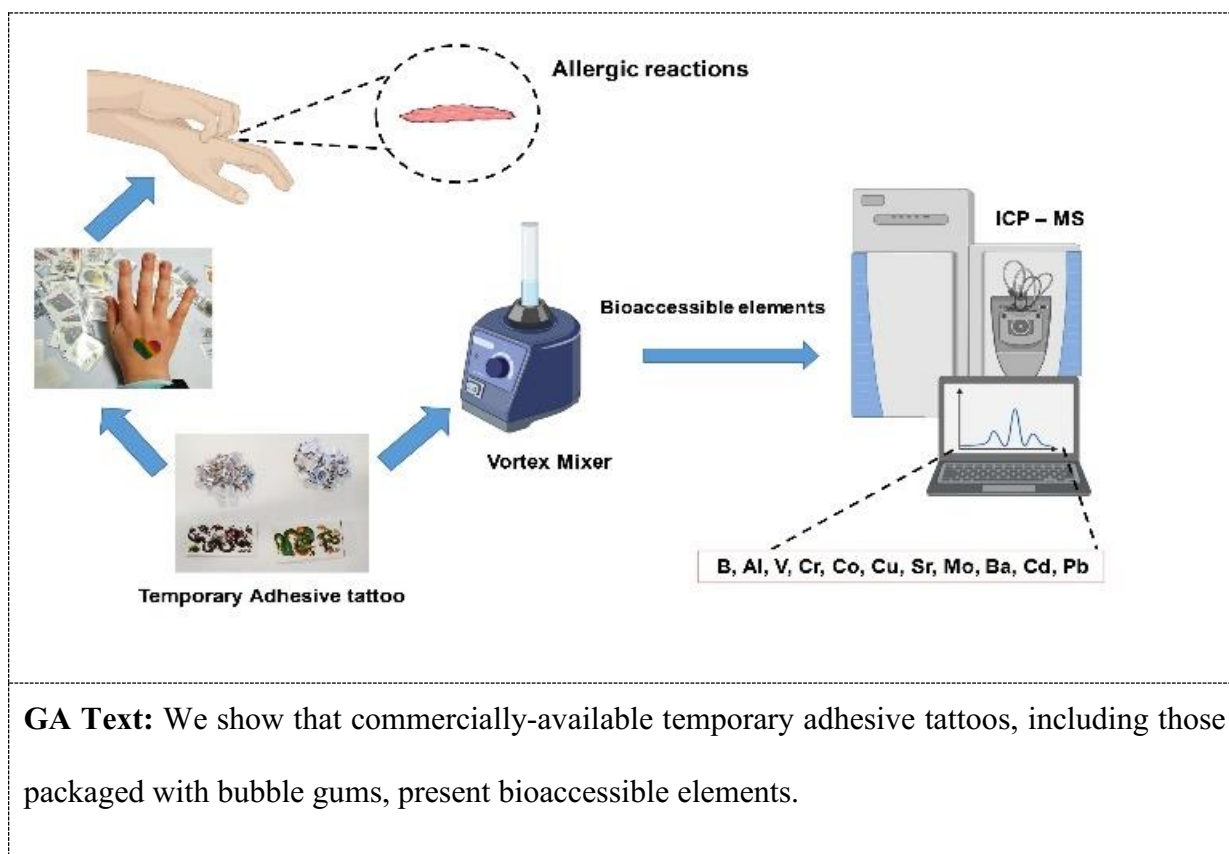
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**Determination of total and bioaccessible elements in temporary adhesive tattoos  
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*Química Nova*

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**Graphical Abstract (GA)**





## **1. Introduction**

### **1.1. A brief history of tattooing**

The art of tattooing has been a part of mankind's culture for a long time, with oldest ever discovered tattoo on human skin being between 5390 and 5120 years old (found on the body of Ötzi the Iceman (DETER-WOLF et al. 2016), meaning it was applied on someone who lived during the Neolithic period (more commonly known as the "Stone Age") (WALKER et al. 2018). Tattoos have been used for many different purposes in many different cultures such as decorations, religious motifs, non-verbal communication, differentiation between societal castes, monetary, and many others (KRUTAK, 2015). The following examples (Fig.1) were provided to illustrate these variations on meaning and aesthetic of tattoos: in ancient Polynesia, on the Samoan tribes tattoos were only executed by well-trained priests during rituals; in North America, Inuit men tattoo the number of hunted whales on their bodies, and woman tattoo their chins to indicate marital status; ancient Greeks and Persians tattooed slaves and prisoners of war, to distinguish these people from law-abiding citizens (PORCELLA, 2009); in modern day Japan various commercial establishments ask patrons to cover their tattoos or refuse service to tattooed patrons due to the strong connection of tattoos with the Yakuza (Japanese criminal organization, Fig. 1).

Our history is full of discovery, loss and rediscovery of methods, objects and knowledge, and tattoos are a prime example of this process. In "modern" history, tattoos were "rediscovered" by the European explorers about 530 years ago, during the "Age of Exploration" when they came in contact with many different cultures from Asia, Africa and the Americas. Because of the disparity in technological advancements and the European social structure at this period, with many rigid societies ruled by authoritarian governments, such as monarchies or empires, alongside the widespread of Abrahamic

faiths (Christianity, Judaism, or Islam), most Europeans considered themselves as the only “civilized” people in the world. This “fact” was “confirmed” by the explorers when confronted with less advanced civilizations, tribes and people, some of which had “desecrated” their bodies (which were made, according to the Europeans religious beliefs, in God’s own image) by marking it with tattoos, and performing tribalistic rituals, “Some of the civilizations that practiced tattooing also practiced human sacrifice.



**Figure 1** (A) example of tattoo found on the body of Ötzi the Iceman (<https://anthropology.net/2009/07/21/otzi-icemans-tattoos-were-born-in-fire/>); (B) example of tattooed Inuit ([statcan.gc.ca](http://statcan.gc.ca/)); (C) example of tattooed Samoan ([tahititourisme.com.br](http://tahititourisme.com.br/)); (D) example of a Thracian Red-Figure Vessel depicting a tattooed person (<https://www.archaeology.org/issues/107-131/features/tattoos/start=5>); (E) example of a tattoo with religious motif ([worldtattoogallery](http://worldtattoogallery.com/)); (F) example of tattooed Yakuza ([Shirtless-Yakuza-Members-At-Sanja-Matsuri-Festival-e1587810365955](http://Shirtless-Yakuza-Members-At-Sanja-Matsuri-Festival-e1587810365955)); (G) Japanese “onsen” sign with the following phrase: “please understand that we cannot accept customers who have tatoos”. Internet free images - (<https://www.google.com/urlsa=i&url=https%3A%2F%2Fmediazink.com%2Ftattoo-tourism-japan/>).

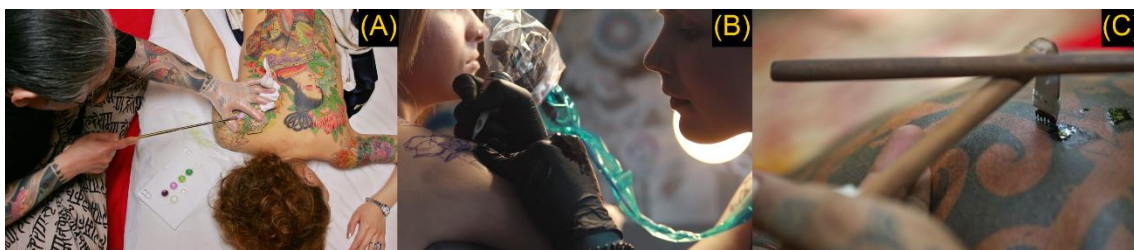
Europeans viewed human sacrifice not only as immoral but also grotesque. Inscribing ink into the flesh and cutting out a human heart to sacrifice to the gods (as practiced among the Aztecs) may have been perceived as equivalent in the minds of Europeans. (PORCELLA, 2009). In this context it is easy to understand why the act of tattooing was seen as something barbaric or primitive, and carried a negative connotation in European society even when done by other Europeans, thus being associated with the lowest individuals in society. During the “Age of Exploration” there was a rise of global trade

and an expansion of the European colonial empires. With that not only foods, animals and products were traded, but there was also an exchange of cultures and ideas. Since during this period the Europeans had the strongest navy and economies in the world their culture was also able to reach and influence the farthest, something that is still visible today around the world. Because of this cultural heritage and other factors, for a long time, tattoos were seen as undesirable by most people in western societies and those who wore them on their skin were usually members of a subcultural group who deviated from the norm (PORCELLA, 2009). In today's world the perception of tattoos has changed, and its popularity increased, although there are still people who discriminate against others with tattoos. This change in how society perceives tattoos is one of the results of many years of struggle and many cultural movements that happened during the late 20<sup>th</sup> century in combination with modern technologies. These movements pushed for a more egalitarian society, in which people of all genders, skin colors, sexual orientation and appearances would be treated as equals, having the same rights and opportunities. Movements such as: Civil Rights Movement, Women's rights, LGBT movements, Punk and Rock movements (GUIDRY, et al. 2003). Because of this cultural change many deviant sub-cultural groups became more popular and by association their looks, including plenty of tattoos. Some individuals from these groups became part of the social elite at the time, in the form of famous writers, musicians or actors, popularizing their style and making it have a positive connotation instead of a negative one, mostly amongst the youth. With this, a positive feedback loop was created, where more young people would see tattoos as something "cool", increasing the likelihood of them getting tattoos and becoming influential tattooed adults themselves. Tattooing and getting tattooed comes with plenty of drawbacks, especially in the past with it being expensive, anxiety inducing, permanent and with the possibility of transmitting or causing illnesses. With

modern technologies they became cheaper, quality increased, there are no more risks of transmissible diseases (so long as the proper sanitary rules are followed), hypoallergenic pigments were developed, tattoos are no longer (necessarily) permanent with the invention of laser removal and temporary tattoos, all these factors also helped popularize tattoos (MATEUS, 2019). Today, tattoos are still increasing in popularity with no sign of slowing or stopping, because of that we must continue studying tattoos and tattooing.

## 1.2. Types of tattoos

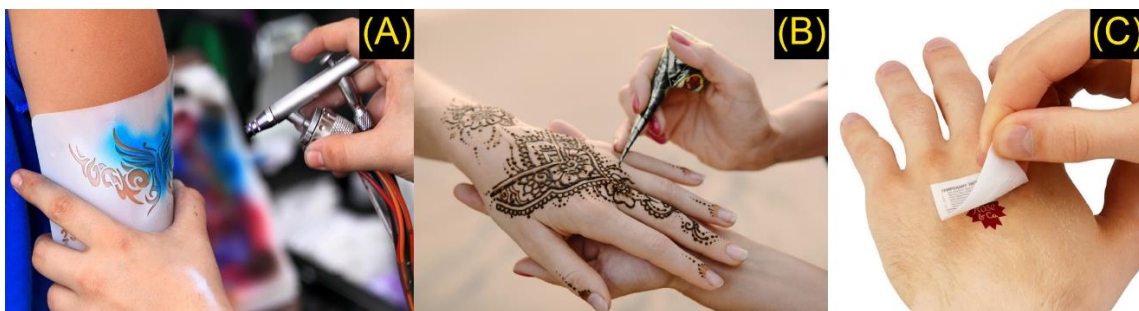
Tattoos can be broadly divided into two categories, permanent and temporary tattoos, with each of these having many different sub-categories. Permanent tattoos are also known as tattoos, tats, tat, ink, permanent makeup and other terms, they are those in which an inert pigment is applied into the dermal layer of the skin using some sort of needle, group of needles or needle-like implement (Fig.2). This type of tattoo cannot be removed/erased from the body without the use of medical procedures, such as laser removal (KENT AND GABER, 2012).



**Figure 2** (A) example traditional Japanese tattooing with a needle-like tool ([http\\_cdn.cnn.com\\_cnnnext\\_dam\\_assets\\_181218104101-tebori-tattoo-2](http_cdn.cnn.com_cnnnext_dam_assets_181218104101-tebori-tattoo-2)); (B) example of modern tattooing with a tattoo gun ([videoblocks-drawing-a-tattoo-on-the-shoulder-close-up-master-tattoo-makes-a-rotary-tattoo-machine-gun\\_r1\\_2il120z\\_thumbnail-1080\\_01](videoblocks-drawing-a-tattoo-on-the-shoulder-close-up-master-tattoo-makes-a-rotary-tattoo-machine-gun_r1_2il120z_thumbnail-1080_01)); (C) example of traditional Polynesian tattooing with needle-like tool (<traditional-polynesian-tattooing-1>). Internet free images: <http://www.historyoftattoos.net/tattoo-facts/tattoo-statistics/>

Temporary tattoos vary greatly on their appearances, inks, application and duration depending on the type of temporary tattoo, but in general they are those in which a pigment is applied on top of the skin. These types of tattoos can be removed/erased by

a variety of means (soapy water, makeup removal products, ethanol and others), depending on the type of temporary tattoo itself. They will also be removed/erased naturally, in a predetermined period, depending on the type of temporary tattoo, that can last from three days to several weeks (FDA <https://www.fda.gov/consumers/consumer-updates/temporary-tattoos-may-put-you-risk>). Amongst the most popular types of temporary tattoos are henna tattoos, airbrush tattoos and press-on tattoos.



**Figure 3** (A) example of airbrush tattoo (temporary-airbrush-tattoo-designs); (B) example of henna tattoo (hennatattoos-1024x684); (C) example of press-on tattoo (0 ZW2SLzXmVChhtVQX). Internet free images: <http://www.historyoftattoos.net/tattoo-facts/tattoo-statistics/>

### 1.3. Temporary press-on tattoo

This type of tattoo is also known as: sticker, sticker tattoo, temporary tattoo, temporary adhesive tattoo, decal, tattoo decal, temporary tattoo decal (Fig.3). For the purposes of this study, the term “temporary tattoo” will be used from this point on when referring to this particular type of tattoo.

Temporary tattoos consist of an image attached to a support/transfer sheet (MOORE et al. 2000), that when in contact with the skin will transfer said image onto the skin, lasting from three days to several weeks (Fig. 4). This tattoo is made of many layers of different materials, layered on top of each other. The image is usually made of three layers, them being a contact adhesive layer, an aqueous spot coating layer and a multi-color ink image layer. The support/transfer sheet is usually made of two layers, them

being a porous paper layer and a slip layer (MOORE et al. 2000). But the construction of these layers can vary greatly, depending on manufacturer, for example, it is not uncommon to find “supports” made out of plastic instead of paper, and many of these tattoos come with two extra layers of easily removable protective plastic that “sandwiches” the tattoo. To apply the temporary tattoo, one would peel of any protective layer on the tattoo, then proceed to “glue” the transfer sheet on the skin as if it were a sticker, then the surface of the tattoo would be moistened with water (if the support were paper) or the tattoo would be lightly massaged onto the skin, after this the transfer sheet would be peeled off leaving the tattoo attached to the skin.

U.S. Patent Jun. 13, 2000 6,074,721

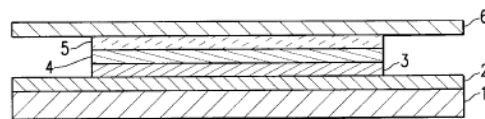


FIG. 1

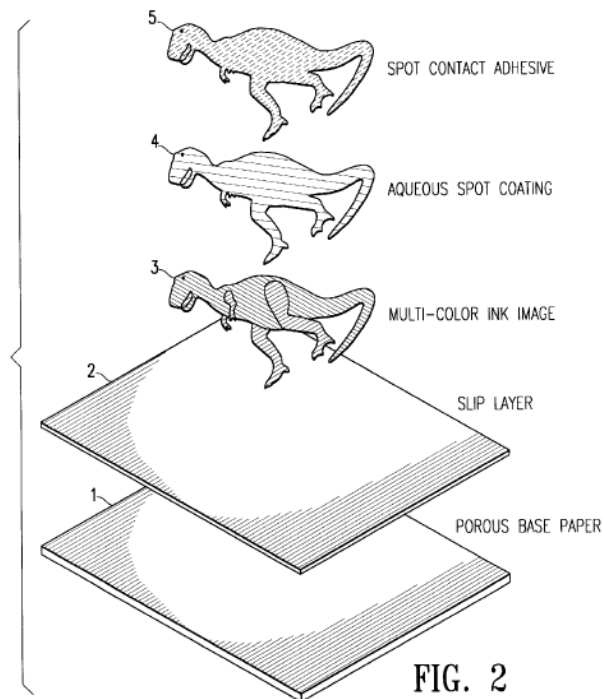


FIG. 2

**Figure 4.** Example of the structure of a temporary adhesive tattoo (patent – free internet image). <http://www.historyoftattoos.net/tattoo-facts/tattoo-statistics/>

## 2. Objectives

This work aimed to verify the bioaccessibility of the elements  $^{11}\text{B}$ ,  $^{27}\text{Al}$ ,  $^{51}\text{V}$ ,  $^{53}\text{Cr}$ ,  $^{59}\text{Co}$ ,  $^{63}\text{Cu}$ ,  $^{88}\text{Sr}$ ,  $^{98}\text{Mo}$ ,  $^{138}\text{Ba}$ ,  $^{113}\text{Cd}$ ,  $^{208}\text{Pb}$  in synthetic temporary tattoos available in the Brazilian market. For this purpose, samples of different brands of temporary tattoos packaged with bubble gums, whose target audience is children, and samples of temporary tattoos sold on cards used mainly by young people and adults were analyzed. The determination was performed by ICP – MS after a simple extraction of the elements with a diluted HCl solution. The sample preparation procedure and the results obtained were performed and compared according to the Brazilian Safety of toys - Part 3: Migration of certain elements of Brazilian Association of Technical Standards (ABNT), International Organization for Standardization (ISO), and Brazilian standards of permitted and prohibited substances in National Health Surveillance Agency (ANVISA).

### 2.1. Justification

The tattooing trend is a relatively new phenomena and we are yet to see the possible consequences and effects it will have on us after several generations, because of that, we believe that there is a need for more studies about tattoos compositions and potential risks derived from skin contact with pigments and other tattoo components. A recent study performed in Brazil (RUBIO et al. 2019) found that around 37% of the population have at least one tattoo, while in other countries this percentage can be higher, for instance in Sweden (47%) and USA (46%), illustrating just how common this art form has become.

The main problem is due to the presence of dyes or other toxic elements that are not approved by FDA (FOOD AND DRUG ADMINISTRATION) and can be harmful for the skin (FDA, 2020). Children are more sensitive to the effects of toxic compounds caused by this exposition, which can cause skin irritation such as redness and swelling

(GUNEY, ZAGURY, 2013; NEGEV et al 2018; RUBIO et al. 2019). Furthermore, there are several reports in the literature showing allergic reactions, local infections or granulomas caused by the different compounds present in temporary tattoos (SIDBURRY, STORRS 2000; ÖNDER et al. 2001; NERI et al. 2002; LEGGIADRO, BOSCAP, SAPADIN 2003; MATULICH, SULLIVAN 2005; HARDWICKE, AZAD 2006; SONNEN 2007; PANFILI, ESPOSITO, DI CARA 2017; FDA, 2020).

Although the several problems previously mentioned earlier, the consumer does not know the composition of temporary tattoos due to inadequate labeling on the packaging (RUBIO et al. 2019). Moreover, these products can be easily found in markets with various shapes, figures and are also packaged with bubble gum. Dyes are the main constituents of these temporary tattoos and, therefore, impurities from the manufacturing process may also be present (RASTOGI, JOHANSEN 2005). Temporary tattoo inks are protected with plastic films and substances such as phthalates may migrate to the inks and, consequently, adhere to the skin when using the product. In addition to these components, aromatic amines, polycyclic compounds with or without azo group, nanoparticles, hydrocarbons and toxic metals can be found in these temporary adhesive tattoos and lead to skin irritation (RUBIO et al. 2019). The quality control of these products is not well established and is confusing. According to Rubio et al. (2019) temporary tattoos must be correctly labeled and the chemical composition must comply with the Safety Standards of Toys, and because the product is in direct contact with the skin, the product must also comply with the regulations of the Cosmetics Regulation.

Rastogi and Johansen (2005) analyzed 36 synthetic adhesive tattoos in order to investigate the presence of different dyes using a method based on solvent extraction and analyzed the samples by high performance liquid chromatography (HPLC) with spectrophotometric detection (UV – VIS). At least 11 compounds were identified in



concentrations more than 4479 mg kg<sup>-1</sup>. The red dye (Barium bis[4-[(2-hydroxy-1-naphthyl)azo]-2-methylbenzenesulphonate) was present in 94% of the temporary tattoos analyzed in a concentration of up to 2391 mg kg<sup>-1</sup>. According to the authors, this dye has already been reported as allergenic due to impurities present in the pigment.

Sukuroglu et al. (2017) analyzed p-phenylenediamine (PPD) by high performance liquid chromatography and Co, Ni, Pb, Cr by inductively coupled plasma mass spectrometry (ICP – MS) in samples of commercial temporary black henna tattoo from Turkey. The authors found the presence of the allergenic additive (PPD) in all samples in the range between 3.37 and 51.6% (w/w). At least 23 samples showed PPD concentration above the limit of 6% (w/w) stipulated by the European Cosmetics Regulation (CEN 2020). In the United States, the FDA has banned the use of PPD in products applied directly to the skin including temporary tattoos (FDA, 2020). For metals, the authors determined the bioaccessible fraction in deionized water. Here, the term bioaccessible is considered as a soluble metal that form hydrate ions in aqueous solution and can be absorbed by the human body or skin (NORDBERG, DUFFUS, TEMPLETON, 2010). The values of bioaccessible metals in deionized water were in the range between 0.15 – 0.18 µg L<sup>-1</sup>, 0.32 – 0.42 µg L<sup>-1</sup>, 0.55 – 0.67 µg L<sup>-1</sup>, and 0.13 – 0.38 µg L<sup>-1</sup> for Co, Ni, Pb and Cr, respectively. The authors stressed that due to the high toxicity, the presence of these elements in cosmetics is prohibited in several countries of the European Union according to the current legislation (CEN 2020). Similarly, these metals are also prohibited in cosmetic formulations in Brazil according to RDC n° 83 of the National Health Surveillance Agency (ANVISA 2020). Moreover, the presence of metals in these tattoos may be related to the presence of inorganic and organometallic pigments, paint impurities, additives or mineral adulterants that was added to the tattoo, in order to give

a metallic and shiny appearance, when the product is applied into the skin (RUBIO et al. 2019).

Besides the effects of toxic elements in the literature being well-known, data related to these contaminants is still scarce in synthetic temporary tattoos, especially those aimed at children. Children can be exposed to chemicals through oral and dermal exposure, and the contact of metallic ions with the skin induces dermatitis and rashes that can be absorbed into the bloodstream (HOSTYNEK 2003; VAN LIERDE et al. 2006; LARESE ET AL. 2007; YOSHIHISA, SHIMIZU 2012; NEGEV et al 2018; MARIN VILLEGAS, GUNEY, ZAGURY 2019; YUAN et al 2019) . In this context, the investigation of the bioaccessibility of potentially toxic elements in temporary tattoos is necessary due to the unknown composition of the ingredients and the consequent possibility of dermal contamination and adverse effects related to the health of children and adults using this type of product.

## 2.2. Possible adverse effects of tattoos

### 2.2.1. Dermatitis

There are known possible side effects of wearing tattoos, be them permanent, temporary, or henna tattoos. These undesirable side effects can vary greatly but are usually some types of dermatitis.

Dermatitis is the term used when describing a vast group of common skin illnesses. They can be described as any alteration of the skin and its attachments that is caused, maintained, or aggravated, directly or indirectly by external agents on the human body (Ali 2009). The symptoms and effects of dermatitis appear as cutaneous alterations that can be but are not limited to the following (Ali 2009): a) rashes; b) allergies; c) eczemas;

d) swollenness; e) fissures; f) changes in coloration; g) hipo/hypersensitivity to temperature changes; h) hypersensitivity to sun light; i) trauma and j) infections.

These illnesses can be caused or influenced by many factors, environmental ones, or external agents. Environmental factors would those related to sun light, humidity, or temperature. External agents are any agent external to the human body capable of affecting the skin on the manner previously described. These agents could be gases, vapors, particulates, radiation, oils, metals, chemical compounds, plastics, etc (Ali 2009). When tattoos do cause a negative reaction on the skin, it usually comes in the form of an allergic reaction, rash, and/or eczema, for temporary and henna tattoos, or as an allergic reaction, rash, eczema and/or infection for permanent tattoos (Fig 5).



**Figure 5.** (A) and (B), example of eczematous reaction on the site of a henna tattoo (henna tattoo reaction – internet free images - <http://www.historyoftattoos.net/tattoo-facts/tattoo-statistics/>).

### 2.2.2. Ink deposition

Another possible side effect of wearing tattoos is the deposition of metals, organic and inorganic compounds on the body due to the migration of this tattoo ink elements from the upper layers of the skin to the blood stream and further into the body. The accumulation of tattoo inks and its components on the body can directly or indirectly cause/aggravate many problems since some of its components are known carcinogens (FOERSTER et al 2020). The migration of tattoo inks and its components can be

exemplified in the case study of Grove et al (2015), where a PET-CT scan (positron emission tomography – computed tomography) resulted in a false-positive due to the deposition of tattoo ink in the common ileac lymph nodes of a patient with cervical cancer which had extensive lower body tattoos.

### 2.3 Metals in tattoo inks

Tattoo inks get their signature colors from the use of various metallic, organic and inorganic pigments. Some of the metals found in tattoo inks are (and by BEUTE et al 2008; FORTE et al. 2009): Iron (Fe<sup>56</sup>); Aluminum (Al<sup>13</sup>); Titanium (Ti<sup>22</sup>); Copper (Cu<sup>29</sup>); Magnesium (Mg<sup>12</sup>); Chromium (Cr<sup>24</sup>); Nickel (Ni<sup>28</sup>); Vanadium (V<sup>23</sup>); Strontium (Sr<sup>38</sup>); Cadmium (Cd<sup>48</sup>); Mercury (Hg<sup>80</sup>); Barium (Ba<sup>56</sup>); Lead (Pb<sup>82</sup>); Molybdenum (Mo<sup>42</sup>); Cobalt (Co<sup>27</sup>).

With this we cannot discard potentially dangerous side effects of metal accumulation on the body, in case the metals present on the tattoos are in fact capable of being deposited on the human body for the long term. The accumulation of metals in the human can lead to several diseases. Just from the metals above mentioned we can cite the following diseases: Alzheimer type II, Parkinsonism, Parkinson disease, DNA damage, cirrhosis, renal stones, neurodegenerative disorders, ataxia, multiple organ failure (muscle, liver, lung, kidney, stomach) and multiple types of cancer (FABIÁN F. L., et al. 2013; ROBERT GOYER, et al. 2004; SANDHYA MISHRA, et al. 2019).

### 3. Material and Methods

All solutions were prepared using high-purity water obtained from a Milli-Q system (Millipore, Germany), resulting in water with resistivity equal to 18.2 MΩ cm.

The analytical reference solutions were prepared in 0.1% (v/v) of HNO<sub>3</sub> by successive dilutions of the 1000 mg L<sup>-1</sup> multi-element solution (Quimlab, Brazil). All solutions were stored in polypropylene bottles.

Kids temporary tattoos were purchased in supermarkets and candy stores. In total, 5 samples of different brands (A, B, C, D and E) were acquired containing bubble gums packed together with temporary tattoos. These samples are manufactured in Brazil, in addition, they are sold in sealed boxes containing 100 units each or are sold individually in smaller quantities. In this specific work, all the samples mentioned were acquired in a sealed box. The temporary tattoo is between the bubble gum and the outer packaging (label) and the drawing containing the inks is protected with a plastic film to prevent contact of the gum with the tattoo ink. The temporary tattoo designs are supported on a paper or plastic substrate, depending on the brand. The dimensions of the applicable area containing the adhesive tattoo inks are variable and depend on the size of the design and the brand. Temporary tattoos from each sample were selected for analysis in such a way that most dyes were present and, in this way, different elements could be extracted and detected.

Other 3 samples (F, G and H) of different brands of temporary tattoos were purchased at the local and online stores. In this case, these tattoos are sold separately and not attached to a product like the ones mentioned above. These samples were acquired as cards containing one or more figures of different sizes and areas containing the applicable ink. In the samples in which the cards contained several drawings, the temporary tattoos were cut with the aid of scissors to remove the excess of unprinted paper with the aid of scissors. All temporary tattoos are printed on a paper substrate and the inks are protected by a plastic film to prevent direct contact with air. The application is similar to those aimed at children; however, the durability is greater, that is, the contact of the ink with

the skin remains for a longer period. The target audience of these tattoos is diverse, it can include children, youth and adults depending on the visual aspect and parental authorization when underage. Figure 6 shows some examples of samples/tattoos packaged together with bubble gums and adhesive tattoos on cards used at work. In total, 9 temporary tattoos were analyzed in this study and classified in A, B, C, D and E as being present in bubble gums aimed at children and F, G and H as temporary tattoos of cards that are most used young and adult audiences (Fig. 6).



**Figure 6.** Examples of the analyzed adhesive tattoos: (A) temporary tattoos present in bubble gum and (B) temporary adhesive tattoos on cards

### 3.1 Bioaccessibility of elements in temporary tattoos and HCl extraction

The procedure for preparing temporary tattoo samples consisted of extracting potentially toxic elements using a solution of  $0.07 \text{ mol L}^{-1}$  HCl according to the Brazilian safety standard of ABNT NBR NM 300-3:2011<sup>35</sup> and ISO 8124-3:2020<sup>36</sup> on element migration in toys. This method is based on the bioavailability of certain elements (metals) after the use of toys whose focus is oral exposure due to suction, swallowing or licking. The bubble gums of each brand were unpacked and the adhesive tattoo separated. Then, the plastic film that protects the paint was removed, leaving the substrate containing the figure. Each temporary tattoo of the 5 different bubble gum brands has figures with different areas, so they have different mass. In this way, the mass used in the extraction procedure was standardized. Approximately 0.6 g of the samples (A, B, C, D and E), which consisted of the respective tattoo attached to the paper substrate) was used. According to the standard safety of toys, the substrate must also be part of the extraction. Temporary tattoos for each brand were added in 5 different polypropylene tubes. Then, 30 mL of HCl ( $0.07 \text{ mol L}^{-1}$ ) solution was added over the tattoos contained in the tubes and stirred at  $37 \pm 2^\circ\text{C}$  for 1 h using a mixer stirrer. After, the solution remained at rest for one more hour. The care with adding the solution ensured that all temporary tattoos accommodated inside the tube were in direct contact with the liquid, ensuring maximum efficiency during extraction. The volume of the solution used in this procedure followed the recommendation of ABNT NBR NM 300-3:2011<sup>35</sup> and ISO 8124-3:2020<sup>36</sup>. Then samples were mixed with HCl ( $0.07 \text{ mol L}^{-1}$ ) using a mass of extracting solution that was 50-fold higher than the mass of sample. The solutions were filtered through a PTFE membrane with a pore diameter of  $0.45 \mu\text{m}$ , stabilized with ultrapure hydrochloric acid to the final concentration of  $1.0 \text{ mol L}^{-1}$  and stored in a polypropylene tube. The same

procedure was applied to temporary card tattoos. However, the plastic film, that was covering the figures, was removed before the experiment.

For large adhesive tattoos, the substrate was cut into smaller parts with a plastic ruler. Initially, the plastic film covering the figure's paint was removed. Each sample was transferred to a polypropylene tube, and the masses were related to the total weight of the card containing the temporary tattoo and the paper substrate. Then, each sample was mixed with a solution of HCl ( $0.07 \text{ mol L}^{-1}$ ) using a mass proportion of 1:50 (HCl: sample) as mentioned before. The mixture was stirred for 1 h at  $37 \pm 2 \text{ }^\circ\text{C}$  and remained for another 1 h of rest. The solutions were filtered, stabilized with HCl and stored in polypropylene tubes for further analysis. The tattoo masses used in the samples (A, B, C, D, E, F, G and H) extracted with HCl were comprised in the range between 0.4 and 0.7 g.

### 3.2. Instrumentation

After the procedure of extracting temporary tattoos with HCl, the solutions obtained were analyzed by inductively coupled plasma mass spectrometry (ICP - MS), model iCAP Q from Thermo Fisher Scientific (Cambridge, England), equipped with a quadrupole mass analyzer and a collision reaction cell set to kinetic energy discrimination (KED) mode, using 99.999% He as collision gas and 99.999% Ar gas was used to carry out the plasma formation and maintenance process. The instrumental parameters used in the operation of the equipment are described in Table 1.



**Table 1** Instrumental parameters used in the operation of ICP – MS.

Parameter	Operational Condition
Radio frequency power (W)	1550
Nebulization chamber temperature (°C)	2.7
Peristaltic pump speed (rpm)	40
Sampling depth (mm)	5
Auxiliary gas flow (mL min <sup>-1</sup> )	0.8
Nebulizer gas flow (mL min <sup>-1</sup> )	0.975
Nebulizer	Concentric
Spray chamber	Cyclonic
Number of replicates	3
Dwell time (s)	0.05
Operation mode	KED (Kinetic Energy Discrimination)
Analyzed isotopes	<sup>11</sup> B, <sup>27</sup> Al, <sup>51</sup> V, <sup>53</sup> Cr, <sup>59</sup> Co, <sup>63</sup> Cu, <sup>88</sup> Sr, <sup>98</sup> Mo, <sup>138</sup> Ba, <sup>113</sup> Cd, <sup>208</sup> Pb
Internal standard	<sup>115</sup> In

Analyses were performed using the optimized instrumental parameters shown in Table 1. All analytical reference solutions were prepared using concentrations of multi-element standards in a range from 0 to 500 µg L<sup>-1</sup>, in order to perform the instrument calibration.

#### 4. Results and Discussion

The concentration of elements in tattoos were determined using an ICP-MS method that had the following figures of merit evaluated: linear range, limits of detection (LOD) and quantification (LOQ). The values obtained for each element are listed in Table 2.

The limits of detection (LOD) and quantification (LOQ) for the determination of elements in temporary tattoo samples were calculated as  $3.3 \times SD/S$  and  $10 \times SD/S$ , respectively, where SD is the standard deviation of 10 readings of blank and *S* the slope (sensitivity) of the analytical curve for each element. The LOD and LOQ calculations were performed as described by the ABNT NBR NM 300-3:2011 standard. The low LODs and LOQs obtained in this study demonstrate the high sensitivity of the method for elemental determination in tattoos samples. The linear range obtained for each metal was wide, with a linear correlation coefficient ( $R^2$ ) greater than 0.998 for all the quantified elements.

**Table 2.** Analytical parameters of the inductively coupled plasma mass spectrometry method.

Element	LOD ( $\mu\text{g g}^{-1}$ )	LOQ ( $\mu\text{g g}^{-1}$ )	Linear range ( $\mu\text{g g}^{-1}$ )	$R^2$
B	0.19	0.64	0.64 – 52.1	0.999
Al	0.32	1.1	1.1 – 52.1	0.999
V	0.029	0.097	0.097 – 111.3	0.999
Cr	0.093	0.31	0.31 – 111.3	0.999
Co	0.0002	0.001	0.001 – 5.17	0.999
Cu	0.009	0.032	0.032 – 5.17	0.999
Sr	0.014	0.046	0.046 – 111.3	0.999
Mo	0.003	0.011	0.011 – 111.3	0.998
Cd	1.2	4.1	4.1 – 111.3	0.999
Ba	0.065	0.22	0.22 – 111.3	0.999
Pb	0.64	2.1	2.1 – 111.3	0.999

#### 4.1. Elementary determination in tattoo samples

The use of synthetic temporary tattoos as a form of toy for children or to follow a fashion trend among young people and adults has become popular. However, knowledge about the composition of the ingredients used in transferable inks is still scarce.

Temporary tattoos are products applied directly to the skin, so skin exposure is similar to the use of cosmetic products. In this way, several substances including toxic metal ions are in direct contact with the human body and if absorbed, they can lead to health problems (ULLAH et al. 2017). However, these patterns are far from being followed. Despite little data obtained in the literature, a study showed the presence of three phthalates and an adipate (dimethyl adipate, DMA) in temporary tattoos that are prohibited in the composition of cosmetics (RUBIO et al. 2019), including in Brazil (ANVISA 2020). In the corresponding section, it was said that the presence and contact of the skin with unregulated substances can cause skin-related problems such as dermatitis or even present carcinogenic potential.

Users remove the film that protects the temporary tattoo and applies the substrate on the skin. The application can be done with or without water to transfer the image into the skin. The long-term exposition of skin to temporary tattoo can cause risk of contamination and allergy due to the unregulated tattoo ink ingredients (FDA 2020; JUHAS 2013). Moreover, some children can easily ingest parts of the tattoos, causing some discomforts (hypersensitivity to pigments or other ink ingredients) or, more rarely, significant health complications (JUHAS 2013).

The ABNT NBR NM 300-3:2011 and ISO 8124-3:2020 standards focus on assessing the chemical safety of toys from oral exposure to bioavailable harmful elements as the relevant route of contamination, as the oral and gastrointestinal absorption of elements is greater than cutaneous absorption (CEN 2016). Thus, as the temporary tattoo is in direct contact with the user's skin for varying periods of time, the results obtained for the elements analyzed in this work were compared with the maximum limits allowed for the same elements found in cosmetic products in Brazil (ANVISA 2020) and national and international toys safety standards (ABNT 2020; ISO 2020).

Table 3 shows the concentration of bioaccessible elements in tattoos and the respective limits allowed in cosmetic products and toys in accordance with Brazilian standards. Among the 11 elements determined in the 8 adhesive tattoo samples, only Mo and Cd were not detected in all samples (< LOD). Cd is a toxic element and is classified as a carcinogen (KLUGER, KOLJONEN 2012). It can be seen that the LOD for the Cd (Table 3) is below the maximum limit allowed for this element according to the toy safety rules. Therefore, the methodology used in this work allows to monitor low levels of Cd concentration in temporary tattoo samples. No work to date has reported the presence of Cd and Mo in synthetic adhesive or henna-based temporary tattoos. On the other hand, a study showed the presence of Cd in cosmetic hair dyes based on henna (OZBEK, AKMAN 2016). Brazilian regulations prohibit the presence of cadmium compounds in cosmetic products (ANVISA 2020), while the Toys Safety standards (ABNT and ISO) establishes a limit of 75 mg kg<sup>-1</sup> of bioavailable Cd (ABNT 2020; ISO 2020).

**Table 3.** Concentration of bioavailable elements after extraction with 0.07 mol L<sup>-1</sup> HCl.

Samples ↓ / Elements→	B (µg/g)	Al (µg/g)	V (µg/g)	Cr (µg/g)	Co (µg/g)	Cu (µg/g)	Sr (µg/g)	Mo (µg/g)	Cd (µg/g)	Ba (µg/g)	Pb (µg/g)
<b>A</b>	< LOQ	3.1 ± 0.1	< LOD	0.403 ± 0,004	< LOQ	0.120 ± 0.002	0.215 ± 0.004	< LOD	< LOD	1.779 ± 0.009	2.6 ± 0.1
<b>B</b>	< LOQ	2.92 ± 0.07	< LOD	< LOD	0.0027 ± 0.0001	0.182 ± 0.002	0.680 ± 0.003	< LOD	< LOD	2.16 ± 0.02	< LOQ
<b>C</b>	< LOQ	< LOD	< LOD	< LOD	0.00463 ± 0.00003	0.219 ± 0.002	0.155 ± 0.005	< LOD	< LOD	5.14 ± 0.02	4.36 ± 0.06
<b>D</b>	< LOQ	< LOD	< LOD	< LOD	0.01935 ± 0.00008	0.354 ± 0.003	0.481 ± 0.005	< LOD	< LOD	5.95 ± 0.02	< LOQ
<b>E</b>	< LOQ	553.3 ± 0.4	< LOD	< LOQ	0.0161 ± 0.0003	0.385 ± 0.002	0.565 ± 0.005	< LOD	< LOD	7.711 ± 0.008	< LOQ
<b>F</b>	2.14 ± 0.07	313 ± 2	< LOD	< LOQ	1.76 ± 0.02	0.875 ± 0.005	9.9 ± 0.2	< LOD	< LOD	11.1 ± 0.1	< LOQ
<b>G</b>	< LOQ	1.97 ± 0.02	< LOD	< LOD	0.0321 ± 0.0002	0.0364 ± 0.0003	4.63 ± 0.07	< LOD	< LOD	1.299 ± 0.003	< LOQ
<b>H</b>	3.54 ± 0.07	35 ± 2	0.295 ± 0.004	< LOQ	0.910 ± 0.002	0.192 ± 0.002	1.49 ± 0.01	< LOD	< LOD	6.35 ± 0.02	< LOQ
<b>Toy limit (ABNT)</b>	NS*	NS*	NS*	60	NS*	NS*	NS*	NS*	75	1000	90
<b>Toy limit (ISO)</b>	NS*	NS*	NS*	60	NS*	NS*	NS*	NS*	75	1000	90
<b>Cosmetic limit</b>	max. 180000 <sup>a</sup>	Allowed	Prohibited	Prohibited	Prohibited	Allowed <sup>b</sup>	35000 <sup>c</sup>	NS*	Prohibited	Allowed <sup>d</sup>	Prohibited

\*NS = Not specified

<sup>a</sup> Maximum permitted concentration in the form of boric acid or boron salts used in products applied directly to the skin <sup>37</sup>.

<sup>b</sup> Permitted in the form of dyes CI 74160 (blue), CI 74260 (green), CI 77400 (brown). The maximum limits allowed are not mentioned <sup>42</sup>.

<sup>c</sup> Concentration allowed in the form of strontium chloride hexahydrate. Strontium lactate and nitrate are prohibited substances for use in cosmetics <sup>37</sup>.

<sup>d</sup> Barium compounds are prohibited with the exception of insoluble barium salts such as barium sulfate, barium sulfide, lacquers, and pigments prepared under conditions that do not release barium ions <sup>37</sup>.

According to Table 3, two samples of temporary bubble gum tattoos (A and C) showed concentrations of bioaccessible Pb. The concentration values were of  $2.6 \pm 0.1 \mu\text{g g}^{-1}$  in A and  $4.36 \pm 0.06 \mu\text{g g}^{-1}$  in C. These values are below the limits established by the toys safety standards, which stipulates a maximum lead value of  $90 \mu\text{g g}^{-1}$  (ABNT 2020; ISO 2020). In all other samples, Pb was detected but it was not possible to quantify because they are below the LOQ of the method. According to cosmetics regulations, the presence of lead and its compounds in products applied on the skin is prohibited (ANVISA 2020). Lead is a highly toxic metal and exposure can cause headaches, memory loss, abdominal pain, problems related to the male and female reproductive system, kidney and cardiovascular problems and in children can cause impaired cognitive development. Studies have shown the presence of lead in hair dyes (LEKOUCH et al. 2001; OZBEK, AKMAN 2016) and temporary henna tattoos (JALLAD, ESPADA-JALLAD 2008; SUKUROGLU, BATTAL, BURGAZ 2017). Ozbek and Askman (2016) determined the concentration of lead in two hair dyes based on henna (green and black) by high-resolution continuum source graphite furnace atomic absorption spectrometry (HR-CS GF AAS). The concentrations obtained were  $0.93 \pm 0.05$  and  $0.60 \pm 0.05 \mu\text{g g}^{-1}$  for the green and black henna, respectively. Sukuroglu et al. (2017) analyzed by ICP – MS the presence of bioavailable lead in 25 temporary henna tattoos using deionized water as extractor solution. The samples analyzed showed that lead concentration was in range between  $1.59 - 17.7 \mu\text{g g}^{-1}$ . With respect to skin absorption, a study realized by Sauber et al. (1994) showed that inorganic lead compounds, such as  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Pb}(\text{CH}_3\text{COO})_2$ , are easily absorbed by human skin and detected in sweat, blood and urine after 6 h of contact with the solutions of these salts on the skin. The authors revealed that of the 5 mg of  $\text{Pb}^{2+}$  applied to the skin in an experiment, 1.3 mg had been absorbed within 24 hours.

The presence of chromium was found only in sample A, which refers to a temporary tattoo packaged together with bubble gums. In this sample, which is used mainly by children, the obtained concentration was  $0.403 \pm 0.004 \mu\text{g g}^{-1}$ . Cr was detected in samples E, F and H, however, the values were found below the LOQ. Sukuroglu et al. (2017) obtained concentrations of bioavailable

chromium between  $0.13 - 0.38 \mu\text{g g}^{-1}$  in temporary tattoos based on henna. Chromium compounds are well known for their negative health effects, and  $\text{Cr}^{6+}$  shows high toxicity and carcinogenicity (JOMOVA, VALKO 2011). In contact with the skin, chromium can cause allergic dermatitis (VAN LIERDE 2006), in addition, *in vitro* studies with human skin have shown percutaneous penetration of different chromium species, such as  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  which can cause negative health effects (GAMMELGAARD ET AL. 1992; VAN LIERDE 2006; LARESE 2007). Salts and other chromium species are prohibited in the composition of any cosmetic product according to the Brazilian resolution (ANVISA 2020). On the other hand, the permitted limit of bioavailable chromium in toys is  $60 \text{ mg kg}^{-1}$  according to the toys safety standards (ABNT 2020; ISO 2020). The chromium value obtained in the adhesive bubble gum tattoo is below the limit established by the toy's safety standards. However, considering the regulation on cosmetics that prohibits any form of free chromium, the tattoo sample is not adequate according to Brazilian resolutions.

Vanadium was found only in a sample that corresponds to the H adhesive tattoo. The found concentration was  $0.295 \pm 0.004 \mu\text{g g}^{-1}$ . The cosmetics regulation prohibits the use of divanadium pentoxide in cosmetic products (ANVISA 2020). The toys safety standards do not mention or stipulate limit values for vanadium ionic compound (ABNT 2020; ISO 2020). For boron, two samples of adhesive tattoos (F and H) presented relatively large concentrations,  $2.14 \pm 0.07$  and  $3.54 \pm 0.07 \mu\text{g g}^{-1}$ , respectively. No acceptable boron limits are reported in the toy's safety standards. On the other hand, for cosmetics, only compounds such as boric acid, borates and tetraborates are allowed with maximum permitted limits of  $0.1 - 18\%$  in the preparation of the products (ANVISA 2020). In the other samples, boron was detected, but it was not quantified because the concentrations were below the LOQ value.

Copper and strontium were detected in 100% of the temporary tattoo samples. For copper, the concentrations were in the range between  $0.037 - 0.875 \mu\text{g g}^{-1}$  while for strontium it varied between  $0.155 - 9.9 \mu\text{g g}^{-1}$ , with emphasis to the sample F which presented the highest concentration. Some compounds like lactate, nitrate and strontium polycarboxylate are prohibited by the resolution of

cosmetic products (ANVISA 2020). However, some compounds, such as chloride, acetate, peroxide and strontium hydroxide, are accepted with restrictions for use in cosmetics (ANVISA 2020). The toys safety standards do not report limit values for the presence of strontium and copper in toys (ABNT 2020; ISO 2020). Copper-based dyes, such as CI 74160 (blue), CI 74260 (green), and CI 77400 (brown), are permitted in cosmetic formulations (ANVISA 2020).

The presence of cobalt was detected in 8 of the 9 samples analyzed according to Table 3. The concentration range obtained for this element varied between  $0.003 - 1.756 \mu\text{g g}^{-1}$ , and the sample F, corresponding to the adhesive tattoo, presented the highest value. Cobalt is an element known to cause allergic reactions in contact with the skin (LARESE 2007; YOSHIHISA, SHIMIZU 2012). In fact, Kang and Lee (2006) determined by flame atomic absorption spectroscopy (FAAS) the bioavailable presence of cobalt in 15 henna tattoos. The authors found the presence of cobalt in 4 different samples with concentrations in the range of  $2.96 - 3.54 \mu\text{g g}^{-1}$ . In addition, it was found in one patient, positive allergic reactions to cobalt caused by skin exposure with henna tattoo. In another study, the concentration of bioavailable cobalt in henna tattoos was obtained in the range between 0.15 and  $0.18 \mu\text{g g}^{-1}$  (SUKUROGLU, BATTAL, BURGHAZ 2017). No limits for cobalt are mentioned in the toy's safety standards. The dye CI 77346 (green), which is cobalt-based dye, is allowed in cosmetic formulations (ANVISA 2020), while other compounds, such as cobalt chlorides, sulfates and benzosulfonates, are prohibited (ANVISA 2020).

Bioaccessible barium was found in all analyzed tattoo samples. The obtained concentrations remained in the range between  $1.779 - 11.116 \mu\text{g g}^{-1}$ . It can be seen that the adhesive tattoos directed to the child audience A, B, C, D and E, and to the young and adult audience F, G and H presented bioaccessible barium concentrations in the order of magnitude of parts per million (ppm). The maximum acceptable limit of bioaccessible barium is  $1000 \mu\text{g g}^{-1}$  according to toys safety standards (ABNT 2020; ISO 2020). In cosmetic product resolutions, barium compounds are allowed only in their insoluble form (ANVISA 2020). That is, it can be seen from Table 3 that the barium compounds present in the tattoo samples are in the soluble form as they were extracted by  $0.07 \text{ mol L}^{-1} \text{ HCl}$ .



Several dyes based on insoluble barium salts are allowed, such as CI 12085 (red) CI 15510 (orange), CI 15540 (red), CI 15630 (red), CI 15850 (red), CI 15865 (red), CI 15985 (red), CI 16255 (red), CI 17200 (red), CI 19140 (yellow), CI 42051 (blue), CI 45370 (orange), CI 45380 (red), CI 45410 (red), CI 45430 (red), CI 77120 (white) (ANVISA 2020). Barium toxicity depends on the solubility of the salts. Barium sulfate is known to be insoluble, however, impurities such as the presence of barium carbonate which is more soluble, causes the release of barium ions. In 2003 in Brazil, about 20 people died of poisoning after ingesting a pharmaceutical product containing barium sulfate (Celobar<sup>®</sup>) used as a radiological contrast agent. Experts pointed out the presence of barium carbonate (13% w/w), which is soluble in the hydrochloric acid of the stomach and releases barium ions (TUBINO, DE SIMONI 2007). Barium intoxication can cause damage to the gastrointestinal tract, respiratory and cardiac paralysis, in addition, it is related to skin allergies as long as compounds containing this metal (JOHNSON, VANTASSELL 1991; OMATA et al. 2018). According to the Agency for Toxic Substances and Disease Registry (ATSDR), there are no reliable data regarding the health effects of humans after direct exposure of the skin with barium ions (ATSDR, 2012).

In 6 samples of temporary tattoos, it was possible to evaluate the concentration of bioaccessible aluminum. The found concentration range was wide and comprised between 1.972 – 553.279  $\mu\text{g g}^{-1}$ . According to Table 3, sample E, which is aimed at children, showed an incredible 553.279  $\mu\text{g g}^{-1}$  of aluminum. Aluminum poisoning can cause anemia, bone disease and impair kidney function. Studies have shown the great capacity of the skin to absorb aluminum present in the cosmetic composition of antiperspirants that acts by blocking the secretion of sweat (PINEAU et al. 2012; DeLIGT et al. 2018). In another study, the use of scanning electron microscopy and energy dispersive X-ray microanalysis allowed the authors to report the presence of granular tumors in the skin induced by hypersensitivity to aluminum in a permanent tattoo (MCFADDEN, LYBERG, HENSTEN-PETTERSEN 1989). The toys safety standard does not mention or establish any maximum permitted limits for aluminum in toy samples (ABNT 2020; ISO 2020). Cosmetic regulations allow the use of a series of aluminum-based substances and dyes (ANVISA 2020).

In view of the obtained results, the presence of toxic elements in most of the analyzed samples is clear. The use of temporary adhesive tattoos in Brazil and in the world is a common practice mainly among children, but it also covers a part of young people and adults who are willing to change the look of the body. Considering the toys safety standard, the metal concentrations in all tattoo samples analyzed are within the required standards. On the other hand, when compared to the regulation of cosmetics, most samples, including those used by children, present metallic ions that are prohibited in the composition of cosmetics, such as Pb, Cr and especially Ba. Although Al is an accepted substance, high levels were obtained in most samples. It is well known that gastric absorption is more efficient than dermal absorption, however, it is necessary to consider that excessive dermal exposure of children and adults with the ingredients of temporary tattoos can lead to allergies and dermatitis. In addition, as has been shown, the skin is able to absorb and transport elements to the bloodstream. It is also likely that the substrate containing the temporary tattoo inks can be taken to the mouth by the children and therefore be ingested. Thus, strict quality control of this type of product is necessary because these products do not present labeled values and the element composition is unknown. The poisoning effects of these elements in certain concentrations and their absorption through skin or by oral ingestion can lead to future health-related problems.

## 5. Conclusions

In this study, the levels of bioaccessible elements were evaluated ( $^{11}\text{B}$ ,  $^{27}\text{Al}$ ,  $^{51}\text{V}$ ,  $^{53}\text{Cr}$ ,  $^{59}\text{Co}$ ,  $^{63}\text{Cu}$ ,  $^{88}\text{Sr}$ ,  $^{98}\text{Mo}$ ,  $^{138}\text{Ba}$ ,  $^{113}\text{Cd}$ ,  $^{208}\text{Pb}$ ) in temporary tattoos used by children and youth/adults. The evaluation was carried out by simply extracting the potentially toxic elements from the tattoos with a  $0.07\text{ mol}^{-1}\text{ HCl}$  solution and analyzed by ICP – MS as described by the national and international toys safety standards. The experimental analytical parameters, such as LOD, LOQ and linear range, confirmed the adequate performance of the methodology and enabled the comparison with the limits of the standards. Mo and Cd levels (<LOD) were not detected in any of the samples. On the other hand, bioaccessible barium was obtained in all 8 samples tested whose concentration varied from

2.001 – 11.116  $\mu\text{g g}^{-1}$ . Chromium was found in one of the tattoo samples used by the child audience, while lead and vanadium were found in two samples, with lead being detected in tattoo samples for children. High concentrations of aluminum were obtained mainly in children's tattoos. Cobalt, a metal known to be allergenic in contact with the skin, was detected in 7 samples. Copper and strontium were found in all tested samples. The concentrations of bioaccessible elements obtained in this study did not exceed the maximum limits established by the Brazilian toy's safety standards. However, bioaccessible species of chromium, lead, barium and cobalt have been detected which are prohibited in cosmetic products applied directly to the skin due to toxic health effects. Thus, it can be concluded that although temporary tattoos are in accordance with toy safety, some toxic elements found in tattoos are in direct contact with the skin of those using the product, especially children. It is then necessary to alert the community and regulatory bodies about the risks involving the use of temporary tattoos due to the unknown composition of the inks. In future works, the identification and determination of the concentration of dyes present in these products may bring more information about the composition of the inks of this type of product.

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