Quantitative analysis of potentially toxic metals in alginates for dental use

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ABSTRACT

Alginate is one the materials most employed in practice to make dental impressions. Substances like zinc, cadmium and lead silicate, which are included in several alginate brands with the aim of improving their physical, chemical and mechanical properties, are a source of serious concern as regards their toxicity. The most serious chronic effect of oral exposure to cadmium is renal toxicity. Assimilation of lead has deleterious effects on the gastrointestinal tract, hematopoietic system, cardiovascular system, central and peripheral nervous systems, kidneys, immune system, and reproductive system. Chronic oral exposures to zinc have resulted in hypochromic and microcyte anemia in some individuals. The aim of the present study was to measure the cadmium, lead and zinc contents of seven brands of alginate for dental use on sale in Brazil. The samples were weighed and placed in the Teflon cups of a closed-system microwave oven. *Aquar regia* (4mL concentrated HCl:HNO₃, 3:1 v/v) and hydrofluoric acid (2mL concentrated HF) were added to the samples, which were then subjected to heating. The samples were then cooled to room temperature and diluted to 25 mL in deionized water in a volumetric glass flask. The samples were diluted in duplicate and analyzed against a reagent blank. The analyses were performed in an atomic absorption flame spectrophotometer. Neither lead nor cadmium was detected. Zinc contents ranged from 0.001% to 1.36% by weight. The alginates exhibited low contents of the metals under study and gave no cause for concern regarding toxicity; even so, it is advisable to monitor potentially toxic materials continually and to analyze their plasmatic levels in the professionals working with them.

Keywords: Cadmium, lead, zinc, alginates, intoxication, irreversible hydrocolloid.

INTRODUCTION

Alginate or irreversible hydrocolloid is one the most acceptable and widely-employed materials used to make dental impressions. Substances like zinc, cadmium and lead silicate, which have been included in several brands of alginate with the aim of improving their physical, chemical and mechanical properties, are a source of serious concern as regards their toxicity (Freitas, 1980), especially now that world opinion is more aware of environmental pollution, caused mainly by heavy metals.

In earlier studies, some brands of alginate exhibited potentially toxic metals, such as cadmium, lead and zinc silicates, either isolated or combined ( Skinner & Phillips, 1960; Smith, 1969; Castagnola & Wirz, 1977, Freitas, 1980). The toxicity is increased if one takes into account the different sources of exposure to these substances and the half-life of metals like cadmium, for instance, which in human beings may remain in the tissues for a period of 10 to 30 years (Levi, 1996).

Cadmium in the human body may cause problems in the nervous (Kumar, 1996), endocrine ( Hamada et al., 1991) and immune ( Sarasua et al., 2000) systems and the salivary glands ( Chiarenza et al., 1989), apart from causing neoplasia in the lungs, prostate and testicles ( Waalkes & Oberdorter, 1990), among other disturbances.

The most serious chronic effect of oral exposure to cadmium, however, is renal toxicity. This critical effect is characterized by tubular proteinuria resulting from renal tubular dysfunction. Friberg et al. (1974) estimated that this critical effect does not occur in humans until the cadmium concentration in the renal cortex exceeds 200 µg/g.

Dietary intake of cadmium has also been implicated in osteomalacia, osteoporosis and spontaneous fractures, conditions collectively termed “itai-itai” (ouch-ouch) disease and originally documented in postmenopausal women in cadmium-contaminated areas of Japan (Goyer, 1996).

Cadmium exposure has also been implicated in hypertensive disorders, a situation that is currently not thoroughly understood or verified (ATSDR, 1993). Satarug et al. (2005) provided the first evidence for a possible link between renal tubular damage and dysfunction caused by environmental cadmium exposure and an increased risk of high blood pressure.

Several researchers have shown that alginates, in particular those manufactured in Europe, contained up to 19% lead. One such brand exhibited an excess of lead...
silicate, approximately 20% by weight. (Smith, 1969; Castagnola & Wirz, 1977; Walter, 1971; Arends et al., 1978; Price & Whitehead, 1978). Dental professionals who employed this material showed an increase in blood lead contents (Price & Whitehead, 1978).

Shiau, CY et al. (2004) investigated time to pregnancy of partners of male lead workers in order to determine the dose-response relation between male blood lead level and decreased fecundity. The results confirmed the hypothesis that a raised blood lead level affects fecundity of the partner. A blood lead level of less than 40 µg/dL may still significantly prolong time to pregnancy.

Patocka & Ceny (2003) disclosed that while the lead is a health hazard for all humans, children, particularly under the age of six, are most at risk of lead poisoning. Lead toxicity causes hematomal, gastrointestinal, and neurological dysfunction, the symptoms usually being noted at blood lead greater than 2 µM. Severe or prolonged exposure may also cause chronic nephropathy, hypertension, and reproductive impairment. Lead inhibits some enzymes, alters cellular calcium metabolism, stimulates synthesis of binding proteins in kidney, brain, and bone, and slows down nerve conduction. Acute lead poisoning is relatively infrequent and results from ingestion of acid-soluble lead compounds or inhalation of lead-containing vapors, but chronic exposure to low levels of the metal is still a public health issue, especially among some minorities and socioeconomically disadvantaged groups. Lead has been used since prehistoric times, and has become widely distributed and mobilized in the environment. Exposure to and uptake of this non-essential element have consequently increased. Both occupational and environmental exposure to lead remain a serious problem in many developing and industrializing countries and a public health problem of global dimensions.

Australian researchers demonstrated that brand-name alginates contained zinc in concentrations varying from 0.0014 to 6.05% (Freitas, 1980). Even though zinc compounds are relatively non-toxic for mammals, zinc intoxication has been reported (Fiske, 1994). Chronic oral exposure has resulted in microscopic and hypochromic anemia and neutropenia in some individuals (Prasad, 1978, Hein, 2003).

On account of the toxicity of heavy metals included in some alginates and a lack of current research on this subject, the aim in this study was to analyze quantitatively the cadmium, lead and zinc contents of alginate brands for dental use on sale in Brazil.

MATERIALS AND METHOD

Materials

The analysis focused on two different batches of seven brands of alginates commercially available in Brazil exhibited on Table 1.

Table 1 - Alginate brands, manufacturers and batch numbers.

<table>
<thead>
<tr>
<th>Brand</th>
<th>Batch 1</th>
<th>Batch 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avagel *</td>
<td>58939</td>
<td>68505</td>
</tr>
<tr>
<td>Deguprint *</td>
<td>041100</td>
<td>1047894</td>
</tr>
<tr>
<td>Hydrogum **</td>
<td>A 043B</td>
<td>1168 B</td>
</tr>
<tr>
<td>Orthoprint **</td>
<td>A 034B</td>
<td>A 1320 B</td>
</tr>
<tr>
<td>Jeltrate *</td>
<td>58880</td>
<td>68080</td>
</tr>
<tr>
<td>Jeltrate Plus *</td>
<td>68560</td>
<td>67454</td>
</tr>
<tr>
<td>Jeltrate Chromatic *</td>
<td>811</td>
<td>4206</td>
</tr>
</tbody>
</table>

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** Zhermack S. p. A. (Italy)

Method

The quantitative analysis of lead was conducted in the Chemical Analysis Laboratory of the Materials Characterization and Development Center of the Federal University of São Carlos-SP, Brasil (CCDM - Laboratório de Análise Química do Centro de Caracterização e Desenvolvimento dos Materiais da Universidade Federal de São Carlos - SP, Brasil).

The samples were digested as follows: 250mg of the material were weighed on a 0.1mg resolution analytical scale and transferred to the Teflon cups of a Millstone microwave oven, model MLS 1200 MEGA. This is a closed system, the most recommended design for elements such as cadmium, which is highly volatile when exposed to high temperatures. This method of sample digestion allows complete dissolution, with the advantage that the equipment vibrates the sample inside the sealed oven. This avoids loss of constituents as well as contamination of the sample. To this material was added 4mL of aqua regia (3HCl + 1 HNO₃) and 2mL of concentrated hydrofluoric acid (HF); then this mixture was subjected to the following thermal cycle: 2 min at 600W, 2 min at 250W and 5 min air fan cooling. Next, the samples were diluted to 25 mL with deionized water in a glass volumetric flask. Duplicate dilutions of the sample and one blank solution were analyzed.

All analyses were performed with the SPECTRA AA640 atomic absorption flame spectrophotometer, manufactured by Varian (USA).

RESULTS

Table 2 exhibits the percent contents of cadmium, lead and zinc in the alginates. Neither cadmium nor lead was detected. In batch 1 of the alginate brands Jeltrate, Jeltrate Plus, Deguprint and Jeltrate Chromatic, zinc was not detected. In batch 2 of these makes, zinc contents were in the lowest detectable range (0.002% - 0.004%). Average zinc concentrations in other brands were: Avagel, 0.30%, Hydrogum and Orthoprint 1.27%. Batch numbers for batches 1 and 2 can be seen in Table 1.
DISCUSSION

The fact that no cadmium was detected in any of the materials studied is very reassuring for the professionals who employ alginates routinely. It was not always so in the past. In the last quantitative study on cadmium, Freitas (1980) analyzed twenty-five brands of alginates on sale in Australia and found worrying values as high as 0.017% and 0.025% (by weight) of cadmium in the brands De Trey and Jeltrate, respectively.

It is well-known that cadmium has no beneficial role in any living system and there is considerable evidence of its toxic effects. It is a pollutant that causes concern worldwide, because of its high toxicity even in very low concentrations: thus, 200 $\mu$g/g is the critical concentration for the renal cortex; also, its half-life is very long, ranging from 10 to 30 years in the human body (Levi, 1996).

Lungs absorb cadmium more easily than the gastrointestinal tract. The amount of this metal absorbed by inhaling was estimated to be 30 to 60% of total absorbed Cd in human beings (Friberg et al., 1974). Once absorbed, cadmium accumulates (Exposure to cadmium leads to its accumulation) in the liver and kidneys. It may also be stored for long times in the tissues of several organs. This metal has been associated with vascular lesions such as arteriosclerosis and hypertension (Yamamoto, 2000).

Lead was also not detected in the samples analyzed, but earlier studies revealed that lead was present in alginates in high concentrations, as reported by Walter (1971), who found up to 17.5% (by weight) of lead. Such values had already been reported by Smith (1969), who described a method for lead extraction by hydrochloric acid that simulated gastric juices.

According to Soremark (1974), use of alginates with high lead contents may produce increased lead levels in the blood of professionals who manipulate alginates for dental impression. Castagnola (1974) reported that since the publication of the work of Walter (1971) and Soremark (1974), many manufacturers have reduced the lead contents in alginates and others have even changed the brand names. On the other hand, Castagnola (1974) evaluated 25 alginate brands on sale in Switzerland and noticed that lead levels in two of them were still excessive, with values of 17.0% (Ca 37) and 18.2% (Protex). Algihard S had 6.8% by weight, whereas Xantalgin and Imprex had only low percentages. The remaining 20 brands were considered to be practically lead-free, exhibiting only traces of this element, and the manufacturers were informed of the need to state the lead content very clearly on the alginate package.

Freitas (1980) tested 25 alginate brands on sale in Switzerland and reported that lead contents ranged from 0.0014 to 6.05%, with an average of 1.02%. Results of analysis revealed that some manufacturers were reducing the lead contents in their products, while at the same time increasing the zinc or fluoride contents. However, he did not report a widespread substitution of lead by other similarly dangerous metals.

Walter (1971) disclosed that the British Standards Institute (BSI) warns that the lead contents of alginates should not exceed 250 ppm and he did not find any consistent relationship between any observed physical property and the lead content of alginates.

Even though the main alterations caused by lead toxicity occur in the erythrocytes, there are reports of changes in the nervous system, kidneys and the reproductive system (Tapeau et al., 2001). Lead absorbed by the organism passes mainly to the blood, soft tissues and bones, where 95% of the lead contents of the body remain. The half-life

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cd (w/w%)</th>
<th>Cd (w/w%)</th>
<th>Pb (w/w%)</th>
<th>Pb (w/w%)</th>
<th>Zn (w/w%)</th>
<th>Zn (w/w%)</th>
</tr>
</thead>
<tbody>
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<td>Batches</td>
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<tr>
<td>Hydrogum</td>
<td>1.26</td>
<td>1.28</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Jeltrate</td>
<td></td>
<td></td>
<td></td>
<td>&lt; 0.001</td>
<td>0.004</td>
<td></td>
</tr>
<tr>
<td>Jeltrate Plus</td>
<td></td>
<td></td>
<td></td>
<td>&lt; 0.001</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Jeltrate Chromatic</td>
<td></td>
<td></td>
<td></td>
<td>&lt; 0.001</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Avagel</td>
<td>0.28</td>
<td>0.32</td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Orthoprint</td>
<td>1.36</td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Deguprint</td>
<td></td>
<td></td>
<td></td>
<td>&lt; 0.001</td>
<td>0.003</td>
<td></td>
</tr>
</tbody>
</table>

(w/w%) = percentage by weight
Quantification limit of the apparatus
Cadmium - 0.001 w/w%; Lead - 0.02 w/w%; Zinc - 0.001 w/w%
of lead in the blood varies from 25 to 36 days, while in the bones it lasts for 27 years (WHO, 1995).

Frank anemia, which is a result of reduced hemoglobin production and shortened lifespan of erythrocytes, is seen in adults at blood lead concentrations of 80 \( \mu \text{g/dL} \) and in children at concentrations of 70 \( \mu \text{g/dL} \). The anemia in lead-exposed individuals is of the hypochromic and normocytic (also microcytic) type and is accompanied by reticulocytosis with basophilic stippling. The shortened lifespan of erythrocytes is due to increased fragility of the blood cell membrane and the reduced hemoglobin production is due to decreased activities of enzymes involved in heme synthesis. Reduced heme synthesis is seen at blood lead levels of 50 \( \mu \text{g/dL} \) in adults and approximately 40 \( \mu \text{g/dL} \) in children (Goyer, 1988).

Effects on the central nervous system, subencephalopathy and damage to the peripheral nerves occur at blood levels of 30-50 \( \mu \text{g/dL} \) in adults (Ehle & Mc Kee, 1990). Desres et al. (2005) reported a neuromotor effect in children at blood lead concentrations below 10 \( \mu \text{g/dL} \).

Chronic nephropathy occurs after prolonged exposure to lead, presenting morphological and functional changes that include a reduced speed of glomerular filtration and tubular dysfunction (Selevan et al., 1985; Cooper et al., 1985).

Exposure to lead is also linked to hypertension, both in the general population and in subjects occupationally exposed to the metal (Ni, 2004), even at low blood levels such as 7 \( \mu \text{g/dL} \), and may predispose individuals to heart attack (US.EPA, 1990). Farmand et al. (2005) demonstrated that the oxidative stress caused by lead as a result of oxidant/antioxidant imbalance plays an important part in the pathogenesis of hypertension.

Research on maternal exposure to lead has provided clear evidence of its adverse effects on reproduction, particularly abortions and stillbirths (Baghurst et al., 1987). Further work has shown that pregnancy may also be affected by paternal exposure to lead (Lindbloom et al., 1991; Shiau et al., 2004). Data available about the possible genotoxic and carcinogenic action of lead are conflicting, as reported by Minozzo et al. (2004). Studies of human carcinogenicity following exposure to lead, which demonstrated the high prevalence of death by stomach and lung cancer were inadequate, since exposure to other metals confused the interpretation of the results (Selevan et al., 1985).

In the present study, it was noticed that alginate zinc concentrations ranged from values below 0.001% to 1.36%. Hydrogum and Orthoprint batches displayed the highest zinc concentrations, 1.28% and 1.36% respectively. These values were lower than those reported by Freitas (1980) who found 6.05% in the Jeltrate brand, while in the present study Jeltrate batches 1 and 2 contained less than 0.001% and 0.004%, respectively.

The main deleterious effects reported for chronic zinc intoxication in animals were anemia and pancreatitis (Broun et al., 1990). According to Fiske (1994), zinc intoxication produces deep changes in bone marrow because it leads to iron deficiency.

The manufacturers advise that the material should be shaken in the container before use, in order to obtain a uniform distribution of the particles. When the container is opened, dust particles fly into the air and so dentists and assistants may be regularly exposed to a large amount of this powder for a short time.

The long-lasting silica collected from aerosols 30 cm above alginate powder, contained 10 to 15% of fibers less than 3 \( \mu \text{m} \) thick and more than 20 \( \mu \text{m} \) long. Such dimensions concur with the fibrinogenic and carcinogenic debris of asbestos and aluminium oxide, whose biological effects depend on the particles’ size (Skinner & Phillips, 1960) and mainly on the aerodynamic median mass diameter (Salgado, 2003), rather than on their chemical and physical composition (Skinner & Phillips, 1960).

Inhaled particles over 10 \( \mu \text{m} \) are deposited preferentially in the extrathoracic parts (before the larynx), while particles of aerodynamic diameter between 5 and 10\( \mu \text{m} \) are deposited in the great airways. Particles between 2.5 and 5 \( \mu \text{m} \) are deposited in the airways near to the bronchioles in normal nasal breathing (Canner & Bakke, 1980 cited in Salgado, 2003).

Consequently, special care should be taken while preparing alginates, eg. wearing masks, keeping the working place clean and in adequate hygiene conditions and good ventilation.

The quantitative results from all batches showed low values of the analyzed metals, so that there is no cause for concern about their toxic effects. It is however advisable to constantly monitor the contents of potentially toxic materials as well as the plasma levels of toxic components in the professionals who use such products.

ACKNOWLEDGMENTS

This work was supported by CAPES.

RESUMO

Análise quantitativa de metais potencialmente tóxicos nos alginatos para uso odontológico

O alginato é um dos materiais mais utilizados na odontologia. Muitas substâncias como o zinco, cádmio, e silicato de chumbo, são adicionadas em algumas marcas de alginatos, com o objetivo de melhorar suas propriedades físicas, químicas e mecânicas, causam preocupação no se refere a toxicidade desse material. O efeito crônico mais sério da exposição oral ao cádmio é a toxicidade renal. O chumbo causa efeitos no trato gastrointestinal, sistema hematólogo, cardiovascular, sistemas nervosos central e periférico, fígado, sistemas imunológico e reprodutor. Exposições orais ao zinco resultaram em anemia microcítica hipocrômica em alguns indivíduos. O objetivo deste trabalho foi analisar quantitativamente o conteúdo de cádmio, chumbo e zinco...
Analysis of metals in alginates

de sete marcas de alginatos para uso odontológico, comercialmente disponíveis no Brasil. As amostras foram pesadas para copos de teflon de forno de microondas, sistema fechado. Adicionou-se às amostras 4 m/L de solução de água régia (3HCL + 1HNO₃) e 2 m/L de HF concentrado e submeteu-se a um programa de aquecimento. A seguir, as amostras foram resfriadas à temperatura ambiente e diluídas a 25 m/L com água desionizada em um balão volumétrico. As amostras foram solubilizadas em duplicata e uma prova em branco. As análises foram realizadas por Espectrometro de Absorção Atômica com chama. Verificou-se que o cádmio e o chumbo não foram detectados. O zinco apresentou valores que variavam de < 0,001 a 1,36% em peso. Embora os resultados quantitativos dos grupos tenham mostrado valores baixos dos metais analisados, não refletindo preocupação com seus efeitos tóxicos, seria interessante o constante monitoramento dos materiais potencialmente tóxicos, assim como a análise dos níveis plasmáticos dos profissionais que utilizam tais produtos.

Palavras-chaves: Cádmio, chumbo, zinco, intoxicação, hidrocolóide irreversível.

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