Arsenic release provided by MTA and Portland cement

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Objective. The aim of the present study was to determine the release of arsenic from 2 gray Portland cements, a white Portland cement, and 2 MTAs (ProRoot and MTA-Angelus).
Study design. The materials were manipulated and placed in plastic tubes, and the tubes were immersed in glass flasks containing water with grade reagent, pH 5.0. After 3 and 168 h, the water in which the material had been immersed was analyzed regarding the presence of arsenic by atomic absorption spectrophotometry with hydride generation.
Results. The levels of arsenic released were similar for Portland cements and MTAs, and were well below those considered to be harmful.
Conclusions. MTA and Portland cements showed very low arsenic presence. The results suggest that MTAs and Portland cements are safe for use in clinical practice in terms of the presence of arsenic.
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Mineral trioxide aggregate (MTA) has been suggested as a good material for retrograde root canal fillings and perforation repairs. The material consists of an aggregate of mineral trioxide, mainly calcium oxide.[1,2] This material shows excellent biological properties[3-9] and good marginal adaptation[10] and sealing ability.[1,11] MTA is commercially available as ProRoot (Tulsa Dental, Tulsa, Okla).

However, in 1999, Wucherpfennig and Green[12] observed that MTA presented macro- and microscopic characteristics and biological behavior similar to those of Portland cement. Estrela et al[13] found a similar composition and antimicrobial action when comparing MTA (ProRoot) and Portland cement, except that Portland cement did not contain bismuth oxide, which is the radiopacifier of ProRoot. Funteas et al,[14] in a comparative analysis, observed no significant difference between 14 elements present in Portland cement and MTA, confirming only the absence of bismuth oxide in Portland cement.

Holland et al,[8] analyzing dentin tubes filled with 2 materials, MTA (ProRoot) and Portland cement, and implanted into rat subcutaneous tissue, obtained similar results for the studied materials. As a continuation of the observation of similarity between Portland cement and ProRoot, Holland et al,[9] in the same year, compared the behavior of the 2 materials in dog dental pulp after pulpotomy and obtained similar results. Saidon et al,[15] using cell cultures and implantation of the material into bone cavities of the guinea pig mandible, confirmed the similarity between Portland cement and MTA.

Portland cement has been suspected to contain undesirable contaminant substances, thus being undesirable for use in humans. In particular, concerns exist regarding the presence of arsenic in Portland cement.

The objective of the present study was to determine the release of arsenic from 2 MTA brands, 2 gray Portland cements, and 1 white Portland cement.

MATERIAL AND METHODS

The materials tested were gray Portland cement (Votorantim Cimentos, Cubatão, Brazil), gray Portland cement Ribeirão (Companhia de cimento Ribeirão Grande, Ribeirão Grande, Brazil), white Portland cement Irajá (Cimento Rio Branco, Rio de Janeiro, Brazil), ProRoot MTA (Tulsa Dental, Tulsa, Okla), and MTA-Angelus (Odonto-Lógika, Prod. Odont., Londrina, Paraná, Brazil).

Other materials used in the present study were water (Millipore, MilliQ Plus, Bedford, Texas), reagent grade HCl (Sigma Chemical, St Louis, Mo), arsenic Titrisol (Sigma Chemical), sodium borohydride (Sigma Chemical), plastic tubes, an atomic absorption spectrophotometer (model 1476; Varian, Victoria, Australia), and a hydride generator (model 76; Varian).

The Portland cements tested were spatulated with distilled water in such a way as to obtain an ideal consistency, and the MTAs were manipulated with fluids available in the kit. On average, 0.038 g cement was placed in 5 plastic tubes (1 cm in length × 1.5 mm in

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Table I. Mean and standard deviation (SD) of arsenic release (in ppm) from each material after 3 and 168 hours

	Votoran		*Ribeirão*		*Irajá white*		*ProRoot*		*MTA-Angelus*	
	3 h	*168 h*	*3 h*	*168 h*	*3 h*	*168 h*	*3 h*	*168 h*	*3 h*	*168 h*
Mean	0.0007	0.0003	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002
SD	0.0006	0.0002	0	0	0	0	0	0	0	0

diameter). Each plastic tube containing the materials was placed in a glass flask containing 25 mL of reagent grade water. The pH of the water was previously adjusted to 5.0 with 6 mol/L HCl. Water was acidified to guarantee that arsenic was released in the form of arsenic III (trivalent salt).

The tubes were maintained in this solution for 3 h, then transferred to another glass flask containing the same solution, and maintained for an additional 168 h. After these periods, the solutions were analyzed quantitatively with an atomic absorption spectrophotometer equipped with a hydride generator. The typical parameters recommended for atomic absorption spectrophotometer and hydride generation were as follows: hydride generation—3 psi nitrogen pressure in the cylinder, nitrogen flow rate of 50 mL/min, 10 mol/L HCl at a flow rate of 1 mL/min, 1% sodium borohydride in 1% sodium hydroxide solution at a flow rate of 1 mL/min, sample flow rate of 8 mL/min, and an integration time of 1 min 30 s; atomic absorption spectrophotometer—wavelength 193.7 nm, arsenic hollow cathode lamp, slit width 0.5, and air-acetylene flame.

Standard solutions at concentrations of 0.02, 0.04, 0.08, 0.1, 0.2 and 0.4 mg/L were prepared from an operational standard solution of 1.0 mg/L arsenic trichloride in reagent grade water, pH 5.0. The concentration of the samples was calculated using the line equation obtained from the evaluation of the standards.

The results of arsenic release from each material were compared statistically at each time point by ANOVA for global comparison and by the Tukey test for pairwise comparisons.

RESULTS

Mean and standard deviation of arsenic release from the materials studied after each period are shown in Table I.

Statistical analysis revealed no significant difference ($P > .05$) in arsenic release between materials after 3 or 168 h.

DISCUSSION

Arsenic is a metallic element with atomic number 33 and was discovered in 1250. This mineral is present in world soils at different proportions, eg, at 2 mg/kg in sedimentary and igneous rocks and ranging from 0.5 to 2.5 mg/kg in other rocks. In some places, arsenic can be found as a contaminant of water and is the component of some insecticides and herbicides.[16] Popular language usually applies the name arsenic to arsenical compounds, especially arsenic trioxide.[17]

The soluble salts of arsenic are absorbed by all mucosae and sites of parenteral administration, and almost all arsenic absorbed is initially found in the erythrocyte fraction of blood. The element rapidly leaves the bloodstream and is deposited in tissues, with the main storage sites being the liver, kidneys, and lungs.[17]

The toxicity of arsenic depends on the compound, with the median lethal dose (LD_{50}) administered orally ranging from 2 to 3 mg/kg for arsenic trioxide, 20 mg/kg for calcium arsenate, 600 mg/kg for sodium arsenate, 10 to 50 mg/kg for sodium arsenate, and 100 mg/kg for Paris green.[16] In food, the presence of arsenic is permitted up to 3.5 ppm.

Portland cement results from the grinding of a product called clinker obtained by cooking a mixture of dosed and homogenized lime and clay until incipient fusion (±30% of the liquid phase) in such a way that all substances only combine with the clayish compounds, without resulting in free lime in harmful amounts after cooking.[16]

The results of the present study showed very low levels of arsenic released by the materials. The highest values were observed for Votoran Portland cement, with values of 0.007 ppm after 3 h and 0.006 ppm after 168 h. The other materials showed levels of 0.002 ppm. All of these values are well below the toxic levels.

If arsenic levels were high in Portland cements and MTAs, these materials would be unlikely to show such satisfactory responses in cell cultures and in animals,[8-10,15] because arsenical compounds bind to sulfhydryl groups, thus acting as an enzyme inhibitor and interfering with cell metabolism.[18]

Enzymes that generate cell energy in the citric acid cycle are adversely affected. This inhibitory action is based on the inactivation of pyruvate dehydrogenase by complex formation with trivalent arsenic and the subsequent inhibition of adenosine-5-triphosphate production. Trivalent arsenic replaces the 2 hydrogen atoms in the thiol group and binds to a sulfur molecule,

forming a chelate complex of dehydrolipoyl arsenite and preventing the reoxidation of dihydrolipoyl which is essential for continuous enzyme activity, thus inhibiting this major step of enzyme activity. As a result, the amount of pyruvate in blood increases, energy production is reduced, and cell damage finally occurs.[16]

Arsenic also shows a carcinogenic effect, and the theory proposing alterations in DNA repair seems to be attractive, because trivalent arsenic compounds such as arsenite can bind strongly to both dithiol and sulfhydryl groups. These protein bonds can lead to the inhibition of DNA repair, mutations at key genetic sites, or an increase in cell proliferation, which can cause subsequent mutation through the inhibition of DNA repair.[16]

Studies[13,14] analyzing the composition of Portland cement and MTA do not mention the presence of arsenic as a component, indicating that, if present, its concentration is minimal, as observed in the present study.

With respect to the method employed, the use of an acidic pH is necessary for the detection of arsenic and atomic absorption spectrophotometer with hydride generation is the adequate method for the quantification of this substance.[19] We quantified trivalent arsenic, which is the most toxic form.[16,19]

The present results show that the concentration of arsenic is low in Portland cements and MTAs and closely similar, thus demonstrating no contraindication for the use of these materials in clinical practice in terms of the presence of this chemical element.

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