Potentiometric stripping analysis of lead and cadmium leaching from dental prosthetic materials and teeth

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Abstract: Potentiometric stipping analysis (PSA) was applied for the determination of lead and cadmium leaching from dental prosthetic materials and teeth. The soluble lead content in finished dental implants was found to be much lower than that of the individual components used for their preparation. Cadmium was not detected in dental implants and materials under the defined conditions. The soluble lead and cadmium content of teeth was slightly lower than the lead and cadmium content in whole teeth (w/w) reported by other researchers, except in the case of a tooth with removed amalgam filling. The results of this work suggest that PSA may be a good method for lead and cadmium leaching studies for investigation of the biocompatibility of dental prosthetic materials.

Keywords: PSA, lead leaching, cadmium leaching, dental prosthetic materials, teeth.

INTRODUCTION

Since its introduction in 1976,[1] potentiometric stripping analysis (PSA) has proved to be a very useful technique for the determination of trace metals in various samples.[2] Although relatively simple and economic, PSA compares favourably with other methods usually employed for trace metal analysis, such as atomic absorption spectroscopy (AAS), inductively coupled plasma-atomic emission spectroscopy (IPC-AES), and X-ray fluorescence (XRF) spectroscopy.[3] One of the most common applications of PSA is for the determination of lead and cadmium in various matrices, which is very important because of the high toxicity of these metals.[2–5] Heavy metals increasingly contribute to the pollution of the environment, playing an important role in the development of human illnesses and toxic effects.

Cadmium is considered to be one of the most dangerous occupational and environmental poisons. Many of the toxic effects of cadmium result from interactions with necessary micro- and macroelements, especially with zinc, copper, iron and calcium.[6] Cadmium

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has a long biological half-life and is present in most tissues, although it is mainly accumulated in the liver and kidneys. This heavy metal is also accumulated in calcified tissues, such as bones and teeth[7] and has shown a positive association with lead levels.[8]

Lead serves no useful purpose in the human body, and its presence can cause toxic effects, regardless of the exposure pathway. Proposed mechanisms for the toxicity of lead involve fundamental biochemical processes including its ability to inhibit or mimic the actions of calcium (which can affect calcium-dependent or related processes) and interaction with proteins. It must be emphasized that lead levels at which health effects have been observed are constantly being revised, and that, for children especially, there may be no threshold for the development of detrimental effects. Lower levels of lead exposure have been shown to have many subtle health effects and for that reason it is important to interdict all lead exposures.[9]

One possible source of lead and cadmium exposure, which has received very little, if any, attention, is dental prosthetic materials used for making ceramic and metal-ceramic implants, crowns, and bridges. Considering the fact that dental implants remain in the human body for a long period of time it is necessary to check their possible harmful effects upon human health. The adverse effects of the use of dental implants may include possible chronic intoxication with heavy metals.

In this paper the results of the application of PSA for the determination of lead and cadmium leaching from dental prosthetic materials and teeth are presented.

<div align="center">EXPERIMENTAL</div>

Reagents

Glacial acetic acid (p.a. grade), hydrochloric acid (suprapur grade), standard solution of lead (1 g/dm^3, "Titrisol") standard solution of cadmium (1 g/dm^3, "Titrisol"), and standard solution of mercury (1 g/dm^3, "Titrisol") were purchased from Merck (Darmstadt, Germany) and were used as received. Working solutions were prepared by the dilution of the standard solutions with doubly distilled water.

TABLE I. Experimental conditions for the determination of lead and cadmium by PSA[10,12]

Experimental conditions	Pb	Cd
Deposition potential (V)	-0.96	-1.15
Final potential (V)	0.1	-0.15
Sample volume (cm^3)	25	25
Deposition time (s)	300	300
Resting time (s)	15	15
Stirring rate (rpm)	4000	4000

Apparatus and instrumental conditions

All analyses were performed by using a commercially available computerized stripping analyzer (Faculty of Technology, Novi Sad and Elektrouniverzal, Leskovac, Serbia and Montenegro). The electrochemical cell consisted of a processing vessel bowl, a mechanical stirrer and a three-electrode system. A glassy carbon disc working electrode was used as an inert support for the mercury film. Before electrode formation, the glassy carbon surface was swept with filter paper first soaked with acetone and then with doubly distilled water. The

mercury film was formed electrolytically from a solution containing 100 mg/dm^3 mercury(II)-ions and 0.02 mol/dm^3 hydrochloric acid, at a constant current of 50 μA for 240 s. An Ag/AgCl/KCl (3.5 mol/dm^3) electrode was used as the reference electrode and a platinum wire as the counter electrode.

Sample preparation

The samples analysed in this study were: one sample of commercially available dental ceramic (basically an alkaline alumosilicate) (Vita, Germany), two different dyes (Vita, Germany), metallic porcelain carrier (Bego, Germany), and metaloceramic crown prepared according to the procedure usually applied in dental prosthetic practice (implant 1 and 2). The sample preparation procedure was similar to the sample treatment used for lead leaching determination from pharmaceutical glassware.[10] One gram of each sample was treated with 100 cm^3 of 4 % acetic acid for 24 h ± 10 min at 22 ± 2 ºC. An aliquot of 25 cm^3 was analyzed by PSA without further dilution.

The teeth analyzed in this study were all permanent teeth of adult persons obtained from the University Dental Clinic in Niš. Both caries-free teeth extracted for orthodontic reasons and a tooth with amalgam filling were investigated. After extraction the teeth were cleaned with a polyethylene scraper and then rinsed with saline solution and finally with doubly distilled water. Before treatment with 100 cm^3 of 4 % acetic acid, the teeth were dried for 6 h at 60 ºC and then fractured to small pieces (approx. 2–3 mm) with pliers in order to increase the accessible surface. However, grinding to a powder was avoided in order to prevent complete dissolution of some sensitive teeth structures and because of the contamination risk.

The amalgam filling was mechanically removed from one tooth, which was then treated in the same way as the caries-free teeth.

PSA of lead and cadmium

A PSA modification with dissolved oxygen as the oxidizing agent was employed assuming diffusion conditions of mass transfer during the analytical step.[11] This PSA modification is the simplest one since it uses already dissolved oxygen as the oxidant thus reducing the contamination risk arising from the application of some externally added oxidizing agent. The parameters for the PSA determination of lead and cadmium in 4 % acetic acid, which also served as the supporting electrolyte, were optimized earlier[10,12] and are summarized in Table I.

Both the calibration curve and standard addition methods were used for the determination of lead and cadmium in the acetic acid extracts of dental materials and teeth. For each sample five replicate measurements were performed.

RESULTS AND DISCUSSION

First the linearity and reproducibility of the PSA analytical signal (τ_{ox} (s)) of lead, and cadmium in solution was checked. The analytical signal was found to be a linear function of the lead concentration within the range of 3–20 μg/dm^3. The dependence of the PSA analytical signal (τ_{ox} (s)) on the mass concentration of lead in solution (c_{Pb}) gave the following equation:

$$\tau_{ox} = 0.4597 + 0.0272\, c_{Pb} \tag{1}$$

For one sample (dental ceramic) a separate calibration curve was used.

The analytical signal was found to be a linear function of the cadmium concentration within the range of 0.5–5 μg/dm^3. The dependence of the PSA analytical signal (τ_{ox} (s)) on the mass concentration of cadmium is solution (c_{Cd}) gave the following equation:

$$\tau_{ox} = 0.2168 + 0.0329\, c_{Cd} \tag{2}$$

According to the high values of the correlation coefficients ($r = 0.9978$ for lead, and $r = 0.9957$ for cadmium), it can be concluded that there was a very good linearity of the PSA analytical signals within the examined concentration ranges of lead and cadmium.

The values for the soluble lead content of dental prosthetic materials are given in Table II. Cadmium was not detected in the extracts of dental materials and implants.

TABLE II. The soluble lead content of dental prosthetic materials ($n = 5$)

Sample	Calibration curve		Standard addition	
	$c_{Pb}/\mu g\ g^{-1}$	RSD/%	$c_{Pb}/\mu g\ g^{-1}$	RSD/%
Dental ceramic	104.30	1.30	105.80	2.70
Dye 1	1.26	3.30	1.31	6.10
Dye 2	1.38	8.70	1.17	8.30
Metal carrier	0.33	10.60	0.29	17.60
Finished implant 1	0.50	7.00	0.54	16.70
Finished implant 2	0.74	4.80	0.69	5.40

n – Number of determinations

From the toxicological point of view, the most interesting result was the very large difference in the soluble lead content between dental ceramic powder and finished implants. This is not unexpected since the procedure for preparing finished implants includes a high temperature firing step which makes the dental ceramic much more dense and compact and, simultaneously, less susceptible to the corrosive action of its surroundings. A subtle point to note is that an improper implant preparation procedure may greatly influence the release of lead (and probably other toxic metals) into the oral cavity besides influencing the mechanical properties of the implant.

The values for the soluble lead content of teeth are given in Table III, and the values for the soluble cadmium content of teeth are given in Table IV.

TABLE III. The soluble lead content of teeth ($n = 5$)

Sample	Calibration curve		Standard addition	
	$c_{Pb}/\mu g\ g^{-1}$	RSD/%	$c_{Pb}/\mu g\ g^{-1}$	RSD/%
Permanent tooth 1	1.89	2.70	2.33	4.20
Permanent tooth 2	1.80	3.40	1.45	5.40
Permanent tooth 3	1.99	1.40	2.61	1.30
Tooth with removed amalgam filling	7.09	11.20	9.63	17.40

n – Number of determinations

The results for the soluble lead and cadmium contents of teeth obtained in this study were slightly lower than the values obtained for the total content of lead and cadmium in whole teeth by PSA[13] or other electrochemical stripping techniques.[14] This small difference between the soluble and total content of lead and cadmium may be indicative of high lead and cadmium mobility in the surface layers of teeth. The notable exception was the

tooth with the removed amalgam filling. The much higher soluble lead and cadmium contents for this sample could tentatively assigned to the high lead and cadmium contents in dental amalgam.

TABLE IV. The soluble cadmium content of teeth ($n = 5$)

Sample	Calibration curve		Standard addition	
	c_{Pb}/µg/g	RSD/%	c_{Pb}/µg/g	RSD/%
Permanent tooth 1	0.06	1.80	0.10	4.60
Permanent tooth 2	0.11	2.10	0.19	6.80
Permanent tooth 3	ND	–	ND	–
Tooth with removed amalgam filling	0.45	4.20	0.58	15.30

n – Number of determinations; ND – not detected

For both dental prosthetic materials and teeth, better reproducibility of the determinations of the soluble lead and cadmium content was achieved by the calibration curve method. However, in both cases the PSA method proved to be applicable for the determination of very small amounts of lead and cadmium leached from dental prosthetic materials and teeth.

Numerous recent studies of elemental release from various dental materials and orthodontic appliances have not included lead and cadmium release[15–18] although the high toxicity of lead and cadmium may cause serious health hazards. It is believed that the results of this study clearly indicate that potentiometric stripping analysis may be a good method for application in lead and cadmium leaching studies during investigations of the biocompatibility of dental prosthetic materials.

ИЗВОД

ПОТЕНЦИОМЕТРИЈСКА СТРИПИНГ АНАЛИЗА ИЗЛУЖЕНОГ ОЛОВА И КАДМИЈУМА ИЗ ДЕНТАЛНИХ ПРОТЕТИЧКИХ МАТЕРИЈАЛА И ЗУБА

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За одређивање садржаја излученог олова и кадмијума из денталних протетичких материјала и зуба, примењена је потенциометријска стрипинг анализа (PSA). Много нижи садржај растворљивог олова је детектован у одговарајућим стоматолошким имплантатима у поређењу са појединачним компонентама које се користе за израду имплантата. При дефинисаним експерименталним условима, кадмијум није детектован у материјалима и финалним производима. Садржај растворљивог олова и кадмијума у зубима, одређен у овом раду, био је испод нивоа који је одређен у целим зубима у радовима других аутора, изузев у случају зуба из кога је механичким путем извађена амалгамска пломба. Резултати овог рада показују да се PSA може

веома успешно примењивати за одређивање садржаја растворљивог олова и кадмијума при испитивањима биокомпатибилности денталних протетичких материјала.

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