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Nuclear techniques to identify allergenic metals in orthodontic brackets

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The present study determines the elementary alloy composition of ten commercial brands of brackets, especially related to Ni, Cr, and Co metals, confirmed allergenic elements. The nuclear techniques applied in the analyses were X-ray fluorescence (XRF) – Centre National de la Recherche Scientifique, France (National Center of Scientific Research), and X-ray energy spectrometry (XRES), and Instrumental Neutron Activation Analysis (INAA) – CDTN/CNEN, Brazil. The XRES and XRF techniques identified Cr in the 10 samples analyzed and Ni in eight samples. The INAA technique identified the presence of Cr (14% to 19%) and Co (42% to 2400 ppm) in all samples. The semi-quantitative analysis performed by XRF also identified Co in two samples. The techniques were effective in the identification of metals in orthodontic brackets. The elements identified in this study can be considered one of the main reason for the allergic processes among the patients studied. This finding suggests that the patients should be tested for allergy and allergenic sensibility to metals prior to the prescription of orthodontic device.

Introduction

Dental literature has described an ever-increasing incidence of allergic contact reactions related to metal orthodontic brackets.

Alloys used in dentistry contain Ni, Cr, and/or Co: Ni-Cr generally contains 69% to 81% of Ni; Cr-Co less than 1% of Ni. Most of these alloys consist of Cr (60% to 65%), Co (27% to 30%), and Mo (5% to 6%).[1] PLATT et al.[2] and ELIADES and BRANTLEY[3] reported that non-precious dental alloys contain stainless steel alloys, and also 18% of Cr, 8% of Ni, and 2% to 3% of Mo, and more recently, Ti has also used in these alloys.

Monkey's epithelial cells, human gingival cells and pulmonary epithelial cells were studied to detect Ni salts cytotoxicity. The results showed that allergic reactions such as stomatitis are related to Ni, Cr and Co present in orthodontic devices.[1]

Nickel increases the resistance of steel used in orthodontic devices, however Ni alloys are directly associated to metals hypersensitivity.[2,4] MARKS and DELEO[5] and RYCROFT et al.[6] state that the contact with Ni is one of the most common causes of contact dermatitis as it can induce a type-4 hypersensitive reaction controlled by hypersensitive mechanism cells.

Studies have shown a statistically significant correlation between nickel sensitivity and intra-oral orthodontic devices.[4,7–10] This hypersensitivity manifests itself as skin eczemas, gingival enlargement, angular cheilitis, and lip desquamation.[10] Allergies caused by Ni are more recurrent in women, most probably because of costume jewelry.[4,6,11,12]

Considering the facts observed, it is necessary to carefully check the chemical elementary composition of the most commonly alloys used in orthodontic brackets.

Experimental

Ten samples of commercial brands of orthodontic brackets were selected for analysis (Table 1). These samples were analyzed using three nuclear techniques: X-ray energy spectrometry (XRES), instrumental neutron activation analysis (INAA), carried out at the Centro de Desenvolvimento de Tecnologia Nuclear/Comissão Nacional de Energia Nuclear [Center of Nuclear Development Technology National Committee of Nuclear Energy (CDTN/CNEN), Brazil] and X-ray fluorescence (XRF), carried out at the Centre National de la Recherche Scientifique [National Center of Scientific (CNRS), France].

XRES does not usually require any sample preparation, but the analysis using the SIGMAX 9050-KEVEX equipment requires sample pulverization and pressing. SIGMAX 9050-KEVEX unit includes a Si(Li) detector, source of excitation, and pre-amplifier. This system uses γ-rays of 60 kV from ^{241}Am of 0.1 Ci activity. Subsequently, qualitative analyses of the samples were obtained.

INAA technique was applied to determine the chemical composition of the samples. INAA requires no chemical processing during preparation, nor while determining the element concentration. k_0-method,[13,14] the most powerful instrumental method, was used. Comparators or monitors are used to calculate the analytical concentrations instead of standards of the analyzed elements.

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Table 1. Samples of orthodontic brackets

Abzil
Ormco
GAC-Accuarch
Dentaurum
GAC-Microarch
A-Company
Morelli G. Line
GAC-Omni
Morelli M.Edwise
Morelli Ni Free

In this study, samples were simply weighed in suitable polyethylene vials and irradiated in the 100 kW research nuclear reactor TRIGA MARK I IPR-R1, located at CDTN/CNEN. In an average thermal neutron flux of $6.6{\cdot}10^{11}$ $n{\cdot}cm^{-2}{\cdot}s^{-1}$, samples were irradiated for 5 minutes to determine the short half-life radionuclides. The samples were irradiated for 4 hours and for 8 hours, to determine medium half-life radionuclides (Au, As, Ga, and Mo) and long half-life radionuclides (Ag, Co, Cr, Fe, Sb, Se, and Zn), respectively. After irradiation and suitable decay time, gamma-spectrometry was carried out using a HPGe detector with 15% nominal efficiency. The element concentration was performed using the k_0-method.

XRF was applied using an ARL ADVANT'XP XRF spectrometer. The geometry of the instrument is optimized to provide the highest sensitivity. It is equipped with an end-window tube with a thin Be window (0.075 mm) and a 4GN Rh anode. The thin window improves the excitation efficiency of elements which are lighter than potassium. The ARL ADVANT XRF spectrometer is equipped with a 3.6 kW power supply with a maximum output of 60 kV, or optionally 70 kV, and a maximum current of 120 mA.

Results

The results of the qualitative analyses of the XREF are shown in Table 2. Results from the INAA are shown in Tables 3 and 4, while the results from the XRF analyses are shown in Tables 5, 6, and 7.

Table 2. X-ray energy spectrometry analysis of orthodontic brackets; CDTN/CNEN– X-ray Energy Spectometry Laboratory

Orthodontic bracket	Element									
Abzil	Ni	Cr	Fe	Mo	Cu	Au	Nb			Sn	Sb
Ormco	Ni	Cr	Fe	Mo						Sn	
GAC-Accuarch	Ni	Cr	Fe	Mo					Ag		
Dentaurum	Ni	Cr	Fe	Mo					Ag		
GAC-Microarch	Ni	Cr	Fe	Mo					Ag		
Morelli Ni Free		Cr	Fe	Mo							
A-Company	Ni	Cr	Fe	Mo			Nb		Ag		
Morelli G. Line		Cr	Fe	Mo				Ti	Ag		
GAC-Omni	Ni	Cr	Fe	Mo	Cu	Au	Nb		Ag		
Morelli M.Edwise	Ni	Cr	Fe						Ag		

Table 3. Instrumental neutron activation analysis (INAA) of orthodontic brackets; CDTN/CNEN – Neutron Activation Analysis Laboratory (in %)

Orthodontic bracket	Element, %					
	Cr	Co	Fe	As	Sb	Mo
Abzil	14(±1)	0.078(±5)	62(±1)		0.0013(±1)	
Ormco	16(±1)	0.18(±8)	63(±1)		0.0019(±2)	
GAC-Accuarch	17(±1)	0.17(±10)	63(±1)		0.0015(±2)	
Dentaurum	17(±1)	0.20(±10)	63(±1)	0.0098(±4)	0.0010(±2)	
GAC-Microarch	15(±1)	0.068(±10)	66(±1)			
Morelli Ni Free	18(±1)	0.0042(±2)	67(±1)		0.00006(±1)	3.6(±0.1)
A-Company	17(±1)	0.15(±10)	64(±1)	0.0039(±2)		0.17(±0.03)
Morelli G. Line	18(±1)	0.006(±3)	68(±1)			3.6(±0.1)
GAC-Omni	16(±1)	0.093(±5)	67(±1)		0.0008(±1)	
Morelli M.Edwise	17(±1)	0.096(±10)	66(±1)		00016(±2)	0.21(±0.02)

Table 4. Instrumental neutron activation analysis of orthodontic brackets; CDTN/CNEN – Neutron Activation Analysis Laboratory (in %)

Orthodontic bracket	Element, %						
	Zn	Mn	Ag	Au	Ga	Se	ni
Abzil		0.8(±0.1)		2.0(±20)		0.0870(±50)	21.03
Ormco		11(±0.1)		3.2(±20)			16.51
GAC-Accuarch		1.4(±0.1)	0.82(±0.02)	0.57(±10)			17.03
Dentaurum		1.3(±0.1)	1.4(±0.1)	0.00081(±0.1)			17.08
GAC-Microarch		0.8(±0.1)	1.2(±0.1)	1.03(±20)			15.90
Morelli Ni Free		7.0(±1)		0.000094(±0.05)	0.062(±70)		4.33
A-Company	0.25(±0.02)	1.5(±02)	1.9(±0.1)	0.00008(±0.1)			15.17
Morelli G. Line		7.0(±1)		0.00023(±0.1)	0.049(±70)		5.34
GAC-Omni		0.7(±0.1)	1.4(±0.1)	0.96(±10)			12.84
Morelli M.Edwise	0.71(±0.02)	2.8(±0.3)	0.94(±0.02)	0.00004(±0.1)	0.05(±80)		29.19

ni: Not identified.

Table 5. X-ray fluorescence analysis in orthodontic brackets; Centre National de la Recherche Scientifique SCA Solaize

Orthodontic bracket	Element, %							
	Ni	Cr	Co	Fe	Si	Mo	Mn	Ca
Abzil	5.42	14.5		67.8	1.2	1.0	1.11	1.57
Ormco	5.70	14.9		60.2	4.5	0.8	1.03	6.26
GAC-Accuarch	6.12	16.1		68.1	1.1	1.0	0.77	0.34
Dentaurum	4.82	17.5		69.2	1.1	0.1	0.85	0.47
GAC-Microarch	5.63	15.9		66.7	0.9	1.1	0.85	0.40
Morelli Ni Free		18.3		60.7	1.5	2.7	3.50	1.12
A-Company	6.56	15.3	0.12	65.5	4.8	0.7	0.47	4.88
Morelli G. Line		15.3		68.7	1.6	1.5	3.46	0.70
GAC-Omni	6.34	16.5	0.19	65.9	1.6	0.9	1.16	0.62
Morelli M.Edwise	5.38	17.2		63.9	1.7	0.2	1.53	4.56

Table 6. X-ray fluorescence analysis in orthodontic brackets; Centre National de la Recherche Scientifique SCA Solaize

Orthodontic bracket	Element, %							
	Hf	K	Mg	Cl	Ge	Ti	Cu	Pt
Abzil		0.13	0.59	0.32	0.20		0.50	
Ormco		0.13		0.30	0.11		0.24	
GAC-Accuarch	3.10	0.10		0.14	0.12		0.47	
Dentaurum	1.18		0.57	0.21	0.11		0.32	
GAC-Microarch	2.37	0.10		0.32	0.19		0.48	0.27
Morelli Ni Free		0.10	0.37	0.14	0.09		0.24	
A-Company		0.08		0.27	0.14			
Morelli G. Line	0.70			0.21	0.24	1.35	0.52	
GAC-Omni				0.21	0.15		0.45	
Morelli M.Edwise	1.02	0.10		0.20	015		0.56	

Table 7. X-ray fluorescence analysis in orthodontic brackets; Centre National de la Recherche Scientifique SCA Solaize

Orthodontic bracket	Element, %							
	Al	Sn	Pb	V	Zn	P	Sr	ni
Abzil	1.23	0.22	0.40			0.13		3.31
Ormco		0.21				0.18	0.08	5.38
GAC-Accuarch		0.27	0.34			0.15		1.46
Dentaurum		0.24	0.26			0.12	0.09	2.75
GAC-Microarch		0.22			0.26	0.07		4.09
Morelli Ni Free	0.75	0.16				0.05		10.93
A-Company		0.16		0.09		0.11		0.27
Morelli G. Line		0.23	1.40			0.23		4.47
GAC-Omni		0.19	1.33	0.04		0.18		0.9
Morelli M.Edwise		0.16	0.28		0.18	0.07		1.38

ni: Not identified.

Discussion

The techniques identified 30 elements in the samples: Ag, Al, As, Au, Ca, Cl, Co, Cr, Cu, Fe, Ga, Ge, Hf, K, Mg, Mn, Mo, Nb, Ni, P, Pb, Pt, Sb, Se, Si, Sn, Ti, V, Zn.

Ni, which is considered the most allergenic metal, was detected in all samples except two: Morelli-Nickel Free and Morelli-Golden Line, by both analyses: XRES and XRF.

Ni concentration varied from 4.82% (Dentaurum) to 6.56% (A-Company) using the fluorescence technique (Table 5). The INAA does not determine Ni, because this element does not have suitable nuclear characteristics for this technique.

Only two samples did not present Ni: Morelli-Nickel Free and Morelli-Golden Line. This result contradicts to findings from some other authors.[15,16] BERGMAN[15] observed that, in general, the brackets, threads, and bands contain Ni in varied concentrations. In stainless steel threads, Ni concentration is 8%, whereas in Ni-Ti threads, Ni concentration is 55%. In the present study, the samples showed no concentrations higher than 6.56% (A-Company) by the fluorescent analyses.

The element Cr was identified in all samples. The concentrations of this element varied from 14% to 18% by INAA (Table 4) and varied from 14.9% to 18% by the fluorescent analyses (Table 5). The samples that showed a higher Cr concentration were Morelli-Nickel Free and Morelli-Golden Line, with 18% in the INAA, and the Nickel Free sample, with 18.3% in the fluorescence technique (Table 4).

The element Co was identified in all samples by INAA (Table 3) where concentrations varied from 42±2 μg/g in the Morelli-Nickel Free to 2000±10 μg/g in the Dentaurum samples. With the fluorescence technique (Table 6), Co was identified in the samples of A-Company (0.12%) and GAC-Omni (0.19%).

SEYMOUR[6] highlighted the presence of Ni in all dental alloys and observed that even the Ni-free Co-Cr alloys show sufficient Ni to induce an allergic reaction. It could be observed in the present study that in all samples the element Cr shows a higher concentration than that of the element Ni, so much that in some samples, the concentration was three times higher. The element Co shows a very low concentration when compared to that of the elements Ni and Cr.

The INAA (Tables 3 and 4) and spectrometry (Table 2) identified a total of 12 elements, and the fluorescence (Tables 5 and 6) identified a total of 26 elements with an average of 96.2% (standard deviation of 1.9%) of the elemental composition of the analyzed samples, whereas INAA identified an average of 84.5% (standard deviation of 4.8%) of the elemental composition of the samples.

The element Fe presented the highest concentration, which varied from 60.2% (Ormco) to 69.2% (Dentaurum) by the fluorescence technique and from 62% (Abzil) to 68% (Morelli-Golden Line) by the INAA.

High toxicity was also detected in other associated metals (As, Sb, Pb, and Al). Such a finding calls for further investigation regarding the potential damage of these metals to the human being. The presence of these elements in orthodontic brackets is scarce in the dental literature.

Other metals, such as Ti, Mg, Au, Mo, Ag, Sn, Nb, Cu, Zn, etc. were also identified, however, they present little threat to toxicity and allergic reaction in dentistry.

Conclusions

The analyses through XRES, INAA, and XRF allowed the identification of the element composition present in orthodontic bracket alloys.

The results of this study show the need for epidemiological investigation and statistics, combined with clinical data and elementary analyses of orthodontic alloys, aimed at identifying the co-relation between allergic reactions and the potential allergenic elements that constitute these alloys.

References

1. H. F. HILDEBRAND, C. VERON, P. MARTIN, Biomaterials, 10 (1989) 545.
2. J. A. PLATT, A. GUZMAN, A. ZUCCARI, D. W. THORNBURG, B. F. RHODES, Y. OSHIDA et al., Am. J. Orthod. Dentofacial. Orthop., 112(1) (1997) 69.
3. T. ELIADES, G. ELIADES, W. A. BRANTLEY, Orthodontic Brackets, in: Orthodontic Materials: Scientific and Clinical Aspects, W. A. BRANTLEY, T. ELIADES (Eds), T. Thieme, New York, 2001, p. 143.
4. M. C. G. PANTUZO, E. G. ZENÓBIO, H. A. MARIGO, M. A. F. ZENÓBIO, Braz. Oral Res., 21(4) (2007) 298.
5. J. G. MARKS, V. A. DELEO Jr., Contact and Occupational Dermatology, Saint Louis, Copyright 1992.
6. R. J. G. RYCROFT, T. MENNÉ, P. J. FROSCH, J. P. LEPOITTEVIN, Textbook of Contact Dermatitis, 3rd ed., Springer, Berlin, 2001.
7. D. G. M. GREIG, Br. Dent. J., 155 (1983) 61.
8. A. L. GREPPI, D. C. SMITH, D. G. WOODSIDE, Univ. Tor. Dent. J., 3(1) (1981) 11.
9. H. KEROSUO, G. MOE, A. HENSTEN-PETTERSEN, Am. J. Orthod. Dentofacial. Orthop., 111(6) (1997) 595.
10. M. MARIGO, D. F. NOUER, M. C. S. GENELHU, L. C. C. MALAQUIAS, V. R. PIZZIOLO, A. S. V. COSTA et al., Am. J. Orthod., 124(1) (2003) 46.
11. L. BLANCO-DALMAU, H. CARRASQUILLO-ALBERTI, J. SILVA-PARRA, J. Prosthet. Dent., 52(1) (1984) 116.
12. H. KEROSUO, A. KULLAA, E. KEROSUO, L. KANERVA, A. HENSTEN-PETERSEN, Am. J. Orthod. Dentofacial. Orthop., 109(6) (1996) 148.
13. F. DE CORTE, The k_0-Standardisation Method; A Move to the Optimisation of Neutron Activation Analysis, Ph.D. Thesis, Ryksuniversiteit Gent, Faculteit Van de Wetenschappen, 1986.
14. M. A. B. C. MENEZES, C. V. S. SABINO, M. B. FRANCO, G. F. KASTNER, E. H. M. ROSSI, J. Radioanal. Nucl. Chem., 257 (2003) 627.
15. M. BERGMAN, Intern. Dent. J., 36(1) (1986) 41.
16. M. S. SEYMOUR, British Dental J., 150(4) (1981) 84.