
The metal content of generic orthodontic brackets compared with proprietary brackets

Morgan Wishney,^{*†} Tom Savage,⁺ Nicholas Proschogo,[‡] Peter Petocz[‡] and M. Ali Darendeliler^{*†}

Discipline of Orthodontics, Faculty of Dentistry, University of Sydney,^{*} Dental Hospital, Sydney South West Area Health Service,[†] School of Geoscience, The University of Sydney,⁺ School of Chemistry, The University of Sydney,[‡] Department of Statistics, Macquarie University,[‡] Sydney, Australia

Background: With minimal manufacturer information, a variety of 'generic' orthodontic brackets are available online from overseas distributors. The present study investigated the metal composition of generic orthodontic brackets compared with two well-known 'proprietary' brands.

Materials and methods: Ranging in price from AU\$2.99 to \$65, five sets of different generic brackets were obtained directly from China via eBay (G1, G2...G5). Proprietary brackets were obtained from American Orthodontics (P1) and Rocky Mountain Orthodontics (P2). The 11, 12, 13 and 14 brackets from each set were liquefied in an acid solution and subjected to trace element analysis using inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES) with respect to nickel, chromium, iron, copper, molybdenum, manganese, cadmium, mercury, arsenic and lead. Statistical analysis investigated the compositional consistency within and between each brand.

Results: The composition of P1 and P2 agreed with the manufacturer's data. The generic groups typically had low molybdenum and higher copper content and approximated either 17-4 or AISI304 stainless steels or a combination of both. No relationship between brand and consistency of manufacture could be identified. The cheapest bracket contained lead.

Conclusions: Generic and proprietary brackets showed differences in their metal composition that may have biocompatibility implications.

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Morgan Wishney: levelandalign@gmail.com; Tom Savage: tom.savage@sydney.edu.au; Nicholas Proschogo: nicholas.proschogo@sydney.edu.au; Peter Petocz: peter.petocz@mq.edu.au; M. Ali Darendeliler: ali.darendeliler@sydney.edu.au

Introduction

In many jurisdictions, orthodontic appliances are classified as 'biomedical devices' and their importation and use fall under the control of regulatory bodies such as the Food and Drug Administration (FDA) in the United States and the Therapeutic Goods Administration (TGA) in Australia. Globalisation and online shopping have posed a challenge to the regulatory bodies as it is relatively easy for individuals to import medical devices directly from overseas suppliers and circumvent administrative oversight. In recent times, dentists have drawn media attention by

importing foreign dental products in an effort save on costs.¹ However the use of imported products may expose patients to possible harm as the product safety profile is seldom established.

Dental products widely available online include orthodontic brackets. Many of these 'generic' orthodontic attachments are a fraction of the cost of locally supplied brackets and typically lack detailed information about their origin or manufacture. It has been shown that orthodontic brackets can undergo corrosion and release metal ions that may bio-accumulate in tissues over time.² Although the

resultant exposure appears to fall below systemic toxicity,³ cell culture experiments have uncovered evidence of cytotoxicity and mutagenicity.⁴ Therefore, in view of the potential for orthodontic brackets to release metals into the body, it is important to determine the composition of imported generic brackets to better understand their safety profile.

The present study sought to investigate the elemental composition of five generic brands of orthodontic brackets obtained from overseas distributors, purchased through eBay, and compare them to two well-known 'proprietary' brands obtained from their respective Australian suppliers and which conform to TGA standards. The primary aim was to quantify and compare the constituent metals, and identify any heavy metals that may be present. A secondary aim was to compare the consistency of the metal composition within each brand.

Materials and methods

Sample acquisition

To obtain the generic sample, a search for 'orthodontic brackets' was performed on eBay (www.ebay.com.au). A total of 157 results were obtained and these were sorted according to price per complete set. Non-metal brackets were not considered. The prices ranged from AU\$2.99 to AU\$65.06 per set including postage. To investigate a possible relationship between price and metal composition, a selection of five brackets was chosen to reflect the cheapest, most expensive and intermediate prices. For the experiment, these were designated as G1 (most expensive) through to G5 (least expensive). A summary of the generic brackets used is provided in Table I.

One set of the Master Series (American Orthodontics, Lot A38402, WI, USA) and one of the FLI®Twins (Rocky Mountain Orthodontics, Lot WO-426557, CO, USA) were obtained as the proprietary group

and designated as P1 and P2 respectively. All brackets were conventional twin brackets except for G1, which was a self-ligating type. All samples were kept in their original (intact and sealed) packaging until the commencement of the experiment.

Sample preparation and analysis

Four brackets in the upper right quadrant from each brand were chosen for analysis (11, 12, 13, 14), in accordance with the sample size used in previous similar investigations.⁵ Two separate analyses of each sample were undertaken using inductively coupled plasma mass spectrometry (ICP-MS) (Nexion 300X, Perkin Elmer, TX, USA) and inductively coupled plasma optical emission spectroscopy (ICP-OES) (720-ES, Agilent, CA, USA). Dual elemental analysis was used to ensure accuracy over a large concentration range since ICP-MS is better suited to elements in the parts per billion (ppb) range, whereas ICP-OES is more accurate for elements in the parts per million range (ppm).

In preparation for elemental analysis, each bracket was weighed and subsequently microwave-digested in a mixture of concentrated hydrochloric acid (HCl), nitric acid (HNO₃), phosphoric acid (H₃PO₃) and hydrofluoric acid (HF) in pressurised Teflon® vessels. A blank (control) solution without a bracket was also prepared using this protocol to control for possible contamination introduced by the acids or any of the volumetric equipment used. After cooling to room temperature, the resulting extract for each bracket was diluted to 50 mL in acid-cleaned plastic flasks. Due to the expected high levels of some elements, samples were further diluted with ultra-high purity water by a factor of 20.

The elements chosen for analysis were the principal potential constituents of stainless steel, including nickel (Ni), chromium (Cr), iron (Fe), molybdenum (Mo), magnesium (Mn) and copper (Cu),⁶ as well as heavy

Table I. A description of the generic brackets used in the experiment. Package branding relates to information found on the packaging. The price was for the complete set, which excluded molar brackets, in all brands except G1. *Price on www.ebay.com.au at 14/2/2017.

Generic bracket	Package branding	Lot number	Cost per set (AUD)*
G1	Self-ligating Bracket	None	\$65.06
G2	Azdent	None	\$9.54
G3	Orthoclassic	MO077189	\$8.34
G4	Bracket	None	\$4.25
G5	Yoka Ortho	None	\$2.99

metals that are potentially found as environmental contaminants, including cadmium (Cd), mercury (Hg), arsenic (As) and lead (Pb).⁷ The analytical instrumentation was calibrated with a calibration blank and three solutions containing the elements of interest in known concentration. From this data, the method detection limit could be calculated.

The experimental design is outlined in Figure 1.

Statistical assessment

The measurements for each metal were analysed using a general linear model with brand, and bracket within brand, as explanatory factors. This provided average concentrations of each metal for each brand. Post hoc pairwise comparisons between brands were carried out using a Bonferroni adjustment for multiple comparisons. Variance components were estimated using an analysis of variance approach with type 1 sums of squares. These gave information on the variability of brackets within brands, and the variability between replicate measurements of the same bracket (the method error). Statistical analyses were performed using Excel (Microsoft, WA, USA) and the SPSS software package (IBM SPSS version 23.0).

Results

The results produced by the ICP-MS and ICP-OES analyses were in agreement for all elements except

for Cr. The Cr results were too high for accurate determination with ICP-MS as they were outside the calibration range for the method. Titanium was excluded due to similar responses in the reagent blanks and the samples. The method limit of detection (LOD) for each element was in the sub parts per billion (ppb) range and is shown in Table II.

The metal composition of each brand by percentage weight (wt%) and the associated standard deviation across the four brackets is shown in Table III. For all reported elements, the precision (method error) was $\leq 5\%$ except for those elements present at extremely low levels (As, Hg and Pb in all samples except G5). Cadmium was below the LOD for all samples and has not been reported. Lead was below the detection limit

Table II. The method limit of detection (LOD) for each element in parts per billion (ppb). 1 ppb = 1×10^{-7} wt%. *below detection limit.

Element	LOD (ppb)
Pb	0.01
Hg	0.025
Mo	0.029
Cr	0.043
Ni	0.06
Cu	0.07
As	0.086
Cd*	0.086
Mn	0.12
Fe	0.825

Table III. Average composition weight (wt%) and relative standard deviation (RSD %) for each metal analysed content across the four brackets from each group (intergroup comparison). Missing values were measurements below the detection limit.

		Ni	Cr	Fe	Mn	Mo	Cu	Pb	As	Hg	TOTAL (%)	
Bracket Group	P1	Average wt%	8.1	14.8	70.1	0.7	1.1	2.2	1.3×10^{-4}	0.002	4.9×10^{-4}	96.9
		RSD %	7.4	3.8	2.8	14.9	16.7	37.8	90.7	25.2	20.7	
	P2	Average wt%	9.3	18.5	69.5	0.5	2.1	0.4	1×10^{-5}	0.001	1.4×10^{-4}	100.1
		RSD %	3.3	3.4	2.8	8.5	6.8	48.0	275.1	16.9	107.3	
	G1	Average wt%	5.0	16.9	73.7	0.8	0.1	3.3	1.8×10^{-4}	0.001	-	99.8
		RSD %	4.4	1.5	2.0	2.8	8.2	3.2	104.3	14.3	-	
	G2	Average wt%	4.0	16.3	74.1	0.7	0.0	4.0	-	0.001	-	99.2
		RSD %	3.4	3.0	1.6	2.1	30.9	1.9	-	26.6	-	
	G3	Average wt%	4.3	15.5	73.8	0.4	0.1	3.9	-	0.001	3.8×10^{-5}	98.0
		RSD %	3.0	3.5	2.0	6.2	4.5	2.1	-	10.1	184.0	
	G4	Average wt%	6.9	16.1	73.5	0.6	0.3	2.3	1.1×10^{-4}	0.002	6.9×10^{-5}	99.7
		RSD %	7.4	2.9	2.1	3.3	5.1	2.6	81.4	9.7	108.9	
	G5	Average wt%	10.8	18.6	70.2	0.1	0.012	0.041	0.031	0.001	2.7×10^{-5}	99.8
		RSD %	3.1	2.4	1.7	45.6	27.9	24.0	33.8	10.8	181.4	

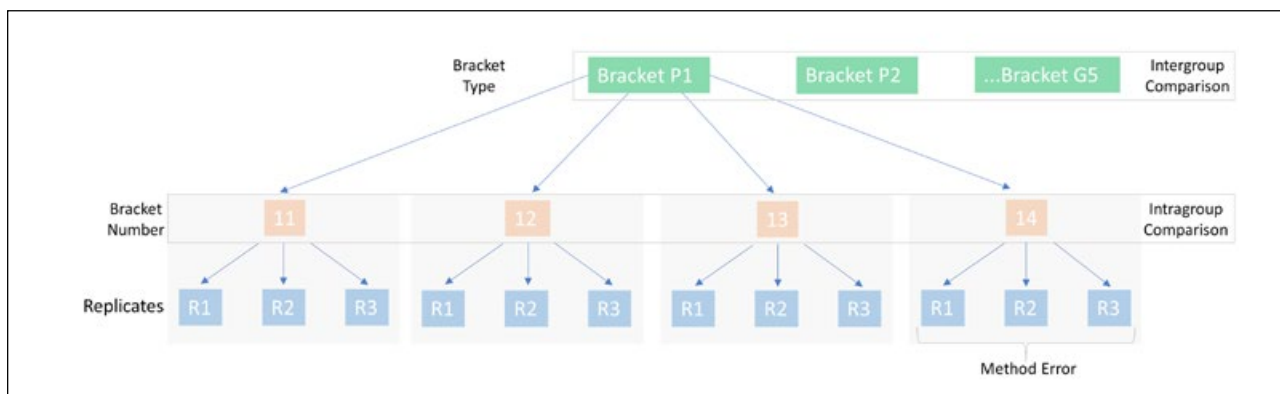


Figure 1. Overview of the experimental design. From each group, the same four brackets from the upper right quadrant were selected (11, 12, 13, 14) and individually analysed. The measurement for each of these brackets was repeated three times to determine the precision of the technique. The average of the triplicate measurements provided the metal composition for each bracket. The average and standard deviation of the measurements from the four brackets from each brand gave the composition and consistency for each group, respectively.

in G2 and G3 whilst Hg was below the detection limit in G1 and G2. It was noted that the elemental totals did not exactly add to 100%, which is consistent with the magnitude of the method error as well as the potential presence of other elements that were not quantified.

Box plots comparing the amount of each metal across the brands are shown in Figure 2. Iron was the most abundant metal and accounted for around 70% of the total metal content in each group (Figure 2c). The next most abundant element was Cr, which accounted for around 15% to 19% across the groups (Figure 2b). Nickel ranged from 4% in G2 to 11% in G5 (Figure 2a), whilst the levels of Cu spanned two orders of magnitude with 0.04% in G5 and 4% in G2 (Figure 2g). The proprietary brands (P1 and P2) showed at least one order of magnitude more Mo than the generic brackets, whilst Mn content was consistently less than 1% across the groups (Figure 2f). As noted above, Pb was either close to or below the detection limit for all groups except G5, which had 0.031% (Figure 2g). Arsenic and Hg were the least abundant elements across all brands (Figures 2e and 2i).

Statistical comparison of the metal content in each brand was conducted using pairwise post hoc comparisons (univariate ANOVA) and Bonferroni adjustment. Almost all metals were present at significantly different levels across with the groups ($p < 0.05$). All metals failed the homogeneity of variance test (Levene statistic) except for Fe ($p = 0.52$), suggesting that the variabilities across each brand are significantly different. Figure 3 presents the relative standard deviations (RSD) for the more abundant elements (Ni, Cr, Fe, Mn, Mo and Cu).

Discussion

Determining the composition of a material represents the first step in exploring its biocompatibility as well as obtaining insights into the quality of the manufacturing process. Complete and accurate quantification of the metals present in the brackets necessitates their destruction and the use of analytical methods with low detection limits such as ICP-MS. With limited exceptions,⁸ most of the comparable investigations previously undertaken have used Electron-probe microanalysis (EPM)⁹ or Energy Dispersive X-Ray Microanalysis (EDX).^{10,11} Whilst these techniques enable the identification of the different metal types that may be present in the base, wing and bracket brazing material, they are limited by relatively high detection limits of a few hundred ppm^{12,13} and confinement to localised sampling of specimens.

A variety of stainless steel grades have been used in the manufacture of orthodontic brackets¹⁰ and the choice ultimately represents a trade-off between physical properties, manufacturing complexity and biocompatibility. Stainless steel is typically graded according to the American Iron and Steel Institute (AISI) system. Stainless steel biomedical implants, as well as many orthodontic brackets,¹⁴ are manufactured from AISI 316L, which is an austenitic stainless steel characterised by 2–3% Mo which confers corrosion resistance in the presence of low levels of chlorides.¹⁵ It is accepted that 316L orthodontic brackets will corrode less in the mouth than another commonly used stainless steel termed 17-4.¹⁶ The corrosion resistance, however, may come as a trade-off with physical properties as AISI 316L steel has a lower

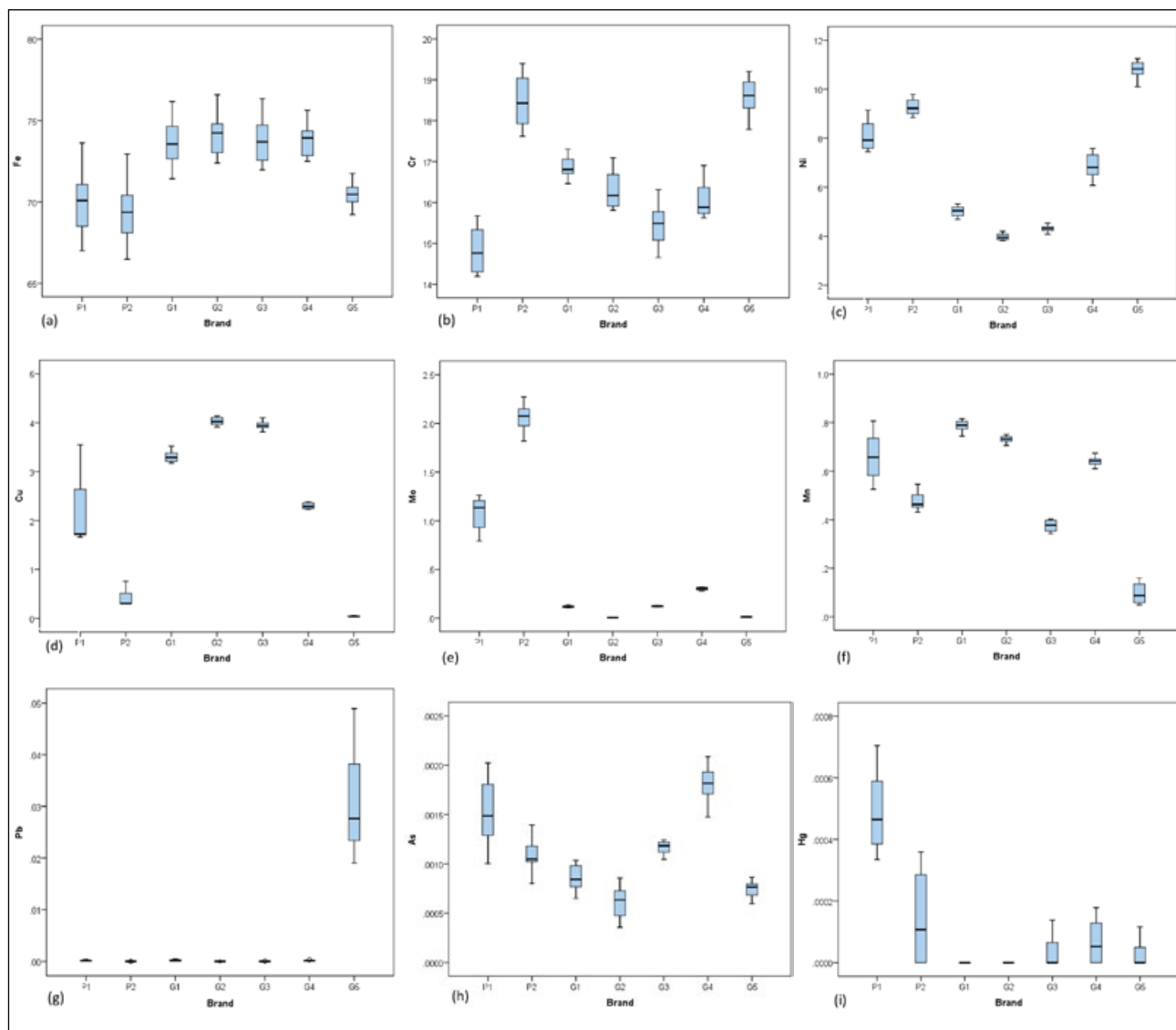


Figure 2 (a) to (i). Box plots for the metal content of each brand of bracket. All values are in wt%. Values below the detection limit are represented by lines at zero.

yield point compared with 17-4 steel. Because they are less hard, it means that clinically, brackets made from 316L may not express torque as well as those made from 17-4 steel.¹⁷

Correspondence with the manufacturers of P1 and P2 revealed that the bracket base of P1 conforms with AISI 316L whilst the wing is 17-4, and that a Ag-Cu-Ni-Pd brazing alloy is used to join the two components. However, the wing and base of P2 are injection moulded AISI 316L, joined with a proprietary brazing material consisting of 20–70% Cu. Despite analysing the total metal content of the brackets, rather than their respective components, the present data is in agreement with the ranges specified

in their respective Safety Data Sheets of the proprietary brackets.^{18,19}

With the knowledge that the Cu in P2 is due to the soldering material only, as well as the composition of the other metals used in P1,⁶ it can be determined that brazing alloy accounts for around 1% of the total mass. Assuming that the brazing alloy therefore makes a negligible contribution to the overall amount of metals present, deductions may be made about the likely composition of the other brackets. In P1, since Mo is only present in the base, it can be determined that the base is approximately 40% and the wing is 60% of the total mass.

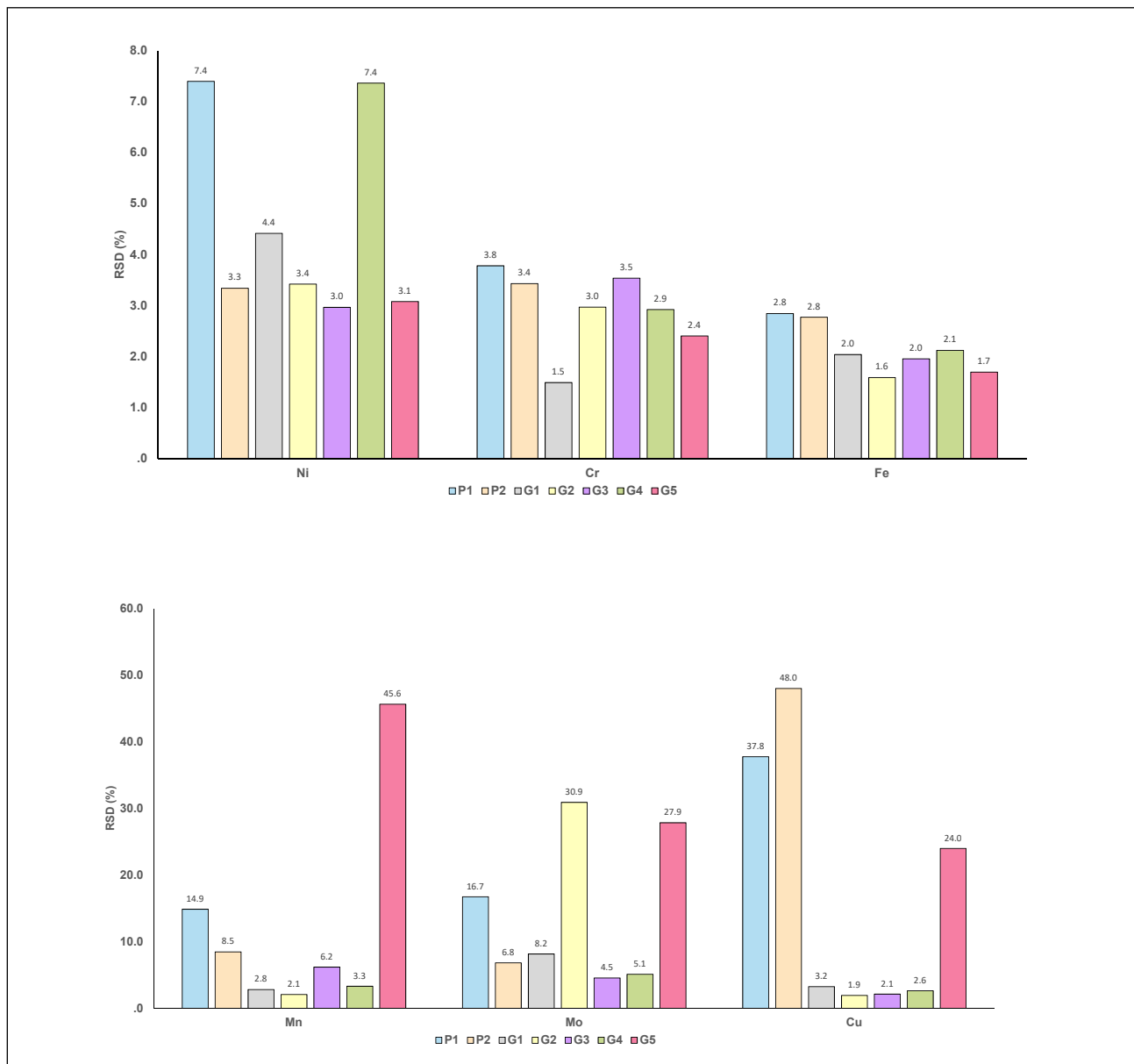


Figure 3. Comparisons of the relative standard deviations (RSD) for (a) Ni, Cr and Fe and (b) Mn, Mo and Cu across each brand of bracket (P1 to G5).

The generic brackets had little to no Mo present and are therefore unlikely to contain 316L. For G1, G2 and G3, the relatively high Cu levels are beyond those that would be expected from a brazing material and suggest that these brackets contain 17-4 stainless steel.⁶ Bracket G5, however, is predominantly Ni, Cr and Fe in proportions that are consistent with AISI 304 stainless steel.⁶ On the other hand, bracket G4 has Ni, Cr and Cu levels in between G5 and the other generic brackets as well as insufficient Mo levels to qualify it as 316L, which may suggest a mixture of AISI 304 and 17-4 steel. It is important to point out

that only inferences can be made about the types of stainless steels that may be present and verification with a different technique, such as EDX, is required. However, it is noted that both 17-4 and AISI 304 are readily available stainless steels and commonly used in orthodontic brackets.^{17,20} The present data identified no clear relationship between consistency of manufacture and cost.

It is important to appreciate that, whilst alloy composition is a significant determinant of the corrosion of stainless steel, it does not necessarily correlate with metal ion release in vitro.¹¹ Speculation

may therefore arise regarding the biocompatibility implications of the present findings. Laboratory⁴ and human²¹ investigations have shown that the metal ions released from stainless steel orthodontic brackets in solution can cause DNA damage and affect cell vitality. Whilst Ni, Fe and Cr ions are all cytotoxic due to their ability to generate free radicals,²² evidence suggests that Cu may be especially cytotoxic.²³ The present results showed that the generic brackets tended to have higher Cu or, in the case of G5, higher Ni levels. Notably, some brazing alloys contain Cd¹⁶ to improve wettability; however, this was not detected in any of the samples in the current study. The presence of ultra-trace levels of Hg across all of the groups is not surprising since trace amounts in the environment are ubiquitous.²⁴ Similarly, trace levels of As may arise from industrial or natural sources in the environment.⁷

Perhaps the most notable finding of the present study was the presence of Pb in the cheapest bracket examined, G5. In absolute terms, 0.031% Pb may be a trace amount, however, the presence of any Pb in a biomedical device is alarming since this metal has a tendency to bio-accumulate and cause multi-organ toxicity.⁷ Although there was an inability to determine how much, if any, Pb could be released into the mouth from these brackets, it is salutary to consider the hypothetical release of only 0.003% of the Pb present would result in 0.01ppm, which is the maximum allowed in drinking water.²⁵ The source of the Pb in the brackets could be in the steel itself, although the high standard deviation observed could indicate it is present in the brazing material (as seen with Cu in P1 brackets) or even the marking paint on the wings, which was found to be relatively large and non-uniform. Further studies looking at metal ion release from these brackets and cell culture responses would be the next logical investigation.

The strengths of the present study are the wide variety of elements analysed, the rigorous analytical techniques used, the low detection limits, the high precision and the fact that it is the first study to compare the metals present in proprietary and generic products. Perhaps the greatest limitation of the study is that it was only possible to infer the types of stainless steels present rather than accurately identify them. Furthermore, the elements of interest in the analysis could have been widened to include other metals that may have been present in either the bracket (e.g., Zn) or the brazing alloy²⁶ (e.g., Ag, Pd).

Conclusion

The compositional differences between the metals in proprietary and generic brackets were identified, particularly with respect to the lack of Mo in generic brackets, which may have corrosion and biocompatibility implications. The cheapest brand was distinguished by the presence of Pb, which was a concern. No relationship between brand and consistency of metal composition between brackets could be identified.

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Corresponding author

Morgan Wishney
Sydney Dental Hospital
Lvl 2 Orthodontics
2 Chalmers St,
Surry Hills, NSW
Australia 2010
Email: levelandalign@gmail.com

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