Original Article

Chromium Release from New Stainless Steel, Recycled and Nickel-free Orthodontic Brackets

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ABSTRACT

Objective: To test the hypothesis that there is no difference in the amounts of chromium released from new stainless steel brackets, recycled stainless steel brackets, and nickel-free (Ni-free) orthodontic brackets.

Materials and Methods: This in vitro study was performed using a classic batch procedure by immersion of the samples in artificial saliva at various acidities (pH 4.2, 6.5, and 7.6) over an extended time interval (t_1 = 0.25 h, t_2 = 1 h, t_3 = 24 h, t_4 = 48 h, t_5 = 120 h). The amount of chromium release was determined using an atomic absorption spectrophotometer and an inductively coupled plasma atomic emission spectrometer. Statistical analysis included a linear regression model for repeated measures, with calculation of Huber-White robust standard errors to account for intrabracket correlation of data. For post hoc comparisons the Bonferroni correction was applied.

Results: The greatest amount of chromium was released from new stainless steel brackets (0.52 $\pm$ 1.083 μg/g), whereas the recycled brackets released 0.27 $\pm$ 0.38 μg/g. The smallest release was measured with Ni-free brackets (0.21 $\pm$ 0.51 μg/g). The difference between recycled brackets and Ni-free brackets was not statistically significant ($P = .13$). For all brackets, the greatest release ($P = .000$) was measured at pH 4.2, and a significant increase was reported between all time intervals ($P < .002$).

Conclusion: The hypothesis is rejected, but the amount of chromium released in all test solutions was well below the daily dietary intake level. (*Angle Orthod.* 2008;79:361–367.)

KEY WORDS: Chromium release; Reconditioned brackets; Nickel-free brackets; Artificial saliva; Batch procedure

INTRODUCTION

Most orthodontic bands, brackets, and archwires are made of stainless steel containing 8% to 12% nickel, 17% to 22% chromium, and various proportions of manganese, copper, titanium, and iron.[1] Although all these elements potentially have adverse effects, nickel and chromium have received the most attention because of their adverse reactions.[2]

The potential health effects from exposure to nickel and chromium and their compounds have been scrutinized for more than 100 years, and it was established that these metals could cause hypersensitivity, dermatitis, and asthma. In addition, a significant carcinogenic and mutagenic potential has been demonstrated for compounds containing these metals.[3] In vitro experiments on cultured human gingival fibroblasts showed that ions released from implanted nickel-chromium alloys can cause altered cellular functions.[4]

Chromium is known to be an essential element for human beings and animals. In general, the most significant human exposure to this metal occurs through the diet, atmosphere, drinking water, jewelry, and iatrogenic uses of articles containing these metals. The average dietary intake for chromium has been estimated to be 280 μg/d.[5]

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In the oral environment, orthodontic appliances are exposed to potentially damaging physical and chemical agents. Factors such as quantity and quality of saliva, salivary pH, plaque, amount of protein in the saliva, physical and chemical properties of food and liquids, and general and oral health conditions may influence corrosion in the oral cavity.

It is known that the presence of chromium in an alloy can increase its corrosion-resistant properties. This metal is added to nickel-based alloys to improve their ability to form a protective oxide film on their surface. Generally, the alloy surface consists of a chromium oxide layer. It has been suggested that a chromium content of 16–27% will provide the optimal corrosion resistance for nickel-based alloys, and the addition of molybdenum will further enhance the corrosion resistance.[6]

The purpose of this investigation was to evaluate and compare the amounts of chromium released from three different kinds of metallic orthodontic brackets: new conventional stainless steel brackets, recycled stainless steel brackets, and nickel-free (Ni-free) brackets. This in vitro study was performed using a classic batch procedure by immersion of the samples in artificial saliva at various acidities over an extended time interval.

MATERIALS AND METHODS

Reagents

All labware was made of low-density polyethylene (LDPE; Essedi Plastik, Senago, Italy), cleaned by soaking in 1:1 nitric acid for at least 48 hours, rinsed with double-distilled water, air-dried in a hood, and stored in plastic bags. All the reagents were of analytical or pure grade to avoid contamination. Solutions were prepared with ultrapure water (Milli-Q; Millipore Corp, Billerica, Mass). Standard solutions of chromium were used to prepare daily dilute solutions for instrument calibration.

Apparatus

A PHM 84 Research pH meter (Radiometer, Copenhagen, Denmark) and a combined ORION glass electrode (Thermo Electron Corp, Waltham, Mass) were used for pH measurements.

An AA-6601G/GFA 6500 graphite furnace atomic absorption spectrophotometer (GF-AAS; Shimadzu Corp, Kyoto, Japan) was used for chromium determination when its concentration in the samples was less than 10 μg/L. Instrumental parameters and thermal programs were the same as previously reported.[7] An ICP JY2301 inductively coupled plasma atomic emission spectrometer (ICP-AES; Horiba Jobin Yvon, Longjumeau, France) was used for chromium determination when the metal concentration in the samples was higher than 10 μg/L.

Orthodontic Brackets

In total, 1080 brackets were evaluated in this study; they were divided in three groups:

- 360 new conventional Victory stainless steel brackets (slot 0.022″; MBT prescription; 3M/Unitek, Monrovia, Calif).
- 360 Victory stainless steel brackets, (slot 0.022″; MBT prescription; 3M/Unitek), recycled by Alpident (Alpident, Villarperosa (TO), Italy). The recycling process (thermal method) involved washing the brackets in a nonacid solution, followed by drying and heating to 350°C for 24 hours. The brackets were then washed twice in a nonacid solution, dried, and electropolished for 20 seconds, and finally sterilized at 250°C.[8]
- 360 Sprint Ni-free brackets (slot 0.022″; MBT prescription; Forestadent, Pforzheim, Germany).

Artificial Saliva

The artificial saliva, used as an immersion test electrolyte, is a modified Tani-Zucchi[9] with the following chemical composition: 5.3×10^{-3} mol/L KSCN, 1.5×10^{-2} mol/L $NaHCO_3$, 2×10^{-2} mol/L KC1, 1.4×10^{-3} mol/L NaH_2PO_4, 0.1 g/L CH_4N_2O (urea), and 0.1 mg/L α-amylase from human saliva. This solution was divided into three aliquots, and in each one the pH was measured potentiometrically and adjusted with a small amount of acid or base. The final pH of the three aliquots was 4.2, 6.5, and 7.6.

Batch Procedure

To simulate the release of chromium from a mouth quadrant (from central incisor to second premolar), five brackets were considered as an individual specimen (quadrant). For each of the three pH values of the artificial saliva (4.2, 6.5, and 7.6), 12 maxillary and 12 mandibular quadrants (each consisting of five brackets) were measured, according to the protocol given in Table 1. Thus, each of the three different orthodontic bracket groups ($n = 360$) was subdivided into 6 subgroups ($n = 60$), depending on the pH of the artificial saliva and the maxillary or mandibular mouth quadrant.

The specimens were rinsed with a mixture of 1:1 ethanol/acetone in an ultrasonic cleaning bath for 30 minutes and air-dried under a cleaned hood. Each group of dried brackets was weighed (analytical balance RE 1614; Sauter, Ebingen, Germany) to facilitate an estimate of the metallic mass exposed to the so-

Table 1. List of the Tested Brackets[a]

Brackets	pH
Victory (3M/Unitek)	4.2
	6.5
	7.6
Victory recycled (Alpident)	4.2
	6.5
	7.6
Sprint (Forestadent)	4.2
	6.5
	7.6

[a] For each pH, 12 maxillary and 12 mandibular quadrants were investigated. Each quadrant consisted of five brackets. In total, 1080 brackets were analyzed; n = 360 for each type of bracket.

lutions. Then, the samples were immersed in cleaned LDPE 100-mL bottles containing 10 mL of artificial saliva, and during the immersion period, they were gently stirred on a shaking plate at room temperature. This procedure allowed that all parts of the brackets were soaked, thus obtaining homogeneous solutions. A blank sample was prepared for each experiment by introducing 10 mL of artificial saliva into a cleaned LDPE 100-mL bottle.

After 0.25, 1, 24, 48, and 120 hours, 0.1 mL of the eluent was removed, diluted, and acidified at pH 2 with HNO_3. Each solution was than analyzed using the GF-AAS or ICP-AES to determine the concentrations of chromium released from the brackets.

At the end, the brackets were rinsed with ultrapure water, air-dried under a cleaned hood, and reweighed to verify if there was a loss of material during the leaching procedure.

Statistical Analysis

Data were analyzed using Stata 9 Software (Stata Corp, College Station, Tex). Descriptive statistics that included the mean, standard deviation, median, and 25th–75th percentiles were calculated for each of the groups tested. A linear regression model for repeated measures was fitted, with calculation of Huber-White robust standard errors to account for intrabracket correlation of data. A two-sided *P*-value less than .05 was considered statistically significant. For post hoc comparisons over time, the Bonferroni correction was applied.

RESULTS

Descriptive statistics for the chromium release of the different brackets are illustrated in Table 2. Chromium concentration is expressed in micrograms of metal released per gram of brackets.

The greatest amount of chromium was released from new stainless steel brackets (0.52 ± 1.083 μg/g), whereas the recycled brackets released 0.27 ± 0.38 μg/g. The smallest release was measured with Ni-free brackets (0.21 ± 0.51 μg/g; Table 2). The difference between recycled brackets and Ni-free brackets was not statistically significant ($P = .13$; Figure 1).

Table 2. Descriptive Statistics (in μg/g) of Chromium Release from the Three Different Bracket Groups

Brackets	Mean	SD	25th Percentile	Median	75th Percentile
Victory	0.52	1.08	0.08	0.14	0.37
Victory R	0.27	0.38	0.005	0.12	0.44
Sprint	0.21	0.51	0.003	0.05	0.44

For all kinds of brackets, the greatest chromium release was measured at acidic pH (pH 4.2). Those values were significantly higher ($P = .000$) than those achieved at pH 6.5 and 7.6. A statistically significant difference ($P = .00$) was also found between the release measured at pH 6.5 and 7.6 (Figures 2 through 4).

When evaluating the effect of time ($t_1 = 0.25$ hours, $t_2 = 1$ hour, $t_3 = 24$ hours, $t_4 = 48$ hours, and $t_5 = 120$ hours) on the chromium release, each kind of bracket showed a significant increase in metal release among all time intervals (t_1–t_2, t_2–t_3, t_4–t_5; $P < .002$).

The comparison between maxillary and mandibular quadrants showed no statistically significant difference ($P = .09$).

DISCUSSION

The aim of this study was to determine the chromium release from three different orthodontic brackets by immersion of the samples in artificial saliva at various acidities (pH 4.2, 6.5, and 7.6) over an extended time interval ($t_1 = 0.25$ hours, $t_2 = 1$ hour, $t_3 = 24$ hours, $t_4 = 48$ hours, and $t_5 = 120$ hours). Two pH values (6.5 and 7.6) were in the range of the human natural salivary pH, whereas the pH 4.2 was investigated to simulate a condition that only occasionally can occur when people feed on acidic foods or drinks (eg, lemon juice, coke). The present investigation showed that the greatest amount of chromium was released from new stainless steel brackets, whereas metal released from recycled brackets and from Ni-free brackets was similar.

Recycled orthodontic brackets may be used for several reasons, for example, to allow patients to reduce costs.[6] Several bracket-reconditioning methods have been introduced.[10–11] The two main commercial processes for recycling orthodontic brackets use a thermal or chemical method to remove the adhesive. The recycling procedure described in the present investigation represents the thermal method.

The adverse effects presented by the reuse of

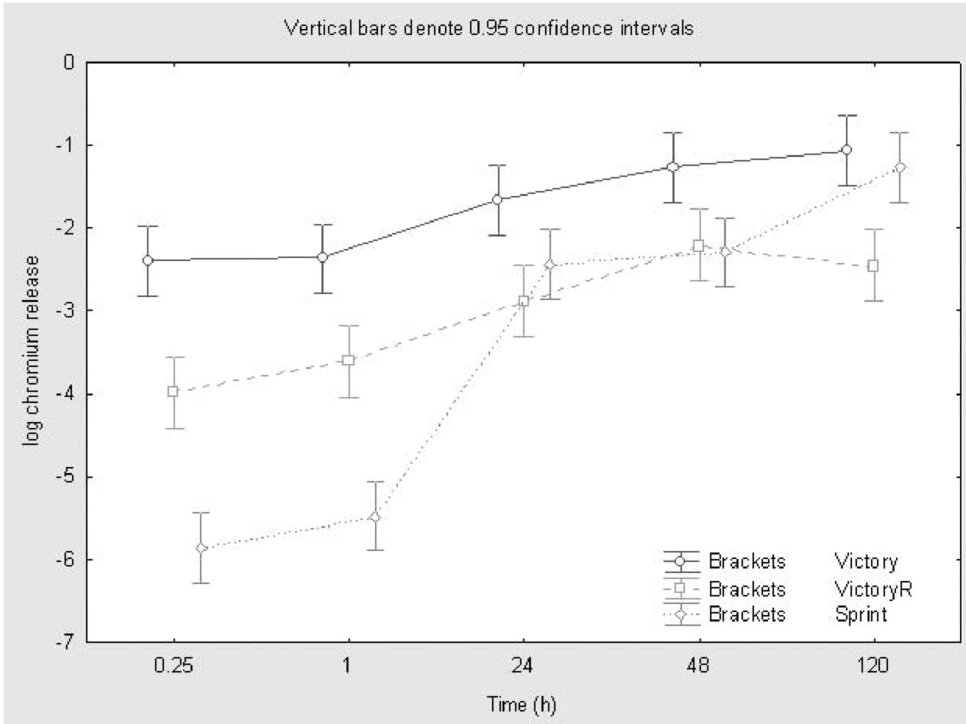

Figure 1. Chromium release from the three different bracket groups depending on immersion time. Values are expressed as logarithmic scale.

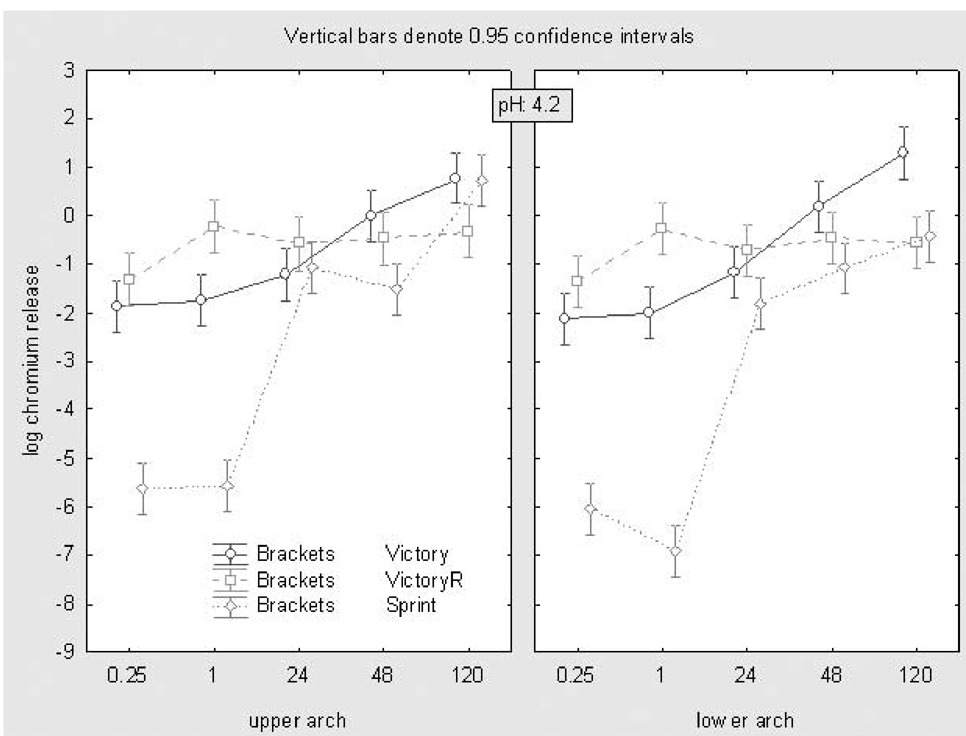

Figure 2. Chromium release at pH 4.2 from the three different bracket groups depending on immersion time and quadrant. Values are expressed as logarithmic scale.

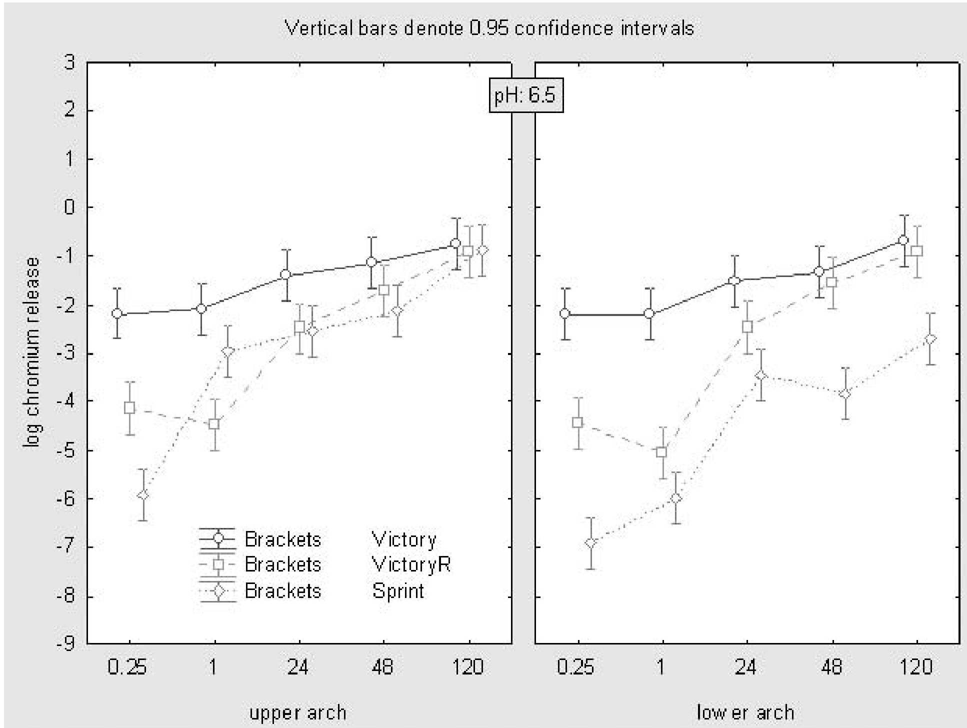

Figure 3. Chromium release at pH 6.5 from the three different bracket groups depending on immersion time and quadrant. Values are expressed as logarithmic scale.

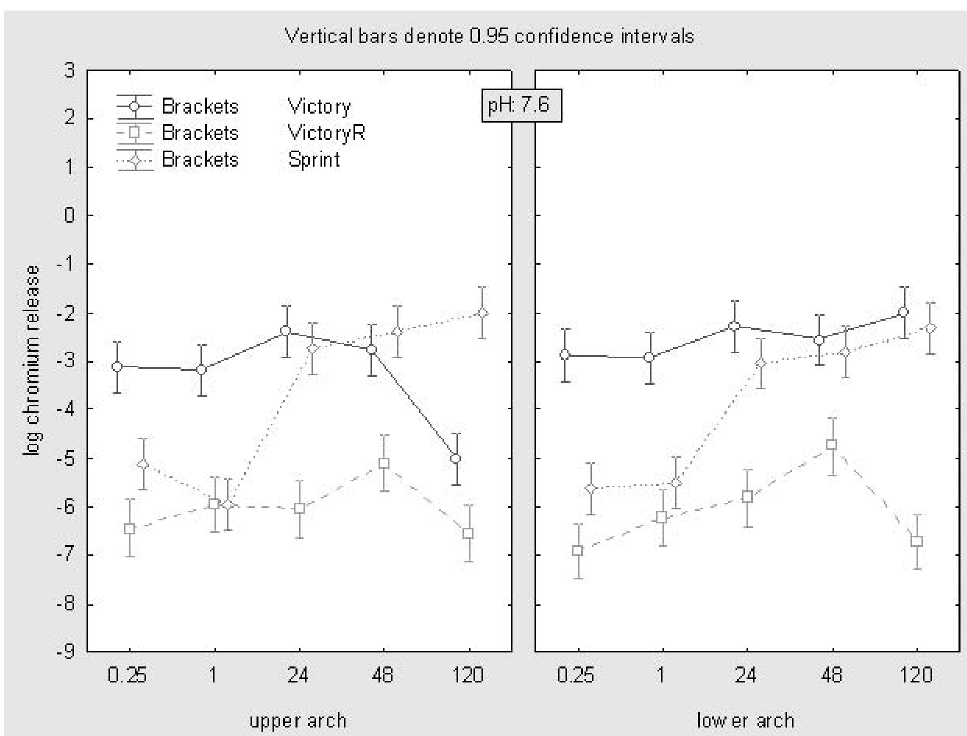

Figure 4. Chromium release at pH 7.6 from the three different bracket groups depending on immersion time and quadrant. Values are expressed as logarithmic scale.

brackets have been examined in the orthodontic literature. Aspects covered include the tensile strength of the metal, corrosion, and the propensity for the release of metal ions that can stain the teeth or induce a hypersensitive reaction in the oral tissue.[12] It is known that the effects of recycling depend on the type of reconditioning process used, the type of steel from which the bracket is manufactured, whether the bracket is milled or cast, and whether the bracket has a mesh pad or a nonmesh undercut integral pad.[8]

Resistance to corrosion can be increased by using an alloy that makes strong chemical bonds with oxygen, creating a protective film on the surface of the materials. Therefore, the content of chromium in stainless steel alloys is responsible for their resistance to corrosion, and a stable film of chromium-oxide results.[12]

The general mechanism for the corrosion and subsequent release of metal ions from stainless steel involves loss of the passive layer of chromium oxide and chromium hydroxide that forms on the surface upon contact with oxygen.[6]

Heat treatment of a metal bracket can alter the surface protection of the alloy. If the steel is heated to high temperatures, a chromium carbide precipitate is formed and, as a result, becomes susceptible to intergranular corrosion, leading to a general weakening of the structure.[13–14] This is the reason why, in general, recycled brackets show higher amounts of ion release than the new samples[15–17] even if other authors reported an increase of nickel/iron content ratio in new orthodontic brackets.[18]

In our investigation, chromium release from recycled brackets was lower than release obtained from new appliances. These results agree with those reported by Huang et al[6] in a previous investigation. A hypothesis could be that the superficial passivation, which is present in new brackets, enriches the surface in chromium. This could produce a slightly higher release of chromium, but also protects the bulk from corrosion and then from other metals release. The recycling process induces also the partial or total etching of this passive film, leaving the bulk uncovered and, as a consequence, the largest metal release except chromium. Stainless steel passivates instantaneously, be it on new or recycled brackets. When ions are released, the metals dissolve in the same ratio as in the alloy.

For all kinds of brackets, the greater release was observed at pH 4.2. These results are in agreement with those by Huang et al[19] that acidic conditions provide a reducing environment in which the stainless steel oxide film required for corrosion resistance is less stable. Similar results were found in previous studies.[20–21]

However, in the present investigation the amount of chromium release in all test solutions was below daily dietary intake level. Our results are in agreement with previous reports when compared with the amount from daily food intake.[19–22]

Generally, the chromium release increased with the immersion period for all the different brackets. Other authors reported similar findings.[5–6] Where the possible sensitivity from dissolving metal ions is concerned, the long-term corrosion resistance of alloys is more important than its initial corrosion resistance.[19]

A previous investigation[23] assessed the in vivo release of chromium into saliva by different metallic brackets. The authors concluded that the chromium ion concentrations increased immediately after placement of the appliance in the mouth for all study groups. This is in agreement with the findings of the present work.

In our study the metal brackets were immersed in artificial Tani-Zucchi saliva in static conditions. A more important factor in metal corrosion is the flow rate of saliva.[22] In the clinical setting, the brackets are mechanically activated to enable movement of the teeth. Movements of wires and friction in the brackets might result in various types of corrosion, which might further enhance the release of ions from the appliance.[6] That is a dynamic situation, as opposed to the static condition used in the present experiment. To mimic the in vivo setting of the oral cavity more closely, a continuous flow system should be employed. Thus, further studies are needed to simulate this additional variable in the analysis of ion release from brackets.

CONCLUSIONS

- The greatest amount of chromium was released from new stainless steel brackets (0.52 $\pm$ 1.08 μg/g), whereas the thermally recycled brackets released 0.27 $\pm$ 0.38 μg/g. The smallest release was measured with Ni-free brackets (0.21 $\pm$ 0.51 μg/g). The difference between recycled brackets and Ni-free brackets was not statistically significant ($P =$ .13).
- For all kinds of brackets, the greatest chromium release was measured at acidic pH (pH 4.2). Those values were significantly higher ($P =$ .000) than those achieved at pH 6.5 and 7.6. Statistically significant difference ($P =$ .00) was also found between the release measured at pH of 6.5 and 7.6.
- When evaluating the effect of time ($t_1 =$ 0.25 hours, $t_2 =$ 1 hours, $t_3 =$ 24 hours, $t_4 =$ 48 hours, $t_5 =$ 120 hours) on the chromium release, each kind of bracket showed a significant increase in metal release among all time intervals (t_1–t_2, t_2–t_3, t_4–t_5; $P <$ .002).
- The comparison between maxillary and mandibular

quadrants showed no statistically significant difference ($P = .09$).
- Chromium release from all types of brackets tested was very low when compared with daily dietary intake.

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