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Brazilian gutta-percha points. Part I: chemical composition and X-ray diffraction analysis

Cones nacionais de guta-percha. Parte I: composição química e análise por difração de raios X

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ABSTRACT: Eight nonstandardized gutta-percha points commercially available in Brazil (Konne, Tanari, Endopoint, Odous, Dentsply 0.04, Dentsply 0.06, Dentsply TP and Dentsply FM) were analysed chemically and by X-ray diffraction, and their chemical compositions were compared. The organic fraction (gutta-percha polymer and wax/resin) of the gutta-percha points was separated from the inorganic fraction (ZnO and $BaSO_4$) by dissolving them in chloroform. The gutta-percha polymer was precipitated with acetone. The inorganic fraction was analysed by elemental microanalysis. Energy-dispersive X-ray microanalysis (EDX) and X-ray diffraction were employed to identify the chemical elements and compounds (barium sulfate and zinc oxide). The barium sulfate content was calculated based on the percentage of sulfur found in the elemental microanalysis. All analyses were repeated three times. The means and standard deviations of the percentage by weight of gutta-percha in the points were: Konne (17.6 ± 0.30), Tanari (15.2 ± 0.30), Endopoint (16.7 ± 0.23), Odous (18.8 ± 0.20), Dentsply 0.04 (15.7 ± 0.17), Dentsply 0.06 (16.6 ± 0.17), Dentsply TP (21.6 ± 0.15) and Dentsply FM (16.3 ± 0.23). The means and standard deviations of the zinc oxide content were: Konne (79.9 ± 0.10), Tanari (81.9 ± 0.07), Endopoint (81.3 ± 0.40), Odous (79.7 ± 0.26), Dentsply 0.04 (77.9 ± 0.03), Dentsply 0.06 (78.2 ± 0.07), Dentsply TP (69.8 ± 0.19) and Dentsply FM (72.6 ± 0.70). The method utilized was appropriate to quantify gutta-percha, wax/resin, zinc oxide and barium sulfate. Cone brands without barium sulfate were found. An unusual high wax/resin percentage was detected in Dentsply FM ($p = 0.0003$). Dentsply TP showed the highest gutta-percha percentage.

DESCRIPTORS: Gutta-percha; Electron probe microanalysis; X-ray diffraction.

RESUMO: Oito marcas de cones de guta-percha disponíveis no mercado brasileiro (Konne, Tanari, Endopoint, Odous, Dentsply 0.04, Dentsply 0.06, Dentsply TP e Dentsply FM) foram analisadas quimicamente e por difração de raios X; e suas composições, comparadas. A porção orgânica (guta-percha e ceras/resinas) foi separada da porção inorgânica (ZnO e $BaSO_4$) através da dissolução em clorofórmio. O polímero guta-percha foi precipitado com adição de acetona. A fração inorgânica foi analisada por microanálise elementar. Microanálise por energia dispersiva de raios X (EDX) e difração por raios X foram utilizadas para identificar os elementos e compostos ($BaSO_4$ e ZnO). A quantidade de sulfato de bário foi calculada através da porcentagem de enxofre detectada na microanálise elementar. Todas as análises foram executadas em triplicata. As médias e os desvios padrões das porcentagens em peso de guta-percha nas diferentes marcas analisadas foram: Konne (17,6 ± 0,30), Tanari (15,2 ± 0,30), Endopoint (16,7 ± 0,23), Odous (18,8 ± 0,20), Dentsply 0.04 (15,7 ± 0,17), Dentsply 0.06 (16,6 ± 0,17), Dentsply TP (21,6 ± 0,15) e Dentsply FM (16,3 ± 0,23). As médias e os desvios padrões das quantidades de óxido de zinco encontrados foram: Konne (79,9 ± 0,10), Tanari (81,9 ± 0,07), Endopoint (81,3 ± 0,40), Odous (79,7 ± 0,26), Dentsply 0.04 (77,9 ± 0,03), Dentsply 0.06 (78,2 ± 0,07), Dentsply TP (69,8 ± 0,19) e Dentsply FM (72,6 ± 0,70). O método utilizado foi apropriado para quantificação dos componentes guta-percha, ceras/resinas, óxido de zinco e sulfato de bário. Foram encontrados cones que não apresentaram sulfato de bário na composição. Foi detectada uma concentração exagerada de ceras/resinas no cone Dentsply FM ($p = 0,0003$). O cone Dentsply TP apresentou a maior porcentagem de guta-percha.

DESCRITORES: Guta-percha; Microanálise por raios X; Difração de raios X.

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INTRODUCTION

The final objective of endodontic procedures should be total cleaning, shaping and obturation of the root canal system[13,14]. According to Schilder[13] (1967), Gutmann, Witherspoon[6] (2002) and de Deus *et al.*[3] (2002), gutta-percha is considered the best material for root canal filling, regardless of the technique applied.

Gutta-percha polymer is a *trans*-1,4-polyisoprene, obtained from the coagulation of latex produced by trees of the *Sapotaceae* family and mainly derived from *Palaquium gutta* bail[6,9]. It was first introduced to the Royal Asiatic Society of England in 1843 by Sir Jose d'Almeida and was introduced into dentistry in the late 1800s. It occurs naturally and is harder, more brittle, and less elastic than natural rubber[15].

Gutta-percha is rigid at room temperature, becomes pliable at 25-30°C, softens at 60°C, and melts at 100°C with partial decomposition[1]. It is a hydrocarbon and is soluble in chloroform, eucalyptone, carbon disulphide, benzene and xylem. When exposed to light and air, gutta-percha undergoes degrading oxidation and becomes brittle[4]. The crystalline phase appears in two forms: 1) the alpha phase and 2) the beta phase. The forms differ only in the molecular repeat distance and single carbon-bond configuration[13,14,15].

Brittleness, stiffness, tensile strength, and radiopacity have been shown to depend primarily on the proportions of organic (gutta-percha polymer and wax/resins) and inorganic (zinc oxide and metal sulfates) components[2]. Zinc oxide is also responsible for the antibacterial activity of gutta-percha points[11]. The particular percentages of components vary according to the manufacturer. It is evident that since the cones differ in their composition, they may differ in their physical properties and even in their biological effect[17].

Friedman *et al.*[4] (1977) have found that the composition of the points is approximately 18 to 22% in gutta-percha polymer, 59 to 75% in zinc oxide and 1.1 to 17.2% in barium sulfate. Marciano, Michailesco[8] (1989) have reported lower ZnO content (36.6%) and higher $BaSO_4$ content (31.2%). Recently, Gurgel-Filho *et al.*[5] (2003) reported the absence of barium sulfate in the composition of three dental gutta-percha brands manufactured in Brazil (Konne, Tanari and Dentsply FM), which had never been reported in the literature.

The purpose of the present study was to determine the chemical composition of eight Brazilian commercially available nonstandardized gutta-percha cones: Konne, Tanari, Endopoint, Odous, Dentsply 0.04, Dentsply 0.06, Dentsply TP and Dentsply FM.

MATERIAL AND METHODS

The gutta-percha contained in eight different dental gutta-percha cones commercially available was analysed. Gutta-percha brands, expiration date and lot number were, respectively: Konne (Belo Horizonte, Brazil), Dec/2005 (no lot number); Tanari (Macapuru, Brazil), Oct/2007 (001003G), Endopoint (Paraíba do Sul, Brazil), Jan/2007 (005); Odous (Belo Horizonte, Brazil), May/2005 (05); Dentsply 0.04 (Petrópolis, Brazil), Nov/2006 (10701); Dentsply 0.06 (Petrópolis, Brazil), Nov/2006 (11106); Dentsply TP (Petrópolis, Brazil), Nov/2006 (8799); Dentsply FM (Petrópolis, Brazil), Jun/2006 (2828). All samples were analysed before the expiration dates established by the manufacturers.

In order to separate gutta-percha point components, the procedure described by Gurgel-Filho *et al.*[5] (2003) was followed: 1 g of commercial gutta-percha points was dissolved in 10 ml of chloroform (Synth, Diadema, SP, Brazil) (24 hours/300 rpm). The resulting solution was then centrifuged (Andreas Hettich GmbH & Co. KG, Tuttlingen, Germany) for 15 minutes at 6,000 rpm. This permits the separation of a solid phase (inorganic components – zinc oxide and metal sulfates) from the supernatant (organic components – gutta-percha, resins and waxes) remaining in the solution.

Since gutta-percha has a low dissolving rate and, in general, undergoes a slow dissolving process[16], the samples were placed in contact with 10 ml of chloroform for 24 h prior to centrifuging. The gutta-percha polymer, insoluble in acetone (Synth, Diadema, SP, Brazil), was coagulated by adding this solvent and weighing after total solvent evaporation. The mass of soluble material in acetone (wax/resin) was determined after the solvent's evaporation.

The organic fraction (gutta-percha polymer and wax/resin) was determined using the procedure described by Gurgel-Filho *et al.*[5] (2003). The barium sulfate content was determined according to the sulfur percentage (elemental microanalysis) obtained, using equation 1. The zinc oxide content was calculated using equation 2 when the specimen contained sulfur, or by equation 3 if it did not.

$$(1)\ BaSO_4\% = S\% \times (BaSO_4 \text{ molar mass})/(S \text{ atomic mass}) = S\% \times 7.28$$

$$(2)\ ZnO\% = 100\% - (\text{gutta-percha polymer}\% + \text{wax/resin}\% + BaSO_4\%)$$

$$(3)\ ZnO\% = 100\% - (\text{gutta-percha polymer}\% + \text{wax/resin}\%)$$

Energy-dispersive X-ray microanalysis (EDX) was utilised to establish qualitatively the presence of chemical elements in the samples. The analysis was carried out on sections of all eight brands mounted on aluminum stubs (Carlo Erba, Rodano, Italy) and carbon coated. A DSM-940A scanning electron microscope (Carl Zeiss, Jena, Germany) with Link System 3.34 Series 300 (Koninklijke Philips Electronics N.V., Eindhoven, Netherlands) with Si(Li) detector was used for the analysis. The sections were analysed at 1,000 X magnification.

The apparatus used for the X-ray diffraction analysis was a Philips MDR Pro (Eindhoven, Holland) operating at 40 kV and 20 mA, using a copper tube. The equipment was calibrated to produce 10^2 cps. Each specimen was observed separately and compared with the X-ray diffraction pattern of zinc oxide and barium sulfate to verify the presence of these two compounds.

The quantitative determination of carbon, hydrogen, nitrogen and sulfur chemical elements in the samples was carried out in a CHNS/O Carlo Erba microanalyser, model 1110 (Rodano, Italy) with combustion at 1,000°C in oxygen atmosphere. A thermal conductivity detector (Carlo Erba, Rodano, Italy) was employed. All the analyses were repeated three times for each material.

RESULTS

The results of the chemical assay according to the organic and inorganic fractions of the eight nonstandardized gutta-percha cones are shown in Table 1. The data obtained were statistically evaluated using the Kruskal-Wallis test (SPSS 12.0, SPSS Inc., Chicago, USA) at the significance level of $p = 0.05$.

The data obtained for gutta-percha percentage revealed values varying between 15.2% and 21.6%. There was no statistical difference between Konne, Endopoint, Odous and Dentsply 0.06 ($p = 0.2987$); and Tanari and Dentsply 0.04 ($p = 0.6033$). Dentsply TP showed the highest percentage of gutta-percha followed by i) Konne, Endopoint, Odous and Dentsply 0.06 ($p = 0.0094$); ii) Dentsply FM ($p = 0.0377$); iii) Tanari and Dentsply 0.04 ($p = 0.0003$).

Dentsply FM showed the highest percentage of wax/resin (10.4%) ($p = 0.0003$). Between the other gutta-percha cones, no statistically differences were found for wax/resin percentage.

The qualitative presence of $BaSO_4$ and ZnO was determined by means of X-ray diffraction, according to the presence and absence of $BaSO_4$, respectively. The energy-dispersive X-ray microanalysis showed all the elements present, such as barium, in all gutta-percha cones studied.

Elemental microanalysis showed the presence of carbon, hydrogen and nitrogen in all specimens. This analysis quantifies these components. The final composition of the eight gutta-percha cones is shown in Table 2. In Table 3, the data obtained from the present study are compared with results of Friedman *et al.*[4] (1977), Marciano, Michailesco[8] (1989) and Gurgel-Filho *et al.*[5] (2003).

DISCUSSION

The root canal system contains lateral canals that communicate with the periodontal tissue in the furcation or at the apex[2]. Every exit from the root canal is to be regarded as a possible route for decomposition products where there is a necrotic pulp[7]. The tendency of apical/periodontal lesions of endodontic origin to heal depends upon a number of factors, including complete filling of the root canal system in three dimensions. An ideal technique to accomplish this was presented in 1967 by Schilder[13], showing that it is possible to produce a three-dimensional bioinert root canal filling by heating a gutta-percha point within the canal[13].

Gutta-percha cones are commercially available and are composed of barium sulfate, zinc oxide, waxes, resins and gutta-percha[8,10]. These different components are combined in various quantities for the different commercial brands[10].

The constituents of eight Brazilian gutta-percha cones were identified by qualitative chemical analysis and their relative percentages were determined. The chemical structures of resins and/or waxes presented were not analysed. The results obtained from these experiments showed

TABLE 1 - Mean and standard deviation (SD) of percentage weights of organic and inorganic fractions after chemical assay of gutta-percha cones.

Gutta-percha cone	Organic fraction (mean ± SD)	Inorganic fraction (mean ± SD)
Konne	20.1 ± 0.30	79.9 ± 0.10
Tanari	18.1 ± 0.30	81.9 ± 0.07
Endopoint	18.7 ± 0.23	81.3 ± 0.40
Odous	20.3 ± 0.20	79.7 ± 0.26
Dentsply 0.04	18.8 ± 0.17	81.2 ± 0.03
Dentsply 0.06	19.0 ± 0.17	81.1 ± 0.07
Dentsply TP	25.6 ± 0.15	74.4 ± 0.19
Dentsply FM	26.7 ± 0.53	73.3 ± 0.70

TABLE 2 - Composition of some Brazilian gutta-percha cones (%).

Gutta-percha cone	Gutta-percha (mean ± SD)	Wax / Resin (mean ± SD)	Barium Sulfate (mean ± SD)	Zinc oxide (mean ± SD)
Konne	17.6 ± 0.30	2.5 ± 0.40	0	79.9 ± 0.10
Tanari	15.2 ± 0.30	2.9 ± 0.13	0	81.9 ± 0.07
Endopoint	16.7 ± 0.23	2.0 ± 0.37	0	81.3 ± 0.40
Odous	18.8 ± 0.20	1.5 ± 0.13	0	79.7 ± 0.26
Dentsply 0.04	15.7 ± 0.17	3.1 ± 0.20	3.3 ± 0.2	77.9 ± 0.03
Dentsply 0.06	16.6 ± 0.17	2.4 ± 0.10	2.8 ± 0.6	78.2 ± 0.07
Dentsply TP	21.6 ± 0.15	4.0 ± 0.36	4.6 ± 0.3	69.8 ± 0.19
Dentsply FM	16.3 ± 0.23	10.4 ± 0.11	1.4 ± 0.0	72.6 ± 0.70

TABLE 3 - Comparison between ranges of component percentage of gutta-percha cones made by different authors using different brands.

Gutta-percha	Wax/resin	Organic fraction	$BaSO_4$	ZnO	Inorganic fraction	Reference
18.9 – 21.8	1.0 – 4.1	22.7 – 23.8	1.1 – 17.3	59.1 – 75.3	75.3 – 76.9	Friedman *et al.*[4] (1977)[a]
–	–	17.7 – 45.7	3.2 – 31.2	36.6 – 74.6	54.3 – 82.3	Marciano, Michailesco[8] (1989)[b]
14.5 – 20.4	1.2 – 3.1	15.7 – 22.4	0.0 – 11.4	66.5 – 84.3	77.6 – 84.3	Gurgel-Filho *et al.*[5] (2003)[c]
15.2 – 21.6	1.5 – 10.4	18.1 – 26.7	0.0 – 4.6	69.8 – 81.9	73.3 – 81.9	This work[d]

[a]Five commercial brands were studied (Premier, Mynol, Indian Head, Dent-O-Lux, Tempryte); [b]Ten commercial brands were studied (Hygienic, Mynol, Roeko, Detrey, Becht, Septodont, Medico-Dentaire, IFKER, SPAD, Endoset); [c]Five commercial brands were studied (Analytic, Konne, Obtura, Tanari, Dentsply); [d]Eight commercial brands were studied (Konne, Tanari, Endopoint, Odous, Dentsply 0.04, Dentsply 0.06, Dentsply TP and Dentsply FM).

heterogeneity among the different brands of dental gutta-percha cones.

X-ray microanalysis and elemental microanalysis provided an overview of the elemental composition of the gutta-percha points. Elemental microanalysis is the most popular technique to quantify Sulfur content. While these methods, as used in the present study, provide qualitative data, assumptions about the quantitative data may be made based on the results. Zinc was universally present in large amounts, reflecting the fact that zinc oxide is the main ingredient in these points, according to many studies[4,5,6,8].

The composition of Tanari points determined here (gutta-percha 15.2%, wax/resin 2.9%, zinc oxide 81.9%) is very similar to that reported by Gurgel-Filho *et al.*[5] (2003): 15.6; 2.4 and 82.0% respectively. This indicates that no composition change was introduced by the manufacturer recently. However, the composition of Konne and Dentsply points is different from previous analysis. The content of gutta-percha in Konne points reported in the literature, for example, was 18.9 ± 0.30%, different from that determined here (17.6 ± 0.30%). This confirms the change in Konne point composition. Analysis of Dentsply FM point composition showed that barium sulfate is indeed present in its chemical composition.

The range of components in gutta-percha points, according to Gurgel-Filho *et al.*[5] (2003), Friedman *et al.*[4] (1977), and Marciano, Michailesco[8] (1989), is 14.5 to 21.8% in gutta-percha, 1.0 to 4.1% in wax/resin, 0 to 31.2% in barium sulfate and 36.6 to 84.3% in zinc oxide (Table 3). The content of gutta-percha, $BaSO_4$, and ZnO in the Brazilian brands, determined in the present work, is in the range reported by said authors. The greatest difference observed was in the wax/resin content observed for Dentsply FM points (10.4%), much higher than the highest value determined in previous analyses (4.1%). The unusual absence of $BaSO_4$, reported by Gurgel-Filho *et al.*[5] (2003), in some Brazilian brands is now observed in four brands (Konne, Tanari, Endopoint and Odous). This absence is no longer unusual.

In the early 1970s, the ideal semisolid root canal filling material should possess the proper combination of flexibility and rigidity to permit the negotiation of almost any root canal, regardless of its anatomic characteristics[4]. Later, advanced methods based on three-dimensional data acquisition became available for the description of canal geometry and enabled changes during cleaning and shaping procedures[12].

Schilder[13] (1967) introduced the concept of cleaning and shaping. Most obturation problems are actually problems of cleaning and shaping. Actually, the endodontist can develop a continuously tapering conical form in the root canal preparation within the regular dentine walls. This fact permits the use of gutta-percha cones having an ideal composition, avoiding the high percentage of inorganic fraction to make the cones rigid, and making the three dimensional root canal system obturation easy using thermoplastic techniques.

The chemical composition of gutta-percha points varies according to the manufacturer, especially considering the proportions of gutta-percha and zinc oxide. This may lead to variations in brittleness, stiffness, tensile strength, and radiopacity[4,6], and also in flow, plasticity, elongation, inherent tension force, and thermal behaviour[4,6,17].

Cones become more rigid with high concentrations of inorganic components and low percentage of gutta-percha[14], making the conventional filling technique easier (lateral condensation). Gutta-percha cones should present at least 17% of gutta-percha and no more than 3% of wax/resin (Dentsply FM and Dentsply TP, 10.4 ± 0.11 and 4.0 ± 0.36 respectively), enabling a good thermal behaviour during warm root canal filling. Barium sulfate and Zinc oxide provide radiopacity[15].

Other studies have been carried out, aiming to correlate physical properties, chemical composition and clinical behaviour (microleakage) of the different brands of gutta-percha cones already available to the practitioner.

CONCLUSIONS

This paper showed that the method utilized was appropriate to quantify gutta-percha, wax/resin, zinc oxide and barium sulfate content. Cone brands without barium sulfate were found (Konne, Tanari, Endopoint and Odous). The gutta-percha and zinc oxide content varied from 15.2% to 21.6% and 69.8% and 81.9%, respectively. An unusual high wax/resin percentage was detected in one brand (Dentsply FM). Dentsply TP showed the highest gutta-percha percentage.

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