



Physicochemical analysis of MTA Angelus[®] and Biodentine[®] conducted with X ray diffraction, dispersive energy spectrometry, X ray fluorescence, scanning electron microscope and infra red spectroscopy

Análisis fisicoquímico del MTA Angelus[®] y Biodentine[®] mediante difracción de rayos X, espectrometría de energía dispersiva, fluorescencia de rayos X, microscopio electrónico de barrido y espectroscopía de rayos infrarrojos

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ABSTRACT

The aim of the present study was to characterize components of commercial cements used in dentistry MTA Angelus[®] White (Angelus Lodrina, Parana Brazil) and Biodentine[™] (Septodont, Saint-Maur-des Fosses, France). Techniques used for said characterization were Scanning Electron Microscope, X-Ray Diffraction, X Ray Fluorescence, Electron Dispersion Spectrometry, and Infrared Spectroscopy. Both cements were mixed according to manufacturer's instructions. A study of surface texture was conducted with Scanning Electron Microscope (SEM), and X Ray Diffraction (XRD) analysis, and X Ray fluorescence analysis (XRF), an analysis of Dispersive Energy Spectrometry (DES), as well as an Infra Red Spectroscopy (IRS) in order to determine functional groups. **Results:** In XRD analysis, a difference was found: Biodentine exhibited Na₂O and ZrO₂. These elements were absent in MTA. MTA presented Cr₂O₃ and BiO₂ which in turn were absent in Biodentine. EDS analysis revealed that differences were found in the radio-opacifying agent, and that Biodentine presented CaCl₂ differing in this from MTA. Statistical analysis conducted revealed statistically significant percentages in contents, even though components were found to be practically the same. SEM analysis revealed marked differences: MTA presented irregular and porous surface whereas Biodentine exhibited irregular and filament form. **Conclusion:** There is a great similarity in the chemical components of MTA Angelus and Biodentine, with the exception of chemical components providing radio-opacity, the size and form of the grain, and, in Biodentine presence of calcium chloride.

RESUMEN

El propósito de este estudio fue caracterizar los componentes de los cementos comerciales para uso en odontología MTA Angelus[®] Blanco (Angelus, Lodrina, Paraná Brasil) y de Biodentine[™] (Septodont, Saint-Maur-des Fosses, Francia) mediante Microscopia Electrónica de Barrido, difracción de rayos X, fluorescencia de rayos X, espectrometría de dispersión de electrones y espectroscopía infrarroja. Los dos cementos se mezclaron según las indicaciones del fabricante. Se les practicó un estudio de textura de superficie mediante el microscopio electrónico de barrido (MEB), un análisis de difracción de rayos X (DRX), un análisis de fluorescencia de rayos X (FRX), un análisis de espectrometría de energía dispersiva (EDS) y un análisis de espectroscopía infrarroja (IR), para determinar los grupos funcionales. **Resultados:** Se presentó una diferencia en el análisis XRD entre Biodentine presentó Na₂O y ZrO₂ mientras que están ausentes en el MTA. El MTA presentó Cr₂O₃ y BiO₂ ausentes en el Biodentine. En el análisis EDS las diferencias fueron en el agente radiopacador y que el Biodentine presentó Cl a diferencia del MTA y en el análisis estadístico realizado a pesar de que prácticamente se presentaron los mismos componentes los porcentajes en los contenidos de éstos fueron estadísticamente significativos. En el análisis de MEB hay una gran diferencia, el MTA presenta una superficie porosa e irregular, el Biodentine una forma fibrilar e irregular. **Conclusión:** Existe una gran similitud en los componentes químicos entre el MTA Angelus y Biodentine con excepción de los componentes químicos para proporcionarles radioopacidad, el tamaño y la forma del grano y en el caso del Biodentine el cloruro de calcio.

Key words: MTA Angelus[®], Biodentine[™], DES, SEM, XRD, XRF, IRS.

Palabras clave: MTA Angelus[®], Biodentine[™], EDS, MEB, DRX, FRX, IR.

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INTRODUCTION

Dental materials have been evolving alongside dentistry due to technological advances, which have assisted these materials to possess better physical, chemical and biological properties.

Retro-filling materials are commonly used in endodontic surgical procedures. An ideal endodontic reparation material should be radio-opaque, biocompatible, with anti-bacterial effect, dimensionally stable, easy to manipulate and not be contaminated or affected by blood. Other desirable characteristics for the selected material would include for it to be osteo-inductor, provide suitable sealing against bacteria and fluids as well as being able to avoid filtrations when placed in humid environment and possessing sufficient resistance to compression and hardness.¹

Many materials have been used to perform retrograde filling. Among them we can count amalgam, zinc oxide-eugenol, polycarboxylate cements, glass ionomer cements, composite resin, epoxy-resin, gutta-percha and mineral trioxide aggregate (MTA) type cements based on Portland cement.

Main disadvantages of the aforementioned materials include micro-leakage, varied degrees of toxicity, as well as sensitivity to presence of humidity.^{2,3} Among these MTA has been recognized as a bioactive material,⁴ hard tissue conductor⁵ hard tissue inductor as well as biocompatible.⁶

MTA is a material commonly used for retrograde filling procedures, apex formation and perforation repairs, nevertheless its handling is less than ideal due to its long setting time and difficulties in preserving mix consistency.⁷

Calcium silicate cements, especially those derived from Portland cement, such as mineral trioxide aggregate (MTA) and others have been designed and are used in clinical dental applications.

Self-adjusting properties of calcium silicate cements are due to the progressive hydration reaction of orthosilicate ions (SiO_4).

When calcium silicate particles react to water a hydrated calcium silicate nanoporous amorphous gel is formed (HCS gel) in the cement particles, while calcium hydroxide (Ca(OH)_2) (portlandite) forms nuclei and grows in available gaps and spaces of the pores. With time, HCS gel polymerizes and hardens, forming thus a solid net which is associated to greater mechanical resistance. HCS gel is soluble in Ca(OH)_2 , released by the cement surface and increases alkalinity of surrounding environment.⁸

The purpose of the present study was to explore the components of MTA Angelus® White cement (Angelus, Lodrina, Paraná Brazil) and Biodentine™ (Septodont, Saint-Maur-des Fosses, France) by means of X-ray diffraction and electron dispersion spectrometry, X-ray fluorescence, as well as observing the surface with scanning electron microscope and infra red spectroscopy.

MATERIALS AND METHODS

Both cements used for the present project were divided into two groups:

- Group 1 MTA Angelus® White (Angelus, Lodrina, Parana, Brazil).
- Group 2: Biodentine™ (Septodont, Saint-Maur-des-Fosses, France).

One gram of the powder provided by the manufacturer was used for XRD and XRF analyses. For DES, SEM and IRS analyses all products were mixed using powder and liquid provided by the manufacturer. Manufacturer's instructions were strictly followed. One 8 mm diameter x 4 mm thickness sample was manufactured for each group. Five points were randomly taken for the analysis.

X ray diffraction analysis was conducted with a diffractometer Phillips Mod 1130/96 (generator) and pw1050/24 (goniometer) using $\text{CuK}\alpha$ at angular intervals ranging from 4° to 70° .

X ray fluorescence analysis (XRF): An X ray fluorescence quantitative chemical analysis was conducted with a Siemens SRS 3000 spectrometer, gauged with Geochemical Reference materials. This analysis was conducted with the sample in dry base, and loss by calcination (LBC) was determined by calcinating 1 g of the sample at 950°C during one hour.

Dispersive energy spectrometry (DES) and scanning electron microscopy (SEM): Once hardened, the samples were placed on the sample holder with a carbon film to which they adhered. Observations were made with Scanning Electron Microscope (leol model 5900 LV, Tokio, Japan). Used magnifications were 500X, 1000X and 2000X.

For the dispersive energy spectrometry analysis (DES) an elemental chemical analysis was conducted with an Oxford device, ISIS model, with 133 eV resolution, with carbon to uranium element detection.

For the present study amplifications of 500X, 1000X and 2000X were used in all samples at four pre-determined points.

Infrared spectroscopy (IRS): Samples were analyzed with attenuated total reflectance technique (ATR) in a Bruker Brand spectrometer, model Vector 33 with 32 scanning and resolution of 4 cm^{-1} . Samples to be analyzed were directly placed on the diamond crystal for analysis, since this technique did not require previous preparation.

RESULTS

XRD results of MTA and Biodentine were the following:

- In both cements presence of calcite and larnite was detected.
- In MTA there was presence of bismite, vesuvianite, and bassanite. These materials were absent in Biodentine.
- In Biodentine there was presence of hatrurite and baddeleyite. These materials were absent in MTA.

In XRF analysis, the following were identified in both cements: SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , CaO , K_2O , P_2O_5 , TiO_2 . MTA exhibited Cr_2O_3 and BiO_2 , these materials were not detected in Biodentine. Biodentine exhibited Na_2O and ZrO_2 , which were absent in MTA Angelus (Table I).

SEM analysis of samples revealed Biodentine structure with fibrillar and irregular shape, with crystal appearance (Figure 1) whereas MTA samples exhibited irregular and porous structure, loose granules were observed and identified as Bismuth (Figure 2).

DES results revealed presence of Bi in Group 1 (MTA Angelus). Bi wasn't present in any other group. In Group 2 (Biodentine) Cl presence was observed, which was absent in Group 1.

C, O, Al, Si, Ca were regularly detected in both groups (Tables II and III).

T Student test was used for statistical analysis. Results revealed that points from where samples were

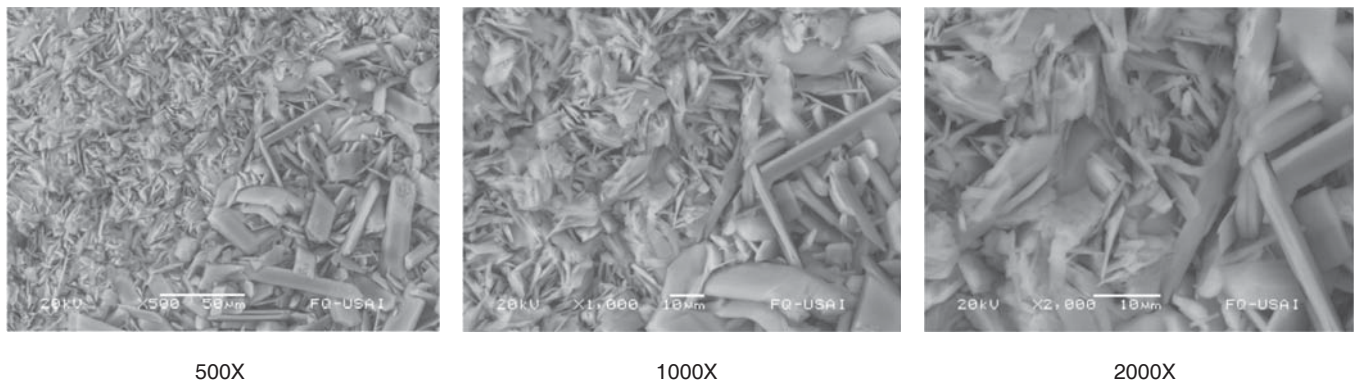


Figure 1. Biodentine Scanning electron micrographs at magnifications of 500X, 1000X and 2000X where irregular and filiform shaped crystals can be observed.

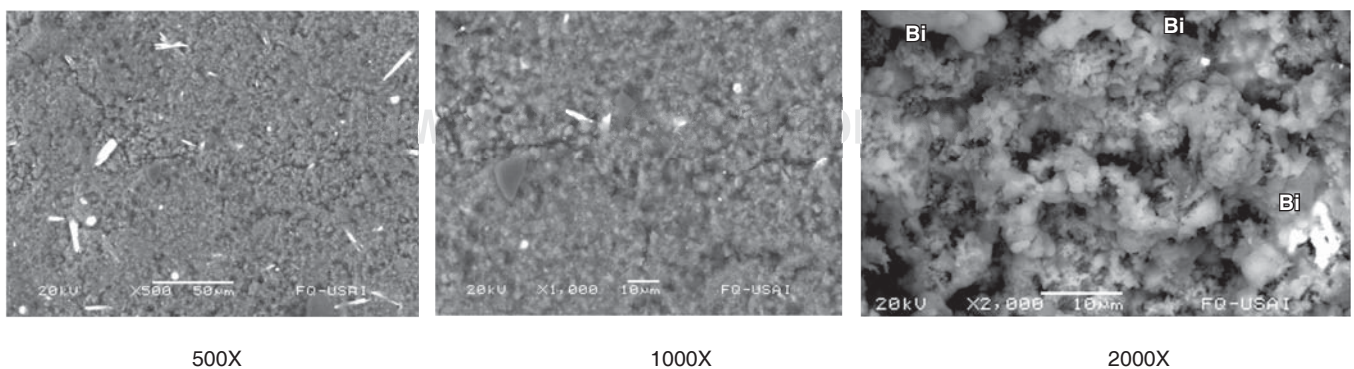


Figure 2. MTA Angelus scanning electron micrographs at magnifications of 500X, 1000X, and 2000X where irregular and porous structure can be observed. Bismuth can be observed in the shape of loose granules.

Table I. Percentages and components found in Group 1 (MTA Angelus) and Group 2 (Biodentine) through ray diffraction procedures.

Cement	SiO ₂ %	Al ₂ O ₃ %	Fe ₂ O ₃ %	MnO %	MgO %	CaO %	Na ₂ O %	Cr ₂ O ₃ %	BiO ₂ %	K ₂ O %	P ₂ O ₅ %	ZrO ₂ %	TiO ₂ %	LBC %	Sum %
Biodentine	20.65	0.247	0.062	0.004	0.072	64.839	0.434	ND	ND	0.036	0.015	6.50	0.009	6.72	99.60
MTA Angelus	21.07	3.47	0.36	ND	0.67	52.49	ND	0.96	16.50	0.021	0.11	ND	0.18	8.56	95.83

ND = Not detected; LBC = Loss by calcination.

Table II. Percentages of elements found in the five samples of each cement.

Element	MTA1 %	MTA2 %	MTA3 %	MTA4 %	MTA5 %	Biode 1%	Biode 2%	Biode 3%	Biode 4%	Biode 5%
C	16.77	14	13.38	14.54	12.92	7.16	9.14	7.65	7.97	9.05
O	38.39	39.69	41.30	39.57	40.24	33.02	32.20	32.33	31.39	30.73
Al	2.15	2.33	2.49	2.26	2.50	0.28	0.32	0.61	0.06	-0.02
Cl	ND	ND	ND	ND	ND	18.52	16.77	16.99	18.49	18.69
Ca	32.50	33.85	32.73	33.63	33.54	41.02	41.56	42.24	41.98	41.46
Si	5.64	6.08	5.59	5.88	5.76	0	0	0.19	0.10	0.10

Table III. Percentages of elements found in the five samples of each cement.

Element	Atomic									
	MTA1 %	MTA2 %	MTA3 %	MTA4 %	MTA5 %	Biode 1%	Biode 2%	Biode 3%	Biode 4%	Biode 5%
C	28.44	24.22	23.09	25.03	22.65	14.14	17.72	15.09	15.79	17.77
O	48.88	51.54	53.50	51.15	52.96	48.95	46.86	47.89	46.71	45.32
Al	1.62	1.79	1.91	1.73	1.95	0.25	0.28	0.53	0.05	-0.02
Cl	ND	ND	ND	ND	ND	12.39	11.01	11.36	12.42	12.44
Ca	16.52	17.55	16.93	17.35	17.62	24.27	24.14	24.97	24.94	24.40
Si	4.09	4.50	4.13	4.33	4.32	0	0	0.16	0.09	0.08
Bi	0.44	0.40	0.45	0.41	0.51	ND	ND	ND	ND	ND

taken were homogeneous, and there were statistically significant differences in the percentages of the varied detected components in both cements with DES tests (Tables IV and V).

INFRARED SPECTROSCOPY

Results obtained from MTA sample (Figure 3) revealed calcium carbonate characteristic groups in the absorption bands in 1410, 869 and 660 cm^{-1} in the C-O group. The band 952 cm^{-1} corresponded to calcium chloride (CaCl_2).

Figure 4 shows the Biodentine sample spectrum. It can be observed that bands at 3567 and 3426 cm^{-1} correspond to groups N-H. The band at 2925 cm^{-1} corresponds to methylene groups (CH_2). The band at

1739 cm^{-1} is assigned to C=O of a carboxylic acid, this is corroborated with bands at 1558 and 1419 cm^{-1} with the group COO⁻ of carboxylic acids. The band at 1620 cm^{-1} can correspond to an aromatic ring or a secondary amine. The aromatic ring can be corroborated in the region of 1410 to 1500 cm^{-1} and the amine group at the 795 cm^{-1} band. The 1168 cm^{-1} band corresponds to the CN group. Bands between 702 and 676 cm^{-1} correspond to monosubstituted groups (in the aromatic ring) C-CH₂ and C-H respectively.

DISCUSSION

Hydroxyapatite as such and other materials which contain Ca exhibit excellent biocompatibility, which

Table IV. Statistical analysis conducted with Student t-test.

Element	Cemento	Average	Standard deviation	T Student	p
Carbon	MTA	14.32	1.499	7.898	0.001
	Biodentine	8.19	0.8722		
Oxygen	MTA	39.83	2.059	12.78	0.001
	Biodentine	31.93	0.887		
Aluminum	MTA	2.346	0.1504	16.65	0.001
	Biodentine	0.258	0.237		
Calcium	MTA	33.25	0.596	24.67	0.001
	Biodentine	41.65	0.473		
Silicon	MTA	5.79	0.197	59.99	0.0001

Table V. Statistical analysis conducted with Student t-test.

Element	Cemento	Average	Standard deviation	T Student	p
Carbon	MTA	24.68	2.798	6.84	0.001
	Biodentine	16.10	1.61		
Oxygen	MTA	51.60	1.80	4.408	0.002
	Biodentine	47.146	1.36		
Aluminum	MTA	1.80	0.134	14.329	0.001
	Biodentine	0.226	0.2057		
Calcium	MTA	17.19	0.4627	27.26	0.001
	Biodentine	24.54	0.386		
Silicon	MTA	4.276	0.164	52.95	0.0001
	Biodentine	0.066	0.0676		

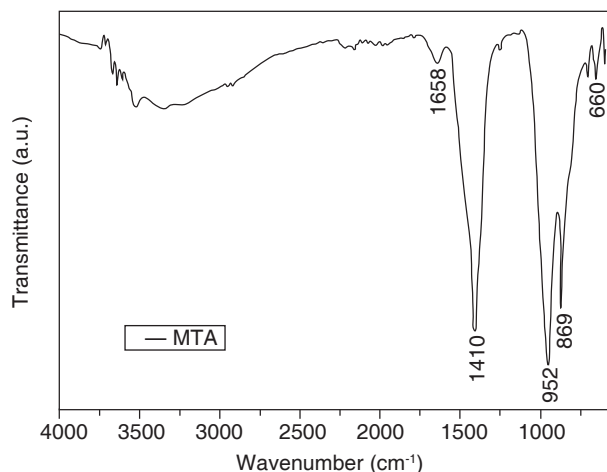


Figure 3. Infra-red spectroscopy of MTA simple.

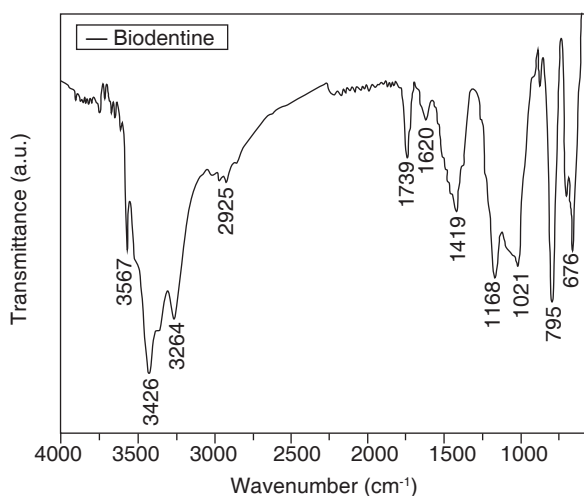


Figure 4. Infrared spectroscopy of Biodentine sample.

is expressed in minimal tissue toxicity and reaction to foreign body, osteoconductivity and osteogenicity (LeGeros, 1991).⁹

The composition of Biodentine powder is tricalcium silicate, calcium carbonate and zirconium oxide (Koubi et al, 2011).¹⁰

Calcium chloride is one of the most efficient accelerators for Portland cement hydration and configuration (Camilleri et al, 2006).¹¹

Calcite (CaCO₃), which was observed in both cements, has two different functions: 1. as active agent involved in the hydration process and 2. as filling which improves the cement's mechanical properties. (Garrault et al 2006).¹²

Hydration of tricalcium silicate (3CaO.SiO₂) leads to the formation of a hydrated calcium, gel silicate

hydroxide (gel CSH) and calcium hydroxide (Ca(OH)₂) (Taylor 1997).¹³

Biodentine surface examined with SEM reveals crystals of varied sizes in the shape of hexagonal plates of Ca(OH)₂ (Taylor 1997)¹³ which differs from the present study which observed crystals of filament shape.

Asgary¹⁴ reported in his XRD analysis of white MTA the presence of CaO, SiO₂, Bi₂O₃, Al₂O₃, MgO, SO₃, Cl, FeO, P₂O₅, TiO₂. In the present study, no Cl was found in MTA and contrary to Asgarty's reports presence of Cr₂O₃, K₂O was observed.

White MTA is composed of a variety of oxides typically of SiO₂, CaO and Al₂O₃. Among oxides, aluminum (Al), a neurotoxin, is harmful to human health due to its ability to alter cellular calcium homeostasis, and promote cellular oxidation (Zatta 2002).¹⁵

Gandolfi¹⁶ reported that in his DES analysis of MTA he obtained the following elements: Ca, Si, Cl, Bi, and O. No Cl was found in the analysis we conducted, and C and Al were found in addition to results reported by Gandolfi.

Song¹⁷ in an DES analysis of MTA reported presence of Ca, Si, C, O, Mg, Al, S and Bi. Our analysis differed from Song's inasmuch as S and Mg were not present.

MTA has a proportion of 4:1 of bismuth, radio-opacity oxide (Camilleri 2007¹⁸, Torabinejad 1995¹⁹) In the present study proportion of bismuth oxide was 16.5% as shown in *Table I*.

Asgary S et al²⁰ reported in DES analysis the highest peaks of calcium, silica and bismuth contents. Nevertheless, aluminum, magnesium and especially iron peaks were significantly lower in white MTA, this could explain color differences. We concur with results obtained in our study.

CONCLUSION

Chemical components of MTA Angelus and Biodentine are very similar, the exception would be in the chemical components which provide opacity, size and shape of grain, and in the case of Biodentine, calcium chloride.

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