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ORIGINAL RESEARCH

Similarities of elemental chemistry and morphology of cements type mineral trioxide aggregate and Portland cement through the use of scanning electronic microscopy and electron dispersion spectroscopy

Similitud de la morfología y química elemental de los cementos tipo agregado de trióxido mineral y cemento Portland, mediante microscopia electrónica de barrido y espectroscopia de dispersión de electrones

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ABSTRACT

Currently, studies on similarities among Portland cement and cements type mineral trioxide aggregate have shown that these compounds exhibit similar performance. This can be due to the fact that they are made based on Portland cement. With the aim of assessing percentages and components of Portland cement and commercial cements type mineral trioxide aggregate Pro-Root® white and Pro-Root® grey, Angelus® and CPM®, five 8 x 4 mm samples of each material were processed. These samples were subjected to a study of surface texture. This study was conducted with the help of a scanning electron microscope as well as a energy dispersive spectrometry analysis. **Results:** Upon comparison, Portland cement and mineral trioxide aggregate cements showed great similarities. The main difference was than in mineral trioxide aggregate there was absence of Fe, Mg, Na and K; in mineral trioxide aggregate cements O, C, Si, Ca, Al, Cl and Bi were found regularly. Ba presence was only detected in CP®. **Conclusions:** The present study established the presence of great similarities among chemical components of Portland cement and mineral trioxide aggregate cements of all commercial brands.

RESUMEN

En la actualidad, los estudios acerca de la similitud entre el cemento Portland y los cementos tipo agregado de trióxido mineral han demostrado que estos compuestos presentan un desempeño análogo, ya que son elaborados con base en el cemento Portland. Con el objeto de verificar los componentes y porcentajes del cemento Portland y los cementos comerciales tipo agregado de trióxido mineral Pro-Root® blanco y Pro-Root® gris, Angelus® y CPM®, se elaboraron cinco muestras de cada material de 8 x 4 mm y se les practicó un estudio de textura de superficie mediante microscopio electrónico de barrido y un análisis de espectrometría de energía dispersiva. **Resultados:** Los cementos mostraron gran similitud entre el cemento Portland y el agregado de trióxido mineral, sólo que en el agregado de trióxido mineral encontramos ausencia de Fe, Mg, Na y K, y en los cementos tipo agregado de trióxido mineral se encontró regularmente O, C, Si, Ca, Al, Cl y Bi; únicamente se detectó la presencia de Ba en el CPM®. **Conclusiones:** Encontramos gran similitud de los componentes químicos entre el cemento Portland y los cementos tipo agregado de trióxido mineral de todas las marcas comerciales.

Key words: MTA type cements, Portland cement, MTA morphology, MTA elementary chemistry.
Palabras clave: Cementos tipo MTA, cemento Portland, morfología MTA, química elemental de MTA.

INTRODUCTION

The material known as trioxide aggregate (MTA) was first developed at the Loma Linda University for surgical use in retro-fillings.[1] This material was patented by Torabinejad[2] in 1995.

MTA Pro-Root® powder (Dentsply Tulsa, Ok USA) consists of small-sized hydrophylic particles, with presence of tricalcium silicate, tricalcium aluminate and silica oxide.[1] This material has been studied in three phases: powder phase, crystalline phase and

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MTA powder hydration phase, forming a colloidal gel which sets with a pH of 10.2 and 12.5 after a three hour mixing process.[1]

Komabayashi et al[3] concluded that white Pro-Root MTA contained smaller particles, with smaller size range than grey Pro-Root MTA. MTA Angelus exhibited less circular, larger ranked particles which were less homogeneous than both white and grey Pro-Root.

Setting time represents another problem which has arisen with MTA use. Torabinejad[4] mentioned that setting time was less than four hours, whereas Kogan et al[5] informed it was 50 minutes when mixed with sterilized water. Differences depended upon the method used to determine the setting process. An example could be the use of a Gilmore needle *versus* vacant Chng et al technique.[6] When following methods established by the International Organization for Standardization, it was reported that setting process, from beginning to end was between 70 and 175 minutes, respectively.

Several methods have been used in order to determine MTA properties. Among them we can count scanning electron microscopy (SEM),[7] spectroscopy[8] and X-ray diffraction.[9] Studies conducted with SEM provide images; nevertheless, they only allow morphological evaluation of the specimens' topographical characteristics.

Estrela[10] and Funteas et al,[11] among others, have reported similarities between MTA and Portland Cement (PC) and their basic components. Camilleri[12] reported the production of calcium hydroxide as resulting product to PC and MTA hydration. Holland et al[13] proposed the theory that PC and MTA mechanisms of action were very similar. In an energy dispersive spectrometry (EDS) analysis, Camilleri et al[12] showed that the components' elements were the same.

With respect to bio-tolerance, Ribeiro DA et al[14] indicated that grey and white MTA Pro-Root were not genotoxic and thus did not cause cellular death. In a similar manner to Camilleri et al[15] informed that in biocompatibility studies, MTA extracts did not elicit grey MTA-derived cytotoxic reactions. They also informed that the addition of bismuth oxide to Portland cement did not interfere with biotolerance.

MATERIALS AND METHODS

The five cements used in the present study were divided into groups in the following manner: Group 1. Portland Cement, Group 2. White Pro-Root MTA (Dentsply, Tulsa, Ok USA), Group 3. Grey Pro-Root cement (Dentsply Tulsa, Tulsa OK USA), Group 4. White MTA Angelus (Angelus, Londrina, Parana, Brazil), and Group 5. MTA CPM (Medix Mexico DF, Mexico).

All cements were mixed with the liquid provided by the manufacturer. Manufacturers' instructions were strictly followed. Bi-distilled water was used with Portland Cement. Five samples were made of all groups. Samples measured 8 mm diameter by 4 mm thickness. All samples were placed in a Hanau oven at 95% humidity at 37.5 ± 5 °C for 24 hours.

Once set, the samples were placed in the sample tray which had a carbon film to which the samples became adhered to. A scanning electron microscope (Jeol Model 5900LV, Tokio Japan) was used to make observations. The microscope possessed magnification range of 18 X to 300,000X. Magnifications used were 500X, 1000X and 2000X.

An elemental chemical analysis was conducted in an Oxford equipment, ISIS model, with 133 eV resolution and detection of elements from carbon to uranium. For the study, magnifications of 500, 1000 and 2000X were used at four points previously determined in all samples, at 2 Sigma, as data variability measure, implying thus it was found to be within 95% of real value.

Comparisons were established among all 5 elements shared in Portland type cement and the four elements found in MTA type cement. Student t test was applied.

At a later point a Kruskal-Wallis non-parametric variance analysis was applied in order to compare all elements of the five cements.

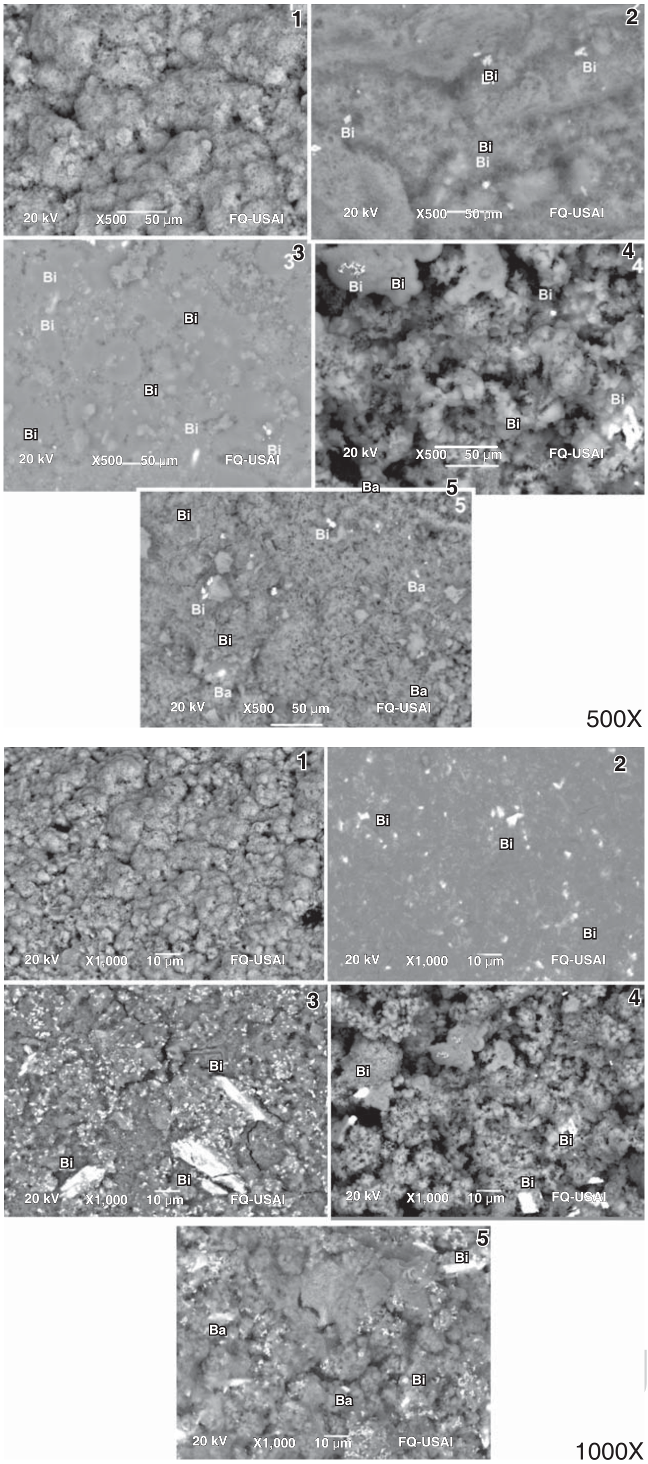
RESULTS

All five elements in shared Portland type cement were compared, as well as all four elements shared in

Table I. Averages of elements common to all five cements.

Element	Average MTA type cement	DE	Portland cement	p
CK	17.84	3.646	14.38	p = 0.154*
OK	24.98	4.057	37.60	p = 00.14
ALK	0.7775	0.2589	1.90	p = 0.002
SiK	2.4475	0.2239	7.92	p = 0.001
CaK	41.79	12.863	33.24	p = 0.276

* In CK element value no statistical significant difference was found.



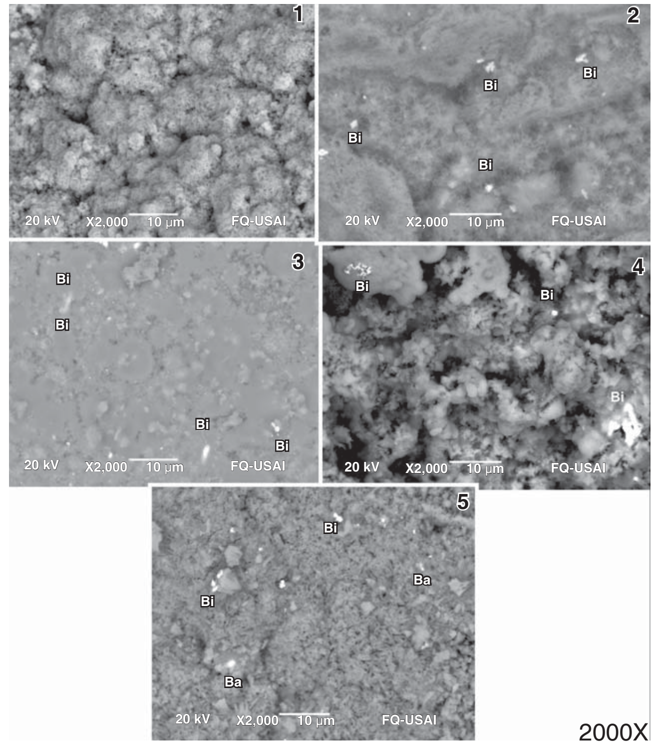


Figure 1. Micro-photographs with 500X, 1000X, and 2000X magnifications. Number 1 shows Portland cement with irregular and porous (rough) borders. Number 2 shows MTA white Pro-Root; Bismuth (Bi) can be observed. Number 3: grey MTA Pro-Root. Number 4, MTA Angelus, and number 5, MTA CPM with presence of bismuth (Bi) and barium (Ba).

Table II. Atomic average values of shared elements by the five cements. Statistically significant difference is shown.

Element	Atomic average	DE	Atomic average Portland cement	p
CK	33.65	4.25	24.57	p = 0.024
OK	37.40	5.44	48.11	p = 0.029
ALK	0.7775	0.2589	17.92	p = 00.01
SiK	2.12	0.955	7.92	p = 0.005
CaK	24.477	6.947	17.02	p = 0.121

MTA type cement. Significant differences were found with exception of CK elements *(Tables I and II)*.

The aforementioned results were obtained applying a Student t test, where a comparison was established between MTA cements *versus* Portland type cement.

A Kruskall-Wallis non-parametric variance analysis was later applied in order to compare all elements of the five cements. K = 0.244, p = 0.993.

In the analysis conducted with the help of the SEM, an irregular and porous micro-structure was observed in hydrated and hardened Portland cement *(Figure 1)*. In hydrated grey and white Pro-Root, as well as in Angelus and CPM, a more homogeneous, irregular porous image was observed, with some loose granules identified as bismuth, and in CPM bismuth and barium were found *(Figure 1)*.

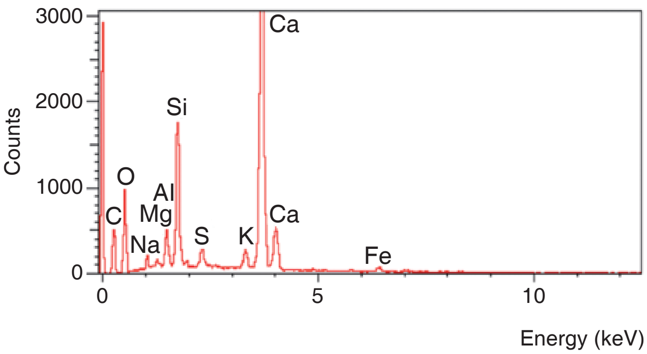


Figure 2. Shows that chemical components detected in Portland cement are Ca, Si, O, C, Na, Mg, Al, S, K, and Fe.

Table III. Portland cement, group 1 ≤ 2 Sigma.

Elmt	Spect Type	Element %	Atomic %
C K	ED	14.38	24.57
O K	ED	37.60	48.11
Na K	ED	1.00	0.90
Mg K	ED	0.42	0.35
Al K	ED	1.90	1.45
Si K	ED	7.92	5.79
S K	ED	1.06	0.68
K K	ED	1.49	0.78
Ca K	ED	33.24	17.02
Fe K	ED	0.98	0.36
Total		100.00	100.00

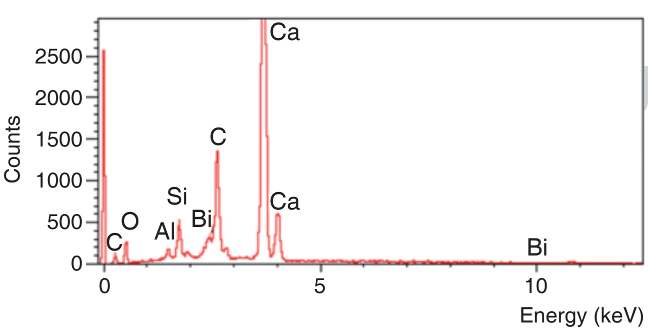


Figure 3. Shows that chemical components detected in MTA white Pro-Root® are Ca, C, Si, O, Al and Bi.

Results obtained with energy dispersive spectrometry (EDS) show that in Portland cement, Group 1, there was presence of Fe, Mg, Na and K *(Figure 2 and Table III)*. These aforementioned elements were absent in the other groups. In groups 2, 3, 4 and 5, O, C, Si, Ca, Cl and Bi were regularly detected *(Figures 3-5 and Tables IV-VI)*. Ba and S were only detected in Group 5 *(Figure 6 and Table VII)*.

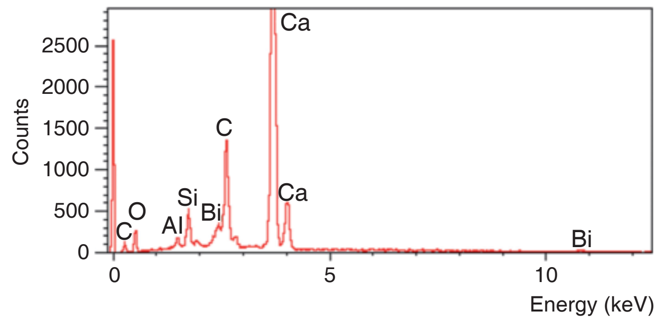


Figure 4. Chemical components detected in MTA grey Pro-Root® are: Ca, C, Si, O, Al, and Bi.

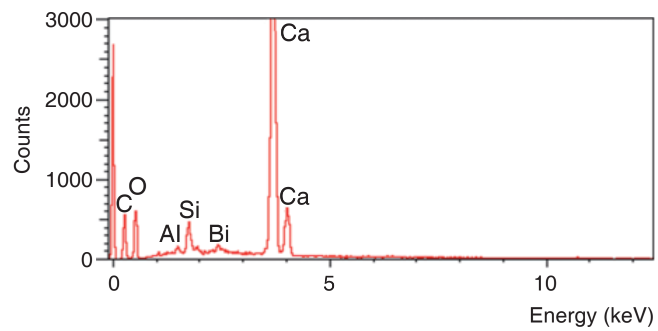


Figure 5. Chemical components detected in MTA Angelus® are Ca, Si, O, C, Al and Bi.

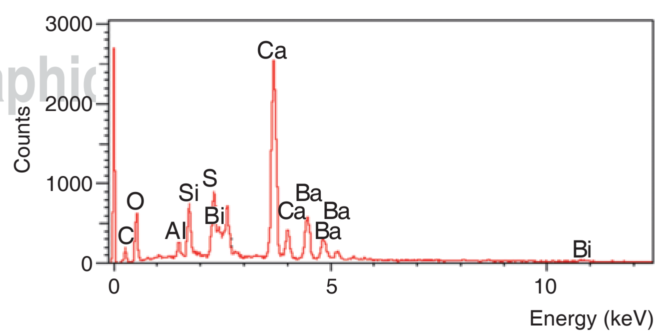


Figure 6. Chemical components detected in MTA CPM® are: Ca, Si, O, C, Mg, Al, S, Bi, and Ba.

DISCUSSION

Many studies have been published on Portland cement, and grey and white MTA with respect to their chemical composition, superficial structural characteristics, sealing abilities, biocompatibilities and capacity to regenerate and repair original tissue.

From the surface analysis perspective, some reports state that there is a material with irregular consistence with granulated areas resembling coral.[16] These characteristics are in agreement with our study, except in the case of white Pro-Root MTA, whose surface is less rough and porous when compared to the surfaces of other studied cements.

Table IV. White Pro-Root, group 2 ≤ 2 Sigma.

Elmt.	Spect. Type	Element %	Atomic %
C K	ED	16.24	33.67
O K	ED	25.47	31.43
Al K	ED	0.73	0.67
Si K	ED	2.59	2.30
Cl K	ED	9.62	6.76
Ca K	ED	50.51	31.39
Bi M	ED	4.46	0.53
Total		100.00	100.00

Table V. Grey Pro-Root, group 3 ≤ 2 Sigma.

Elmt.	Spect. Type	Element %	Atomic %
C K	ED	23.27	37.30
O K	ED	24.92	37.45
Al K	ED	0.76	0.63
Si K	ED	1.50	1.20
Ca K	ED	46.64	26.17
Bi K	ED	2.51	0.27
Total		100.00	100.00

Table VI. Angelus, group 4 ≤ 2 Sigma.

Elmt.	Spect. Type	Element %	Atomic %
C K	ED	15.40	27.69
O K	ED	33.04	44.60
Al K	ED	0.54	0.43
Si K	ED	2.08	1.60
Ca K	ED	47.35	25.52
Bi M	ED	1.61	0.17
Total		100.00	100.00

Table VII. CPM, group 5 ≤ 2 Sigma.

Elmt.	Spect. Type	Element %	Atomic %
C K	ED	16.47	35.97
O K	ED	24.50	36.13
Al K	ED	1.08	1.05
Si K	ED	3.62	3.38
S K	ED	4.85	3.97
Ca K	ED	22.66	14.83
Ba L	ED	19.87	3.80
Bi M	ED	6.96	0.87
Total		100.00	100.00

Asgary et al[17] reported the fact that MTA presented significantly lesser amounts of ferric oxide, as well as aluminum oxide and manganese oxide. In our EDS study, no presence of Fe and Mg and aluminum oxide was detected, no significant differences were observed although, regularly, amounts were always smaller than those found in Portland cement.

In the SEM study conducted by Oliveira et al[18] it was reported that they found chemical components which were very similar among all studied materials. Percentages only exhibited minimal differences. Bismuth was the only additional element. Our study agrees with this report; bismuth was the additional element. Only in the CPM cement, additional elements were bismuth and barium. Our study also agreed with Oliveira's study with respect to surface analysis: when using scanning electron microscope, differences were observed in textures and in each material's particles.

With respect to bismuth percentages, Funteas et al[16] reported that this material was insoluble, and was incorporated to the Pro-Root® MTA formulation in order to provide radio-opacity to the material. He reported an average 9.2 bismuth percentage. In our study, this percentage was lower, since 4.46% was detected in white Pro-Root®, 2.51% was detected in grey Pro-Root®, 1.61% was detected in Angelus® and 6.96% was detected in CPM. General average was 3.10%. Barium percentage detected in CPM® was 19.87.

J. Camillleri[19] reported in his study that MTA was aluminum-deficient. He suggested the material had been prepared in rotary ovens, as is habitual for Portland cement manufacturing. In the process of hydration, this affects ettringite and monosulfate production, which are usually formed during hydration of Portland cement. Bismuth affects the material's hydration mechanism in MTA type cements, it is part of the C-S-H structure and also affects precipitation of calcium hydroxide in the hydrated paste. He also states that MTA possesses a more fragile microstructure when compared to Portland cement.

CONCLUSIONS

There is a great similarity of chemical components when comparing Portland Cement and MTA type cements of all commercial brands, with exception of chemical components which provide opacity such as bismuth oxide and barium oxide. Nevertheless, further studies are required geared to researching processes of decreasing setting time and increasing compressive forces in order to then be able to consider them suitable restorative materials.

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