Chemical analysis of powder and set forms of Portland cement, gray ProRoot MTA, white ProRoot MTA, and gray MTA-Angelus

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Objective. To evaluate the chemical composition and crystalline structures of Portland cement, gray ProRoot MTA (gray MTA), white ProRoot MTA (white MTA), and gray MTA-Angelus.

Study design. X-ray diffraction analysis was used to identify and characterize crystalline phases, and energy dispersive x-ray spectrometer was used to determine the chemical composition of the test materials. Both powder form and set form were examined.

Results. The crystalline structure and chemical composition of gray and white MTA were similar except for the presence of iron in gray MTA. Both were composed mainly of bismuth oxide and calcium silicate oxide. Portland cement was composed mainly of calcium silicate oxide and did not contain bismuth oxide. Gray MTA-Angelus had a lower content of bismuth oxide than ProRoot MTA. There were no noticeable differences in the chemical composition and crystalline structures between the powder and set forms of any of the material tested.

Conclusion. Portland cement differed from the MTA by the absence of bismuth ions and presence of potassium ions. Gray MTA contained a significant amount of iron when compared with white MTA. In addition, gray MTA-Angelus had a lower content of bismuth oxide than ProRoot MTA. (Oral Surg Oral Med Oral Pathol Oral Radiol Endod 2006; 102:809-15)
also shown the Portland cement to exhibit properties similar to MTA.

Recently, white MTA has been developed and marketed to replace gray MTA to address esthetic concerns. A number of studies have been performed on this new material to determine if it exhibits the same properties as gray MTA. These studies comparing white and gray MTA have yielded conflicting results in terms of biocompatibility, sealing ability, and ability to induce tissue regeneration. A leakage study by Ferris and Baumgarnter and a biocompatibility study by Holland et al. have shown them to have similar properties. Camilleri et al. reported that osteoblasts had the same biocompatible reaction to both types of MTA. An in vivo study by Menezes et al. showed that when white MTA, gray MTA, and white Portland cement were applied as a pulpotomy agent, all the samples resulted in healing of the pulp and a hard tissue bridge formation.

However, some in vitro studies, such as by Perez et al., have reported that osteoblastic cell line grown on gray MTA adhered and differentiated better than the cells grown on white MTA. A leakage study by Matt et al. showed that gray MTA demonstrated significantly less dye leakage when compared to white MTA.

In light of the conflicting findings in comparing the sealing ability, biocompatibility, and tissue-regenerating ability of gray MTA and white MTA between these studies, there is a need to compare the chemical composition of the MTA products available. The purpose of this study was to analyze and compare the chemical composition of Portland cement, gray MTA, white MTA, and gray MTA-Angelus. Both the powder and the set forms were examined. X-ray diffraction (XRD) was used to identify and characterize crystal phases, and an energy dispersive x-ray spectrometer system (EDS) was used to determine the chemical composition of the examined materials.

MATERIALS AND METHODS
Preparation of the sample (powder)
MTA powder was mixed with acetone and applied onto the frosted surface of a glass slide and left in air for 30 seconds until the acetone had evaporated completely, leaving the MTA powder attached to the slide. The prepared slide was mounted onto the XRD apparatus. Three samples of each material, Portland cement, gray MTA, white MTA and gray MTA-Angelus, were investigated by XRD.

Preparation of the sample (set)
Each MTA sample was mixed with distilled water according to the manufacturer’s direction for use. Portland cement sample was also mixed in the same manner. The mix was stored in an incubator at 37°C and 100% humidity for 3 days. The set samples were then mounted onto the XRD apparatus for analysis.

XRD analysis
The prepared sample material was mounted onto the XRD apparatus (Geigerflex Horizontal diffractometer with a graphite crystal monochrometer; Rigaku/MSC, Woodlands, TX). The x-ray beam angle 2θ range was set between 3 degrees (3000) to 70 degrees (70000) and scanned at 2 degrees per minute. The Cu x-ray source was set at accelerating voltage of 45 KV and the current in the electron beam at 30 mA and on continuous scan mode. The peaks on the diffraction pattern were marked using the Rigaku software (version 2.8). Then the peaks were compared and matched with that of the standard material in the powder diffraction file (JCPDS International Center for Diffraction Data 1998, Pennsylvania) using a micro powder diffraction search and matching analysis program.

Preparation of the sample for EDS
Each sample powder was placed on an aluminum stop with double-sided carbon tape. Carbon coating was applied before running the scanning electron microscopy (SEM).

EDS
Analytical scanning electron microscopy was performed on JEOL 6400 SEM (Tokyo, Japan). This microscope was equipped with an Oxford energy dispersive x-ray spectrometer (EDS) and wavelength dispersive x-ray spectrometer (WDS). The EDS system was used to determine the chemical composition of the examined materials.

RESULTS
XRD
The chemical composition and its crystal structure of gray and white MTA were similar (Fig. 1, Table I). The only exception was that gray MTA contained significant amount of iron when compared with white MTA. Both materials were composed mainly of bismuth oxide crystalline structure and calcium silicate oxide. Although present, other crystal phases contributed to a very small proportion of the material. Portland cement did not contain bismuth oxide but it was composed of many different crystal phases. Gray MTA-Angelus differed from the gray ProRoot MTA in that it contained less bismuth oxide and more of other crystalline phases, many of which could not be identified (Fig. 1; Table I).

For each of the cement types, there were no notice-
able differences in the composition and crystalline structure between powder and set form.

**EDS**

The chemical composition of Portland cement, gray MTA, and white MTA were very similar. The only difference observed between the 2 types of MTA was the lack of iron ions in white MTA. The Portland cement differed from MTA by the lack of bismuth ions and the presence of potassium ions (Figs. 2-4; Table II).

**DISCUSSION**

Several studies have compared the chemical composition, surface characteristics, sealing ability, biocompatibility, and ability to regenerate original tissues of Portland cement, gray MTA, and white MTA. The surface characteristics of Portland cement and
gray MTA have been shown to be irregular, consisting of either cuboidal discrete crystals or areas of granular material with a coral-like characteristic when viewed under high magnification.\textsuperscript{16,18,20} This was not the case for the white MTA, which showed different surface roughness when viewed under SEM.\textsuperscript{27}

Holland et al.\textsuperscript{22} clinically observed 2 differences with these materials: the color and the setting time, which was greater in white MTA.

Ferris and Baumgartner\textsuperscript{24} compared white and gray MTA for their sealing ability of furcal perforation using a bacterial leakage model. Their results demonstrated no difference between the 2 in allowing passage of \textit{F. nucleatum}. However, a leakage study by Matt et al.\textsuperscript{28} showed that gray MTA demonstrated significantly less dye leakage than white MTA.

Abdullah et al.,\textsuperscript{20} Holland et al.,\textsuperscript{22} and Saidon et al.\textsuperscript{23} showed that the biocompatibility and the potential to promote bone healing of Portland cement are comparable to that of gray MTA in their in vitro studies. There are not many studies published comparing the new white MTA and the extensively studied gray MTA. Perez et al.\textsuperscript{27} compared their effects on osteoblasts. Under the conditions of their study, primary osteoblasts bound and survived on gray MTA and initially bound to white MTA but did not survive on the surface. On the other hand, Holland et al.\textsuperscript{22,25} implanted white MTA and gray MTA on the connective tissue of rats and reported that the mechanisms of action of white MTA are very similar to those of gray MTA despite the differences in the material.

This study examined the presence and intensity of the peaks from the XRD patterns. Over 50% of the crystalline structure present in ProRoot MTA was in the form of bismuth oxide, and calcium silicate oxide crystalline contributed to approximately 30%. Gray MTA-Angelus consisted of about 40% of the bismuth oxide phases and 30% of calcium silicate oxide. This study is in agreement with that by other authors who compared the chemical composition of Portland cement and gray MTA and showed that they contain the same chemical elements except that gray MTA also contains bismuth oxide.\textsuperscript{18,19,21} This study is also in agreement with that of Dianamnti et al.,\textsuperscript{18} who found that iron oxide was absent in white MTA; however, their observation of absence of calcium sulfate (plaster anhydride) only in gray MTA was not observed in this study. Asgary et al.\textsuperscript{29} found that white MTA contained significantly less iron oxide as well as aluminum oxide and magnesium oxide than gray MTA. Our results also showed that there was more of the magnesium compound phase in gray MTA than in white MTA. Metal oxides such as
aluminum and iron oxides have been known to cause abnormal tissue reactions equivalent to a chemical insult. The effect of iron oxide in gray MTA at this point is not clear. Also, the trace amount of other compounds detected in the Portland cement and gray MTA-Angelus may or may not play a significant role in the short- and long-term clinical application, and this warrants further studies.

Fig. 2. Energy dispersive x-ray spectrum of Portland cement.

Fig. 3. Energy dispersive x-ray spectrum of gray MTA.

Fig. 4. Energy dispersive x-ray spectrum of white MTA.
Table II. Energy dispersive x-ray spectrometer results showing the composition of Portland cement, gray MTA, and white MTA

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<th>Portland cement</th>
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<th>White MTA</th>
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CONCLUSION

The difference observed between the 2 types of MTA was the lack of iron ions in white MTA. They were similarly composed of bismuth oxide and calcium silicate oxide crystalline structures, and other crystalline components comprised a very small proportion of the material. Portland cement differed from MTA by the absence of bismuth ions and presence of potassium ions. In addition, ProRoot MTA appeared to have more homogeneous composition than Portland cement and gray MTA-Angelus. For each of the cement types, there were no noticeable differences in the composition and crystalline structure between powder and set form.30

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REFERENCES


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