X-ray diffraction analysis of mineral trioxide aggregate and Portland cement

I. Islam, H. K. Chng & A. U. J. Yap
Faculty of Dentistry, Department of Restorative Dentistry, National University of Singapore, Singapore

Abstract

Islam I, Chng HK, Yap AUJ. X-ray diffraction analysis of mineral trioxide aggregate and Portland cement. *International Endodontic Journal*, **39**, 220–225, 2006.

Aim To compare the major constituents present in ProRoot mineral trioxide aggregate (MTA), ProRoot MTA (tooth coloured formula), ordinary Portland cement and white Portland cement using powder X-ray diffractometery.

Methodology X-ray diffractometery of the four materials was carried out with the divergence and scatter slits set at 1° and the receiving slit at 0.10 mm. The scan range was set at 5–70° and continuous scans for the θ–2θ range were run with a scan speed of 2° min^{-1}. The patterns obtained were then compared with the Powder Diffraction Files (PDF) found in the International Centre for Diffraction Data database. The three strongest peaks were used for the identification of the constituents. The relative intensities were plotted against the angle 2θ and compared with the plots in the PDF.

Results The main constituents were found to be tricalcium silicate, tricalcium aluminate, calcium silicate, and tetracalcium aluminoferrite in all the four cements with the additional presence of Bi_2O_3 in ProRoot MTA and ProRoot MTA (tooth coloured formula).

Conclusions The four cements had similar major constituents. Data on Portland cement may be used for the further development or modification of ProRoot MTA in order to improve its physical characteristics and expand its scope of clinical applications.

Keywords: mineral trioxide aggregate, Portland cement, root-end filling materials, X-ray diffraction analysis.

Received 2 March 2005; accepted 31 October 2005

Introduction

Mineral trioxide aggregate (MTA) has emerged as a popular root-end filling material both because of its biocompatibility (Torabinejad *et al.* 1995a,b, 1998, Torabinejad & White 1995, 1998, Hayashi *et al.* 2004) and superior sealing ability (Torabinejad *et al.* 1993, 1995a,b, Torabinejad & White 1995, Fischer *et al.* 1998, Adamo *et al.* 1999). MTA has also been successfully used for direct pulp caps (Ford *et al.* 1996), repair of furcal perforations (Pitt Ford *et al.* 1995, Arens & Torabinejad 1996) and in the management of teeth with open apices (Hayashi *et al.* 2004). Although MTA is popular, there have been concerns about its cost and difficult handling characteristics. It has been reported that the MTA mixture loses consistency in the presence of excessive liquid, even at the proportion recommended by the manufacturers and results in a fluid mix (Fridland & Rosado 2003). Lee (2000) stated that the long setting time of MTA results in an initial looseness which can make handling rather difficult.

Mineral trioxide aggregate is a fine powder consisting of hydrophilic particles of tricalcium silicate (C3S), tricalcium aluminate (C3A), tricalcium oxide and silicate oxide (Schwartz *et al.* 1999). The United States Patent no. 5,415,547 and 5,769,638 for MTA states that the base material for MTA is Portland cement and bismuth oxide has been added to make the mix radiopaque (Torabinejad *et al.* 1995a,b, 1998). This has generated interest in the evaluation of

Correspondence: Dr Hui Kheng Chng, Faculty of Dentistry, Department of Restorative Dentistry, National University of Singapore, 5, Lower Kent Ridge Road, Singapore 119074, Singapore (Tel.: +65 67724954; fax: +65 67732603; e-mail: rsdchk@nus.edu.sg).

Portland cement as an alternative to MTA, as Portland cement is less costly and widely available. Funteas *et al.* (2003) analysed samples of MTA and Portland cement for fifteen different elements using inductively coupled plasma emission spectrometry (ICP-ES). Comparative analysis revealed that there was a significant similarity except there was no detectable quantity of Bismuth in Portland cement. They concluded that there is no significant difference between the 14 different elements in both Portland cement and MTA. The biocompatibility of MTA and Portland cement has also been compared and both materials were found to be biocompatible (Abdullah *et al.* 2002, Saidon *et al.* 2003).

The hydration behaviour of MTA in various physiological environments has also been investigated (Lee *et al.* 2004). Using X-ray diffraction analysis (XRD), the authors determined the crystalline phases of MTA before and after hydration. They observed several sharp peaks of C3S, C3A, calcium silicate (C2S) for the sample of unhydrated MTA. They observed sharp peaks at $2\theta = 27.3°$ and multiple peaks at 32° and 34°. They also observed that in hydrated samples the same three phases of C3S, C2S, and C3A were observed in the same locations, but the line intensities were reduced. They stated that as these reactants dissolved in water to form hydrated products, a reduction in quantity was observed.

X-ray diffraction is a method widely used to investigate the structure of alloys (Brantley *et al.* 1995). It has also been used for the study of dental alloy oxidation (Ohno *et al.* 1983) and metal-ceramic interfaces (Brantley *et al.* 1996). X-ray diffraction is also a useful analysis technique for the study of cements. It enables identification of the major crystalline products in a cement sample.

Mineral trioxide aggregate is currently available commercially in two formulations: ProRoot MTA (PMTA), a grey variety and ProRoot MTA (tooth coloured formula) (WMTA) (Dentsply Tulsa Dental, Tulsa, OK, USA). Most of the earlier studies on MTA were conducted using PMTA. The number of studies conducted using WMTA is limited as it is a relatively new product. Like MTA, Portland cement is also available in grey (ordinary Portland; OP) and white (white Portland; WP) varieties. Although XRD of grey variety of MTA has been carried out (Lee *et al.* 2004) and the elements present in grey MTA and OP were compared (Funteas *et al.* 2003), studies comparing the major constituents of PMTA and WMTA with Portland cement are still not available. The aim of this study was to use X-ray diffraction to compare the major constituents present in PMTA, WMTA, OP and WP (Asia Cements Pte. Ltd, Singapore).

Materials and methods

Sample preparation

Specimens were prepared by packing dry powder into an X-ray holder, which was placed on a flat glass slab. The X-ray holder consists of rectangular aluminium plates having a rectangular window for packing the sample. Powder was compacted by applying pressure with a flat spatula. The excess powder was removed from the surface of the sample holder by a single sweep with the edge of a glass slide. The holder was checked to ensure complete and uniform coverage of the holder. A powder X-ray diffractometer (Shimadzu Corporation, Kyoto, Japan) with Ni filter and CuK_α radiation (λ–0.154 nm) running at 30 kv voltage and 30 mA current was used. The divergence and scatter slits were set at 1° and the receiving slit at 0.10 mm. The scan range was set at 5–70° and continuous scans for the θ–2θ range were run with a scan speed of 2° min^{-1}.

Interpretation of data

Each component of a mixture or a compound has a characteristic diffraction pattern, independent of other components in the mixture. Powder diffraction patterns are usually plotted with scattered intensity as a function of Bragg angle, 2θ. The diffraction pattern of the material is peculiar to the material and on this basis it is possible to conduct qualitative analysis of the material. The diffraction pattern of the unknown material is compared with documented diffraction patterns of known materials. Diffraction patterns of known materials are documented in the Powder Diffraction Files (PDF) found in the International Centre for Diffraction Data (ICDD) database (Powder Diffraction File 2004). In the ICDD card, the diffraction pattern of materials is indicated by the interplanar spacing *d*, corresponding to each diffracted X-ray and the relative intensity of the diffracted X-ray. The materials are represented by the value of the three strongest X-ray peaks and the relative intensity *I*. The relative intensity indicates the quantity of a compound or constituent present in the material. These cards have two types of indices.

i. Alphabetical index of each substance by name, which facilitates searching by the name of the material and the chemical formula.

ii. Numerical index by three strongest X-ray peaks, which facilitates searching by diffraction patterns.

After the experiment was run, the values of relative intensity I and θ were plotted. The proper group representing the strongest peak was located in the numerical index. Then the closest matches for the other two peaks were located and the relative intensities were compared with the tabulated values. When good agreement was found for all the three strongest lines, the proper data file was located and the relative intensities of all the lines were compared to complete the identification.

Results

The results of the XRD are presented as graphs in Figs 1–4.

For WMTA, a large peak representing C3S was observed at $2\theta = 31.9°$. In addition, peaks representing C2S and C3S were also observed at $2\theta = 31.99$, 30.55 and 41.66°. A peak was also observed at $2\theta = 37.67°$ and this represented C3A. Another peak was observed at $2\theta = 34.56°$ and this represented tetracalcium aluminoferrite (C4AF). A peak was also observed at $2\theta = 27.2°$. This represented bismuth oxide.

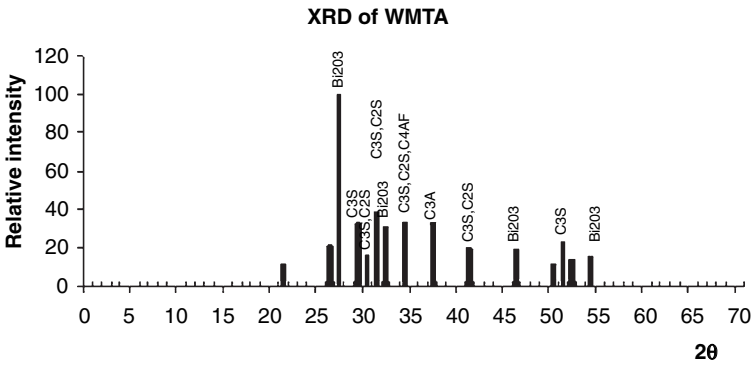

Figure 1 X-ray diffraction analysis of ProRoot MTA (tooth coloured formula).

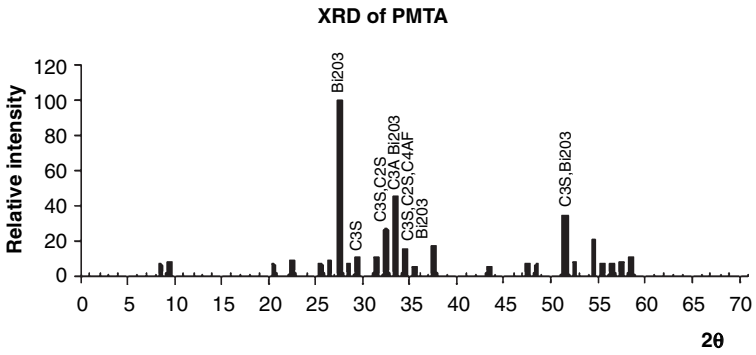

Figure 2 X-ray diffraction analysis of ProRoot MTA.

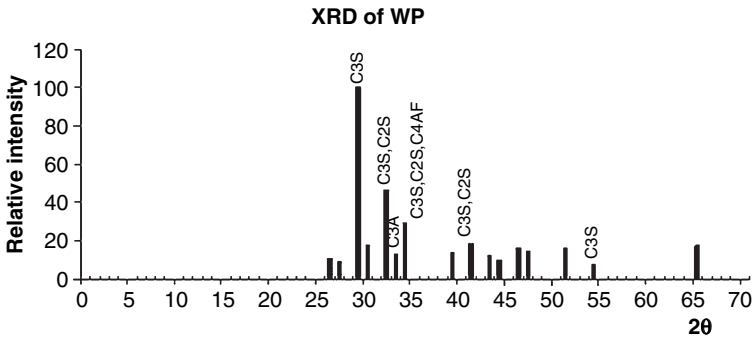

Figure 3 X-ray diffraction analysis of white Portland.

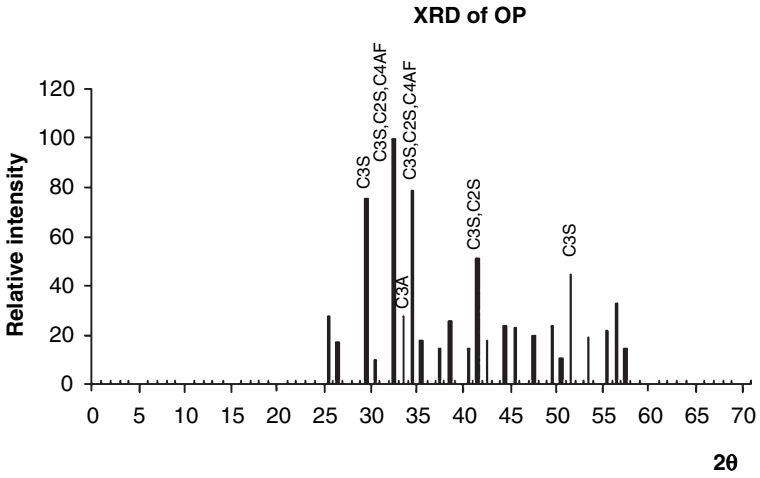

Figure 4 X-ray diffraction analysis of ordinary Portland.

For PMTA, a large peak was observed at $2\theta = 29.3°$ representing C3S. Peaks representing C2S was observed at $2\theta = 32.45°$ and at $2\theta = 34.26$. A peak representing C3A was observed at $2\theta = 33.1°$. Another peak representing C4AF was observed at $2\theta = 34.26$. Similar to WMTA, a peak representing bismuth oxide was observed at $2\theta = 27.2°$.

For WP, peaks representing C3S were observed at $2\theta = 29.38°$ and at $2\theta = 32.44°$. Peaks representing C2S were observed at $2\theta = 32.44°$ and at $2\theta = 35.26°$. Another peak representing C3A was observed at $2\theta = 33.26°$. A peak representing C4AF was observed at $2\theta = 34.26°$.

For OP, peaks representing C3S were observed at $2\theta = 29.38°$ and at $2\theta = 32.13°$. Peaks representing C2S were observed at $2\theta = 32.13°$ and at $2\theta = 34.32°$. Another peak representing C3A was observed at $2\theta = 33.26°$. A peak representing C4AF was observed at $2\theta = 34.32°$.

The XRD results indicated that in all four materials tested, the major constituents were C3S, C3A, C2S, and C4AF. Thus WMTA, PMTA, WP and OP have the same major constituents. However bismuth oxide was found in ProRoot MTA and this was not present in PC.

Discussion

Using ICP-ES, Funteas *et al.* (2003) were able to identify the elements present in MTA and Portland cement. Although they have shown that the elements present were similar, it was not known if the major compounds present in MTA and Portland cement were the same. The use of XRD permitted the identification of the major constituents or compounds present in a material or mixture. Further, samples of WMTA and WP, which were not compared in previous studies, were included. Although PMTA and WMTA appeared different on visual examination because of their colour, the results of this study showed that in fact, the two products shared the same major constituents. Using XRD, Lee *et al.* (2004) demonstrated presence of multiple peaks of C3S, C3A and C2S for unhydrated MTA. They observed sharp peaks at $2\theta = 27.3°$ and multiple peaks at 32° and 34°. The results of the present study for PMTA corroborated these findings.

The identification of the major constituents of a material is important as it will lead to understanding of its physical, chemical and mechanical properties. Although ProRoot MTA is a relatively new material in Dentistry, Portland cement has been used in the construction industry for a long time. As ProRoot MTA has major constituents similar to Portland cement, the vast amount of information and knowledge available on Portland cement may be used to improve certain characteristics of ProRoot MTA. For example accelerating admixtures such as metal hydroxides or aluminates can be added to Portand cement to reduce its setting time and improve its strength. As the major constituents of ProRoot MTA and Portland cement are similar, it is likely that the admixtures will have similar effects on the setting time and strength of ProRoot MTA. A modified ProRoot MTA with faster setting time or higher compressive strength may potentially have expanded clinical applications, including use as a coronal dental restorative material.

Although both MTA and Portland cement have been found to be biocompatible (Torabinejad *et al.* 1998a, Torabinejad & White 1998, Abdullah *et al.* 2002, Saidon

et al. 2003), industrially manufactured Portland cement does not meet with the stringent guidelines required in the manufacture of medical devices. ProRoot MTA was successfully modified from Portland cement and was approved for use by the Food and Drug Administration (FDA) in 1998 (Schwartz *et al.* 1999) after extensive *in vitro* and *in vivo* tests demonstrated it was biocompatible. ProRoot MTA, like all medical devices, is manufactured under strict regulations, conforming to the USA FDA good manufacturing practices and the European Medical Device Regulations. FDA requires a disclosure from the manufacturers regarding the safety and efficacy testing of the devices according to appropriate ADA and ISO regulations, prior to commercialization of the device. The Federal Code of Regulations also requires that manufacturers have a quality system that continues to ensure product quality. The Federal system of disclosure and monitoring of manufacturing processes leads to high quality standards for products. Any further modified form of ProRoot MTA, for example, by addition of a suitable admixture to improve the handling characteristic and setting time of ProRoot MTA, should similarly be subjected to rigorous *in vitro* and *in vivo* testing, as well as be manufactured under such stringent conditions, before it can be recommended for clinical use.

White Portland cement differs from OP in its lower iron content. The lighter colour of WP is because of the reduction in the ferrite phase. During the production of WP, the ferrite component is usually reduced by producing the cement clinker under reducing conditions and by rapid quenching (Bye 1999). WP also has lower compressive strength compared with OP and is used commercially in civil engineering works as a repair material and in architecture because of its aesthetic value. It is unclear if WMTA was formulated using WP as base material. The physical and mechanical properties of WP and WMTA are likely to be similar if WP was the base material for WMTA. When WMTA is used as a root-end filling material, a slight decrease in compressive strength compared with PMTA is not critical, as root-end fillings are not subjected to direct occlusal load. However, PMTA may be more suitable for use as a base material if it is to be modified and developed into a coronal restorative material.

X-ray diffraction is a reliable, precise and reproducible method to quantify the relative phase abundances in the Portland cement clinker and Portland cement (Walenta & Fullman 2004). In theory, positive identification of any substance whose diffraction pattern is included in the PDF should be possible. However, in practice, various difficulties arise, which include errors in the diffraction pattern of the unknown, overlapping peaks and errors in the PDF. A given substance will always produce a characteristic diffraction pattern, whether that substance is present in the pure state or as one constituent of a mixture of substances (Cullity & Stock 2001). However, the absolute amounts of phase contents cannot be determined if there are overlapping peaks. The classical method of determining the amount of a phase in a mixture is the comparison of the peak height and peak area. This method has been used in the analysis of free lime content in Portland cement clinker (Walenta & Fullman 2004), but the almost complete overlap of the C3S and the C2S phases in this study makes quantitative analysis by determining peak heights or peak areas impossible. Alternative techniques will be required to determine the quantity of the various phases present in the cements. In addition, XRD of the hydrated cements should be performed to ascertain the compositional changes, which the cement undergoes during setting. This can provide valuable insight to aid in the further development or modification of ProRoot MTA so as to improve its characteristics and expand its scope of clinical applications.

Conclusions

The XRD results indicated that in all four materials tested, the major constituents were C3S, C3A, C2S and C4AF. Thus, WMTA, PMTA, WP and OP have the same major constituents. However, bismuth oxide was found in ProRoot MTA and this was not present in PC. Given the similarity in the composition of ProRoot MTA and Portland cement, the vast amount of information and knowledge on Portland cement may be used to aid in the further development or modification of ProRoot MTA so as to improve its physical characteristics and expand its scope of clinical applications.

Acknowledgements

This research was supported by a grant from the Academic Research Fund, National University of Singapore, Singapore. We are also grateful to Dentsply Tulsa Dental, Tulsa, OK, USA for providing the ProRoot MTA used in this study.

References

Abdullah D, Ford TR, Papaioannou S, Nicholson J, McDonald F (2002) An evaluation of accelerated Portland cement as a restorative material. *Biomaterials* **23**, 4001–10.

Adamo HL, Buruiana R, Schertzer L, Boylan RJ (1999) A comparison of MTA, Super-EBA, composite and amalgam as root-end filling materials using a bacterial microleakage model. *International Endodontic Journal* **32**, 197–203.

Arens DE, Torabinejad M (1996) Repair of furcal perforations with mineral trioxide aggregate: two case reports. *Oral Surgery, Oral Medicine, Oral Pathology, Oral Radiology and Endodontics* **82**, 84–8.

Brantley WA, Cai Z, Foreman DW, Mitchell JC, Papazoglou E, Carr AB (1995) X-ray diffraction studies of as-cast high-palladium alloys. *Dental Materials* **11**, 154–60.

Brantley WA, Cai Z, Papazoglou E *et al.* (1996) X-ray diffraction studies of oxidized high-palladium alloys. *Dental Materials* **12**, 333–41.

Bye GC (1999) *Portland Cement Composition, Production and Properties*, 2nd edn. UK: Thomas Telford Limited.

Cullity BD, Stock SR (2001) *Elements of X-ray Diffraction*, 3rd edn. London, UK: Prentice-Hall International.

Fischer EJ, Arens DE, Miller CH (1998) Bacterial leakage of mineral trioxide aggregate as compared with zinc-free amalgam, intermediate restorative material, and Super-EBA as a root-end filling material. *Journal of Endodontics* **24**, 176–9.

Ford TR, Torabinejad M, Abedi HR, Bakland LK, Kariyawasam SP (1996) Using mineral trioxide aggregate as a pulp capping material. *Journal of the American Dental Association* **127**, 1491–4.

Fridland M, Rosado R (2003) Mineral Trioxide Aggregate (MTA), solubility and porosity with different water-to-powder ratios. *Journal of Endodontics* **19**, 814–7.

Funteas UR, Wallace JA, Fochtman EW (2003) A comparative analysis of MTA and Portland cement. *Australian Endodontic Journal* **29**, 433–4.

Hayashi M, Shimizu A, Ebisu S (2004) MTA for obturation of mandibular central incisors with open apices: case report. *Journal of Endodontics* **30**, 120–2.

Lee ES (2000) A new mineral trioxide aggregate root-end filling technique. *Journal of Endodontics* **26**, 764–5.

Lee YL, Lee BS, Lin FH, Yun Lin A, Lan WH, Lin CP (2004) Effects of physiological environments on the hydration behavior of mineral trioxide aggregate. *Biomaterials* **25**, 787–93.

Ohno H, Kanzawa Y, Takanohashi S (1983) State analysis of iron oxides formed on gold alloys for porcelain-metal bonding by an X-ray microanalyzer. *Dental Materials* **2**, 179–91.

Pitt Ford TR, Torabinejad M, McKendry DJ, Hong CU, Kariyawasam SP (1995) Use of MTA aggregate for the repair of furcal perforations. *Oral Surgery, Oral Medicine, Oral Pathology, Oral Radiology and Endodontics* **79**, 756–63.

Powder Diffraction File (2004) *Search Manual. PDF-2 Release International Centre for Diffraction Data*. Pennsylvania, USA: Powder Diffraction File.

Saidon J, He J, Zhu Q, Safavi K, Spangberg LS (2003) Cell and tissue reactions to mineral trioxide aggregate and Portland cement. *Oral Surgery, Oral Medicine, Oral Pathology, Oral Radiology and Endodontics* **95**, 483–9.

Schwartz RS, Mauger M, Clement DJ, Walker WA III (1999) Mineral trioxide aggregate: a new material for endodontics. *Journal of the American Dental Association* **130**, 967–75.

Torabinejad M, Watson TF, Pitt Ford TR (1993) Sealing ability of a mineral trioxide aggregate when used as a root end filling material. *Journal of Endodontics* **19**, 591–5.

Torabinejad M & White DJ (1995) *United States Patent 5,415,547 USPTO Patent full Text and Image Database.*

Torabinejad M, Hong CU, Pitt Ford TR, Kettering JD (1995a) Cytotoxicity of four root end filling materials. *Journal of Endodontics* **21**, 489–92.

Torabinejad M, Smith PW, Kettering JD, Pitt Ford TR (1995b) Comparative investigation of marginal adaptation of mineral trioxide aggregate and other commonly used root-end filling materials. *Journal of Endodontics* **21**, 295–9.

Torabinejad M & White DJ (1998) *United States Patent 5,769,638 USPTO Patent Full Text and Image Database.*

Torabinejad M, Ford TR, Abedi HR, Kariyawasam SP, Tang HM (1998) Tissue reaction to implanted root-end filling materials in the tibia and mandible of guinea pigs. *Journal of Endodontics* **24**, 468–71.

Walenta G, Fullman T (2004) Advances in quantitative XRD analysis for clinker, cements, and cementious additions. *Powder Diffraction* **19**, 40–4.