Susceptibility to localized corrosion of stainless steel and NiTi endodontic instruments in irrigating solutions

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Abstract

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Aim To evaluate the pitting and crevice corrosion characteristics of stainless steel (SS) and NiTi endodontic files in R-EDTA and NaOCl irrigating solutions.

Methodology The corrosion behaviour of two H-files produced from different SS alloys (Mani, AISI 303 SS, Dentsply Maillefer, AISI 304 SS) and one file produced from NiTi alloy (Maillefer) was determined in R-EDTA and NaOCl irrigating solutions by the cyclic potentiodynamic polarization method. The cutting flutes of 12 files of each material were embedded in an epoxy resin, polished, exposed to the irrigating solutions and used as an electrode. An Ag/AgCl electrode was used as a reference, a platinum plate was used as a counter electrode and polarization curves were obtained for all files in R-EDTA and NaOCl irrigating solutions in 37 °C with a potential scan rate of 5 mV min^{-1}. Corrosion potential (E_{corr}), Corrosion current density (I_{corr}) and Pitting potential (E_{pit}) were calculated from each curve. The results were statistically analysed with two-way ANOVA and Student-Newman-Keuls (SNK) multiple comparison test with materials and irrigating solutions serving as discriminating variables ($a = 0.05$).

Results Cyclic polarization curves presented negative hysteresis implying that pitting or crevice corrosion are not likely to occur for all the materials examined in both irrigating solutions. In NaOCl all materials showed significantly higher E_{corr} ($P = 0.011$) as well as lower I_{corr} compared with R-EDTA reagent. Moreover, all materials demonstrated equal E_{pit} in NaOCl, which was to be found significantly lower ($P = 0.009$) than the value of E_{pit} in R-EDTA.

Conclusions None of the tested materials is susceptible to pitting or crevice corrosion in R-EDTA and NaOCl solutions and from this standpoint are appropriate for the production of endodontic files.

Keywords: corrosion, NiTi files, stainless steel files.

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Introduction

Intracanal fracture of endodontic files during chemomechanical preparation of root canals may jeopardize the outcome of endodontic therapy (Grossman 1969, Cohen & Burns 1984, Ingle 1984, Lambrianidis 2001).

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Information on the failure process of stainless steel (SS) endodontic files has been gained by a limited number of *in vivo* studies. These studies concern K-files (Sotokawa 1988) and H-files (Zinelis & Margelos 2002), which were retrieved after clinical use; the conclusions were that metal fatigue is the primary failure mechanism under clinical conditions. The fatigue failure mechanism has been also adopted for NiTi instruments (Yared *et al.* 2000, Gambardini 2001), although limited studies based on *in vivo* data imply that fracture occurs due to a sudden overloading rather than a progressive fatigue process (Zinelis &

Margelos 2001, 2003). Fracture caused by fatigue failure mechanism occurs due to crack initiation at the cutting surfaces and propagation toward the file's axial centre (Sotokawa 1988, Kuhn *et al.* 2001, Zinelis & Margelos 2001). Although, there are no reports in the literature about corrosion failure of files, it is likely that pitting or crevice corrosion might occur first and promote fatigue failure altering the fracture mechanism from conventional fatigue failure to corrosion fatigue (Sprowls 1987). Corrosion mechanism might be activated during chemomechanical preparation, chemical disinfection or sterilization. Although the corrosion behaviour of several materials used for file manufacture has been studied in different irrigating solutions (Speck & Fraker 1980, Edie *et al.* 1981, Mueller 1982, Rondelli 1996, Stratovetsky *et al.* 1998, Stokes *et al.* 1999, Dartar Öztan *et al.* 2002, Gurappa 2002), data regarding the potential of pitting or crevice corrosion of endodontic files are deficient.

The aim of the present work was to evaluate and compare the electrochemical behaviour and the potential of pitting and crevice corrosion of representative SS and NiTi files when immersed in two commonly used irrigating solutions (NaOCl and R-EDTA).

Materials and methods

Twelve files (ISO size 25) from each company listed in Table 1 were used. The files of each company are made of three different alloys (AISI 303 and AISI 304 SS and NiTi) as presented in Table 1. The irrigating solutions used were 5.25 wt% NaOCl with a pH 10.6 and 17 wt% R-EDTA solution with a pH 7.5; both solutions were prepared before testing. For each solution, six different files of each material were tested in order to evaluate their corrosion behaviour.

The apparatus and the polarization cell conformed to ASTM G5-94 standards. An Ag-AgCl electrode was used as a reference and a platinum plate as an auxiliary counter electrode. The files were embedded along their longitudinal axis in an epoxy resin with good edge retention and were wet polished with SiC papers up to 1000 grits. The latter ensures that all the surfaces have the same roughness, which is a critical parameter in measuring corrosion behaviour (Stratovetsky *et al.* 1998). The size of the exposed area after polishing was measured using an optical microscope and an image analysis procedure.

The corrosion behaviour of files was determined electrochemically by cyclic potentiodynamic polarization, which is capable of measuring localized corrosion susceptibility of iron- and nickel-based alloys (ASTM G61-81). The solutions were heated to 37 °C and this temperature was held until the end of the tests. Before testing, the specimens were cleaned in an ultrasonic bath with distilled water and were left to dry. Then, they were placed in the polarization cell for 1 h before initiating polarization. Polarization curves were obtained with a potential scan rate of 5 mV min^{-1} by using a potentiostat (Versa Stat II; EG & G Instruments, Princeton, TN, USA). The corrosion parameters determined from the cyclic potentiodynamic polarization curve are shown schematically in Fig. 1. The results were statistically analysed with two-way ANOVA and the SNK multiple comparison test, with material (SS AISI 303, SS AISI 304 and NiTi) and irrigating solutions (R-EDTA and NaOCl) serving as discriminating variables ($a = 0.05$).

Table 1 Lot numbers and alloy type for all materials tested

Manufacturer	ISO no.	Lot no.	Alloy type
Mani, Tochigi-Ken, Japan	15-40	5980180400	AISI 303
Dentsply, Maillefer, Ballalgues, Switzerland	15-40	377632	AISI 304
Dentsply, Maillefer, Ballalgues, Switzerland	15-40	348527	NiTi

Results

Figure 2(a–c) presents typical cyclic polarization curves of AISI 303, AISI 304 and NiTi, respectively, in

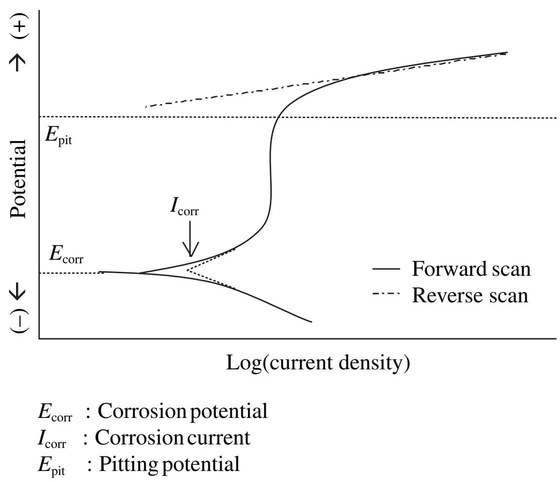

Figure 1 Corrosion parameter obtained by a cyclic potentiodynamic polarization curve.

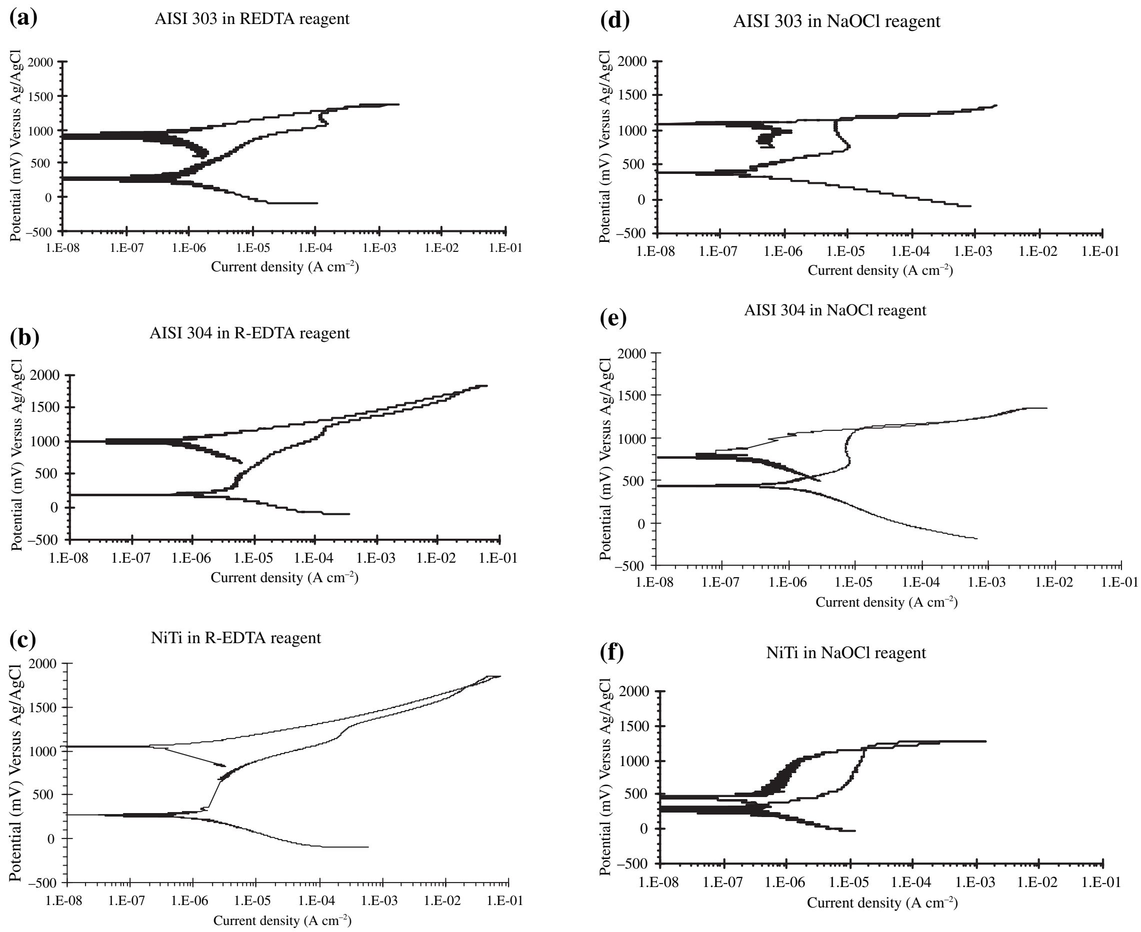

Figure 2 Representative cyclic polarization curves of tested materials, in R-EDTA (a–c) and NaOCl (d–f) irrigating solutions.

R-EDTA, whilst Fig. 2(d–f) presents the cyclic polarization curves of the same materials in NaOCl reagent. It can be observed that all the polarization curves showed negative hysteresis as in the reverse anodic scan the current density was less than that for the forward scan. Figure 3 demonstrates the mean value and standard deviations for E_{corr}, I_{corr} and E_{pit} obtained for all materials tested in R-EDTA and NaOCl irrigating solutions. Significant differences were found for E_{corr}, between AISI 303 and AISI 304 in R-EDTA, whilst significant differences were located amongst all materials in NaOCl. However, all materials showed significantly higher E_{corr} in NaOCl (Fig. 3a) reagent as well as lower I_{corr} (Fig. 3b). Only AISI 303 and NiTi depicted significantly equal I_{corr} in NaOCl. Moreover, all materials demonstrated equal but significantly lower E_{pit} in NaOCl compared with that in R-EDTA (Fig. 3c), whilst AISI 303 demonstrated lower E_{pit} than NiTi in R-EDTA. For all measured variables, there was no statistically significant interaction between materials and irrigating solutions.

Discussion

ISO 3630-1 (1992) states that endodontic files should be made from plain carbon steel or SS without any other specific requirements regarding the alloy type. Unfortunately there is no available information for the type of SS currently used in the production of endodontic files. However, recent studies with EDS analysis (Darabara *et al.* 2003) pointed out that only two types of SS alloys are currently used for the production of endodontic files and for this reason the specific endodontic files were selected as representative of AISI 303 (17–19Cr, 8–10Ni, max 2 Mn, max 1 Si and 0.6 Mo, all in wt%) and AISI 304 (18–20Cr, 8–10.5Ni, max 2 Mn, max 1 Si, all in wt%) SS alloys (Table 1).

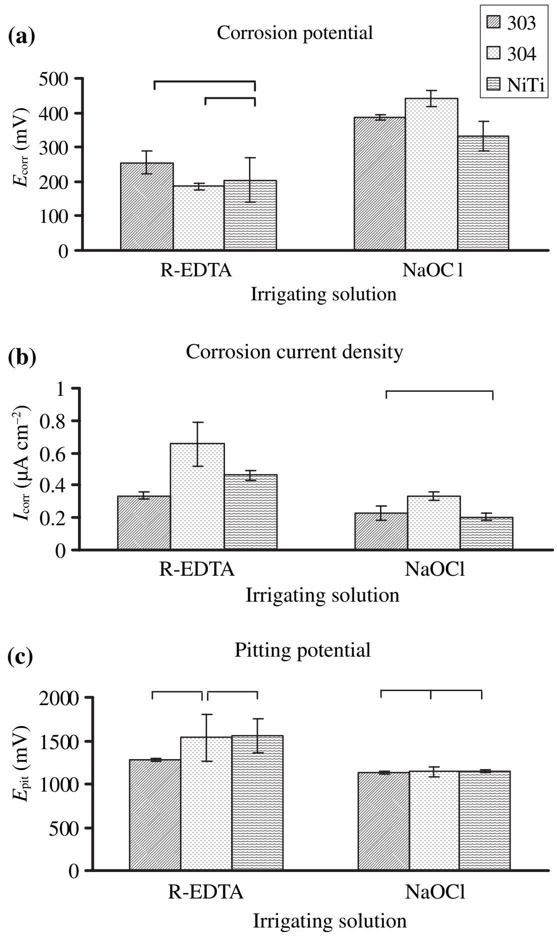

Figure 3 Corrosion parameters, obtained from the cyclic potentiodynamic polarization curves shown in Fig. 2. (a) Corrosion potential (E_{corr}), (b) corrosion current density (I_{corr}) and (c) pitting potential (E_{pit}). Bars connect mean values without statistical significant differences ($P = 0.05$).

Generally, E_{corr} value is indicative for the ionization tendency of materials in specific media. The ionization tendency is decreased towards higher E_{corr} values. According to the results of this study all materials demonstrated higher E_{corr} in NaOCl compared with R-EDTA accompanied with lower corrosion rate (I_{corr}) in the same reagent. These differences should be attributed to the lower pH of R-EDTA (7.5) compared with NaOCl (10.6), behaviour that has also been recorded for a variety of precious, semiprecious and base dental alloys (Bayaramoglu *et al.* 2002). Nevertheless, the lower corrosion rate I_{corr} of all materials tested in NaOCl is in contrast with the findings of Dartar Öztan *et al.* (2002) for SS K files. However, these differences are likely to be related to the fact that in this study a laboratory fresh made reagent was used compared with a commercially available solution used in the study of Dartar Öztan *et al.* (2002). Ordinarily, NaOCl is ionized in Na^+ and OCl^- (Daumer *et al.* 2000) and thus does not contain Cl^- as erroneously reported in previous studies (Dartar Öztan *et al.* 2002). This is also corroborated by the basic pH of this reagent. However, storage of stock solutions even for short periods (3–4 months) leads to the decomposition of NaOCl to Cl^- increasing the reactivity of the reagent (Sidgwick 1950, Sneed *et al.* 1954, Downs & Adams 1973). In general, a yellowing of the solution could identify decomposition of NaOCl. Previous studies reported that caution should be exercised when using NaOCl, as even new solutions demonstrated signs of decomposition (Daumer *et al.* 2000).

In standard potentiodynamic polarization tests, pitting resistance is evaluated by the type of hysterisis in reverse scan and pitting potential (E_{pit}) (Ralph *et al.* 1987). Figure 2 demonstrates that all the cyclic polarization curves present negative hysteresis, implying that pitting or crevice corrosion is not likely to occur for all the materials examined in both irrigating solutions. The passive film formed on the surface of the specimens is protective and self-healing. So in the case where a preexisting crack tends to propagate, a protective film will be instantly developed, preventing further expansion of the crack due to pitting corrosion. E_{pit} represents conservative measures of anodic pitting tendency because it shows minimum potential below which pitting cannot be sustained.

Although all the examined materials present better values for E_{corr} and I_{corr} in NaOCl (Fig. 3) the pitting potential (E_{pit}) in R-EDTA reagent was extended to higher potential values compared with NaOCl, meaning that the passive film formed is more stable and durable in an R-EDTA environment. This may be attributed in turn to the ability of R-EDTA to form complexes with metal ions (i.e. Fe, Ni, Cr, Co, etc.) at low pH values (<4) that is attained in the pit (Reinhard *et al.* 1992) promoting the passivation. Another explanation could be that the large molecules of R-EDTA have greater difficulty in concentrating and orienting the pit so as to increase the acidity to adequate values for trigger corrosion.

AISI 303 and AISI 304 demonstrated equal pitting resistance in NaOCl (Fig. 3) although it would be expected that AISI 303 should have higher pitting resistance than AISI 304 due to the presence of small quantities of Mo (<0.6 wt%) (Ralph *et al.* 1987, Davis

2000) which in combination with Cr is very effective in terms of stabilizing the passive film in the presence of Cl^-, increasing the resistance to the initiation of pitting and crevice corrosion. However, as mentioned above, NaOCl reagent does not contain Cl^- and thus the beneficial effect of Mo is eliminated.

The results of this study for the high corrosion resistance of SS agree with previous findings that continuous irrigation and prolonged contact with 2.5% NaOCl does not corrode SS files (Eicher *et al.* 1976, Scott & Walton 1986). The high corrosion resistance of SS and NiTi alloys in specific irrigating solutions are also in accord with the clinical observation where mechanical rather than corrosive reasons are responsible for file failure (Zinelis & Margelos 2002, 2003). In addition, the results of this study suggest that crack propagation cannot be accelerated by the combined action of stresses and corrosion for the specific alloys in R-EDTA and NaOCl irrigating solutions. In conclusion, the AISI 303, AISI 304 and NiTi alloys easily withstand the corrosive attack of R-EDTA and NaOCl and from this standpoint they are appropriate for use in endodontic files.

Conclusions

Pitting or crevice corrosion of endodontic files are not likely to occur in R-EDTA and NaOCl irrigating solutions whilst all the examined materials showed higher pitting resistance in R-EDTA irrigating solution. Both stainless steel and the NiTi alloys demonstrate high corrosion resistance in NaOCl and R-EDTA irrigating solutions.

References

Annual Book of ASTM Standards (1999a) Standard reference test method for making potentiostatic and potentiodynamic anodic polarization measurements (G5-94). In: Allen RF, Baldini NC, Donofrio PE, *et al. 03.02 Wear and Erosion; Metal Corrosion*. Easton, MD, USA: ASTM, pp. 54–64.

Annual Book of ASTM Standards (1999b) Standard test method for conducting cyclic potentiodynamic polarization measurements for localized corrosion susceptibility of iron-, nickel-, or cobalt-based alloys (G61-86). In: *03.02 Wear and Erosion; Metal Corrosion*. Easton, MD, USA: ASTM, pp. 237–41.

Bayaramoglu G, Alemdaroglu T, Kedici S, Aksut A (2002) The effect of pH on the corrosion of dental metal alloys. *Journal of Oral Rehabilitation* **27**, 563–75.

Cohen S, Burns RC (1984) *Pathways of the Pulp*, 3rd edn. St Louis, MO: CV Mosby Co., pp. 804–6.

Darabara M, Bourithis L, Zinelis S, Papadimitriou GD (2003) Assessment of elemental composition, microstructure and hardness of K and H endodontic files and reamers. *Journal of Endodontics* **30**, 523–6.

Dartar Öztan M, Akman AA, Zaimoglu L, Bilgiç S (2002) Corrosion rates of stainless-steel files in different irrigating solutions. *International Endodontic Journal* **35**, 655–9.

Daumer K, Khan A, Steinbeck M (2000) Chlorination of pyridinium compounds. *The Journal of Biological Chemistry* **44**, 34681–92.

Davis JR (2000) *Corrosion: Understanding the Basics*. Materials Park, OH, USA: ASM International, p. 359.

Downs AJ, Adams CJ (1973) In: Bailar JC, Emeleus HJ, Nyholm R, Trotman-Dickenson AF eds. *Comprehensive Inorganic Chemistry*. Oxford, UK: Pergamon Press, pp. 1400–8.

Edie JW, Andreasen FG, Zaytoun PM (1981) Surface corrosion of nitinol and stainless steel under clinical conditions. *The Angle Orthodontist* **51**, 319–24.

Eicher MA, Schoen DM, Goldman M, Kronman JH (1976) Effect of protein and sodium hypoclorite on endodontic instruments. *Journal of Endodontics* **2**, 335–8.

Gambardini G (2001) Cyclic fatigue of nickel-titanium rotary instruments after clinical use with low- and high-torque endodontic motors. *Journal of Endodontics* **27**, 772–4.

Grossman LI (1969) Guidelines for the prevention of fracture of root canal instruments. *Oral Surgery* **28**, 746–52.

Gurappa I (2002) Characterization of different materials for corrosion resistance under simulated body fluid conditions. *Materials Characterisation* **49**, 73–9.

Ingle JI (1984), *Endodontics*, 2nd edn. Philadelphia: Lea and Febiger, pp. 606–8.

ISO 3630-1 (1992) *Dental Root-Canal Instruments. Part 1: Files, Reamers, Barder Broaches, Rasps, Paste Carries, Explorers and Cotton Broaches*, 1st edn. Geneva: International Organization for Standardization.

Kuhn G, Tavernier B, Jordan L (2001) Influence of structure on nickel-titanium endodontic instruments failure. *Journal of Endodontics* **27**, 516–20.

Lambrianidis T (2001) *Risk Management in Root Canal Treatment*, 1st edn. Thessaloniki, Greece: University Studio Press, pp. 205–39.

Mueller HJ (1982) Corrosion determination techniques applied to endodontic instruments – irrigating solutions systems. *Journal of Endodontics* **8**, 246–52.

Ralph MD, DeBold T, Johnson MJ (1987) Corrosion of stainless steel. In: Davis JR ed. *Corrosion*. Materials Park, OH, USA: ASM International, pp. 561–4.

Reinhard G, Radtke M, Rammelt U (1992) The role of the salts of weak acids in the chemical passivation of iron and steel in aqueous solutions. *Corrosion Science* **33**, 307–13.

Rondelli G (1996) Corrosion resistance tests on NiTi shape memory alloy. *Biomaterials* **17**, 2003–8.

Scott GL, Walton RE (1986) Ultrasonic endodontics: the wear of instruments with usage. *Journal of Endodontics* **7**, 279–83.

Sidgwick NV (1950) *The Chemical Elements and Their Compounds*. Oxford, UK: Clavendon Press, pp. 1213–6

Sneed MC, Maynard JL, Brasted RC (1954) *Comprehensive Inorganic Chemistry*. New York, NY, USA: Van Nostrad Co., Inc., pp. 152–5.

Sotokawa T (1988) An analysis of clinical breakage of root canal instruments. *Journal of Endodontics* **14**, 75–82.

Speck MK, Fraker CA (1980) Anodic polarization behavior of Ti-Ni and Ti-6Al-4V in simulated physiological solutions. *Journal of Dental Research* **59**, 1590–5.

Sprowls DO (1987) Evaluation of corrosion fatigue. In: Davis JR ed. *Corrosion*. Materials Park, OH, USA: ASM International, pp. 291–3.

Stokes OW, Di Fiore PM, Barss JT, Koerber A, Gilbert JL, Lautenschlager R (1999) Corrosion in stainless-steel and nickel-titanium files. *Journal of Endodontics* **25**, 17–20.

Stratovetsky D, Khaseler O, Yahalom J (1998) Corrosion behaviour of heat-treated intermetallic titanium-nickel in hydrochloric acid solutions. *Corrosion* **54**, 524–30.

Yared GM, Bou Dagher FE, Machtou P (2000) Cyclic fatigue of Profile rotary instruments after clinical use. *International Endodontic Journal* **33**, 204–7.

Zinelis S, Margelos J (2001) Assessment of fracture mechanism of endodontic files. In: Lambrianidis T ed. *Risk Management in Root Canal Treatment*, 1st edn. Thessaloniki, Greece: University Studio Press, pp. 239–43.

Zinelis S, Margelos J (2002) Failure mechanism of Hedstroem endodontic files in vivo. *Journal of Endodontics* **28**, 471–3.

Zinelis S, Margelos J (2003) In vivo aging of endodontic instruments and materials. In: Eliades G, Eliades T, Brantley WA, Watts DC eds. *Dental Materials In Vivo: Aging and Related Phenomena*, Chapter 11, 1st edn. New York, NY, USA: Quintessence, pp. 179–92.

