# Quantitative and Qualitative Elemental Analysis of Different Nickel–Titanium Rotary Instruments by Using Scanning Electron Microscopy and Energy Dispersive Spectroscopy

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## Abstract

This study was designed to determine if the alloy composition shares an influence with the geometric design on the physical behavior of nickel-titanium rotary endodontic instruments. ProTaper, HERO, and K3 files were selected. After sterilized and cleaning with alcohol, surface analysis was performed using energy dispersive spectroscopy. Measurements were performed on the active part and on the shank. SEM images of fractured instruments were also obtained and assessed. All three types of instruments were composed mainly of Nickel (54.3%, SD ± 0.8) and Titanium (45.2%, SD ± 0.9). SEM images revealed similar aspect with the presence of Kirkendall voids regularly distributed in the alloy. The results indicate that the difference in properties and behavior of these three endodontic rotary shaping instruments is solely related to the respective geometric characteristics of the instrument design. *(J Endod 2008;34:53–55)*

## Key Words

Elemental composition, energy dispersive spectroscopy, Kirkendall effect, nickel-titanium

Titanium has been suggested as biomaterial for medical purposes since the 1960s, and nickel-titanium alloys have since been designed, developed, and tested for medical and dental applications because of their biocompatibility, strength, and ductility [1, 2]. Nickel-titanium alloys can exhibit the well-known shape memory effect and superelastic behavior [3, 4] through their unique reversible phase transition between the low-temperature martensite phase and the high-temperature austenite phase. Nickel-titanium hand files were first introduced by Walia et al. (5), but the alloy is presently mostly used to manufacture rotary endodontic instruments. On the basis of their superelastic properties, nickel-titanium rotary instruments are described as being able to maintain the original canal shape without creating severe irregularities such as zip, ledge, or perforation, particularly in narrow curved canals (6–8). An increasing number of nickel-titanium rotary file systems are currently available and possess unique design properties in terms of cross-sectional shape, taper, the number and angle of flutes, and so forth. Furthermore, these instruments are intended to reduce procedural steps and treatment time (9–11). Commercially presented as having similar properties, such instruments present major differences in their clinical behavior as reported by many studies (12–14). Although nickel-titanium alloys are described by Thompson [15] as containing approximately 56% nickel and 44% titanium, no studies comparing the elemental composition of the alloys of the different marketed systems exist, and little or no information is available on their metallurgical composition; each manufacturer understandably keeps their manufacturing processes secret. As a direct result, it is not known whether the differences in physical characteristics of these instruments are solely related to their geometric design, or whether these differences are influenced by their metallurgic composition as well. If the metal composition of such files is identical, then the difference between them would be directly associated to their design characteristics. The aim of this study was to determine whether the alloy composition shares an influence with the geometric design on the physical behavior of nickel-titanium rotary endodontic instruments. The null hypothesis was that there is no difference between ProTaper, HERO, and K3 instruments with regards to qualitative and quantitative elemental composition.

## Materials and Methods

ProTaper (F2; Dentsply-Maillefer, Ballaigues, Switzerland), HERO (0.06-20; MicroMega, Grenoble, France), and K3 (0.06-25; SybronEndo, Orange, CA) nickel-titanium rotary endodontic shaping files representing 3 different brands were selected. Five nickel-titanium rotary shaping instruments were randomly selected for each brand from 5 boxes with different batch numbers. All the instruments that were selected were size 30 with a 0.06 taper, except for ProTaper. Because ProTaper has a variable taper, size F3 with a 0.30-mm tip size was chosen. The instruments were sterilized individually by using an autoclave (Statim; SciCan, Toronto, Canada; 3-minute cycle). They were placed in glass tubes containing 90% alcohol. One hour later, they were suspended in another tube containing absolute alcohol and vibrated in an ultrasonic bath for 15 minutes to remove any debris and obtain clean, noncontaminated surfaces. Instruments were mounted on the staging platform of a low-vacuum JSM-6360LV scanning electron

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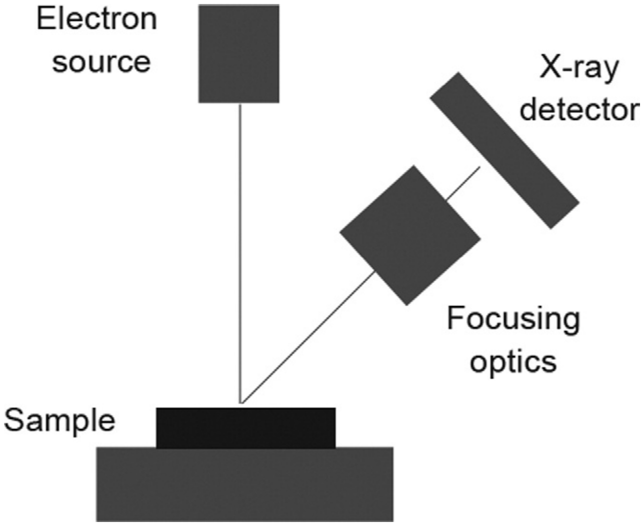

**Figure 1.** Schematic principle of energy dispersive spectroscopy. Energy dispersive x-ray spectroscopy (EDS) is a chemical microanalysis technique performed in conjunction with a scanning electron microscope (SEM). The technique uses x-rays that are emitted from the sample during bombardment by the electron beam to characterize the elemental composition of the analyzed volume. The EDS x-ray detector measures the number of emitted x-rays versus their energy. The energy of the x-ray is characteristic of the element from which the x-ray was emitted. A spectrum of the energy versus relative counts of the detected x-rays is obtained and evaluated for qualitative and quantitative determinations of the elements present in the sampled volume.

microscope (JEOL, Tokyo, Japan), and surface analysis was performed on each instrument with energy dispersive spectroscopy (Energy Dispersive Spectroscopy JEOL-EDS System, ISIS System; Oxford Instruments, Japan) (Fig. 1). The standards used were aluminum, titanium, and nickel. Measurements were performed on 2 locations for each instrument, halfway on the active part and 2 mm from the active part on the shank. Furthermore, high-resolution scanning electron microphotographs of the section of instruments fractured by cyclic fatigue loading in a steel phantom about 3 mm from the tip were taken at 1000× magnification.

## Results

Energy dispersive spectroscopy analysis gave the composition of the samples in percent of elements detected (Table 1). When compared with the expected composition of the alloy (nickel, 55% and titanium, 45%), no significant differences could be found with the Pearson $\chi^2$ test. All 3 types of instruments were composed mainly of nickel (54.3%; standard deviation, 0.8) and titanium (45.2%; standard deviation, 0.9). Traces of aluminum were detected in all samples at the shank level and for the HERO instruments at the flutes level as well. Traces of silicon were detected in the HERO instruments at the shank level. Scanning electron microscopy images revealed similar aspect, with the presence of voids regularly distributed in the alloy. The large standard deviation calculated for trace elements is explained by the fact that they were not present in all samples.

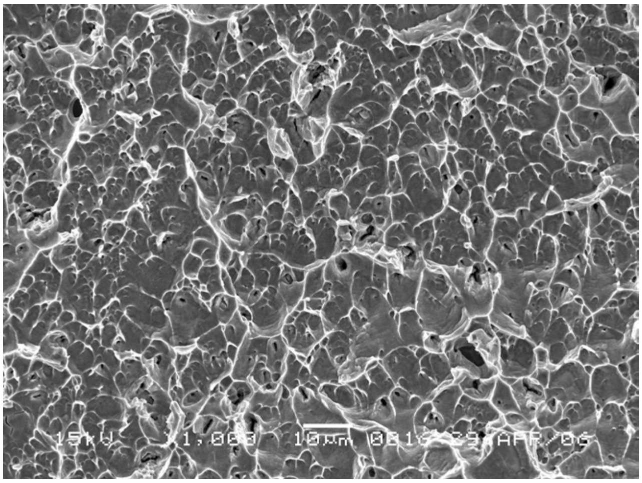

**Figure 2.** Scanning electron microscopic view of fractured surface of ProTaper instrument showing shallow dimples (characterizing a ductile fracture pattern) and Kirkendall porosities of different size and shapes. Scanning electron micrographs of HERO and K3 instruments showed similar aspect.

## Discussion

Differences in physical properties between endodontic instruments might be related to either the metal itself or to the design features. This study was designed to assess the atomic composition of 3 different types of nickel-titanium endodontic rotary instruments. Because there was no difference, the null hypothesis was accepted.

Similar if not identical fabrication processes of nickel-titanium alloys are understandable because transformation temperatures of these alloys are extremely sensitive to a small variation in nickel or titanium concentration. For alloys having greater than 55.0 weight percent nickel, a one weight percent deviation in nickel (or titanium) concentration will result in approximately a 100°C shift in transformation temperatures. This extreme sensitivity puts a strict requirement on any melting practice to tightly control the nickel/titanium ratio to meet the required tolerance in transformation temperatures (16). Because nickel-titanium alloys cannot be cold worked because they work harden rapidly, round wires are produced by die drawing processes. In this aspect, they require multiple reductions and frequent interpass annealing at 600°–800°C until the final dimension is obtained (16).

The traces of aluminum detected near the shank are probably due to the final assembly of the files during which the machined nickel-titanium file is yanked under pressure in the aluminum-made shank. The traces of silicon might be due to the presence of silicone stoppers as for the 3 brands tested; silicone stoppers were provided from the manufacturer and were already fitted on the files.

It is noteworthy that the scanning electron microphotographs of the fractured section of these instruments showed the same aspect

**TABLE 1.** Mean Elemental Composition (Standard Deviation) in Percent at Flutes Level (f) and Shank Level (s) for ProTaper, HERO, and K3

| Element | ProTaper (f) | ProTaper (s) | HERO (f) | HERO (s) | K3 (f) | K3 (s) |
|---|---|---|---|---|---|---|
| Si | | | 0.0 (0.0) | 0.2 (0.3) | | |
| Al | | 0.2 (0.1) | 0.1 (0.2) | 0.5 (0.4) | | 0.2 (0.2) |
| Ti | 45.2 (0.5) | 44.8 (0.5) | 44.9 (0.4) | 46.7 (0.1) | 45.2 (0.2) | 45.1 (0.1) |
| Ni | 54.8 (0.5) | 55.0 (0.4) | 54.7 (0.2) | 54.1 (0.7) | 55.1 (0.5) | 53.1 (0.2) |

The high standard deviation for Si and Al is due to the fact that these traces were not present in all samples.

at high magnification (Fig. 2). An interesting point is the presence of small voids regularly distributed in the bulk of the material. These voids are very possibly due to the manufacturing process, because when melting the elemental nickel and titanium ingots, the speed of diffusion of nickel atoms into the titanium is different from that of titanium atoms inside the nickel. This accounts for the presence of voids known as Kirkendall porosities (or Kirkendall effect) (17). Because the size and distribution of these voids are characteristic of the metallurgical process, the presence of similar voids in all 3 types of instruments would indicate that their alloys underwent similar fabrication processes (18). These voids seem to play an important role in the mechanical behavior of instruments. Nagumo (19) indicated that hydrogen can be absorbed into the alloy from oral liquids, then diffused through interstitial sites, dislocations, and grain boundaries, and reacted with lattice atoms to form hydride phases, stable at room temperature and considered to be the cause of hydrogen embrittlement. Asaoka et al. (20) also reported that the diffusion of hydrogen through the nickel-titanium alloys forms brittle hydride phases in the vicinity of the alloy surface. Furthermore, because the thickness of the brittle hybrid layer is not uniform, microcracks are formed on the surface when abrasion is induced by external force or when deformation is forced. Because the hydrogen is easily concentrated at the crack tips and forms brittle hydrides, this deterioration is effective in developing cracks in the alloy. Thus, the adsorption of hydrogen might be a highly important factor in determining the service life of the alloy in biologic circumstances (20). This could possibly not be very relevant during regular clinical use because this mechanism might not have adequate time to produce damage; however, it might be of importance during cleaning and sterilization procedures where the instrument is in contact with ionized fluids for extended periods of time. Further research is required to determine the extent of hydrogen uptake by nickel-titanium instruments during sterilization procedures.

Differences in physical properties between endodontic instruments might be related to either the metal itself or to the design features. Within the limitations of this study, the results seem to indicate that the difference in properties and behavior of these 3 endodontic rotary shaping instruments is solely related to the respective geometric characteristics of the instrument design, whether cross-section aspect, helical angle, pitch, number of blades, or cutting angle.

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