Natural radioactivity in zirconia-based dental ceramics.

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Abstract. Zirconia-based ceramics are being increasingly used in dental prosthetics in substitution of metal cores, which are known to induce local toxic reactions and delayed allergic responses in the oral tissues. Some concerns have been however raised about the use of zirconia, since it is known that unpurified zirconia materials may contain non negligible levels of natural radionuclides of the U/Th series. Combined measurements of alpha and gamma spectrometry as well as beta dosimetry were conducted on zirconia samples used for dental applications. Samples were available in form of powder and/or solid blocks. The results showed that the beta dose rate in zirconia ceramics was on average only slightly higher than the levels measured in natural teeth, and generally lower than the values measured in feldspatic and glass ceramics. These materials are indeed known to deliver a beta dose significantly higher than that measured from natural teeth, due to the relatively high levels of $^{40}\text{K}$ (between 2 and 3 kBq·kg$^{-1}$). The content of radionuclides of the U/Th series in the zirconia sample was estimated to be lower than 15 Bq·kg$^{-1}$, i.e. doubtlessly below the exclusion level of 1 kBq·kg$^{-1}$ recommended by IAEA in the Safety Standard Series. Beta dosimetry measurements, however, gave indications of possible inhomogeneous clusters of radioactivity, which might give rise to local doses above the background.

KEYWORDS: beta dosimetry, uranium, thorium, dental ceramics, zirconia.

1. Introduction

Feldspathic and glass ceramics are widely used restorative materials in dental prosthetics due to their consistency and aesthetic properties [1, 2]. However, due to their inherent brittleness, ceramics cannot withstand the elevated forces released during mastication. Therefore, they require coupling with a reinforcing layer (core), above which the porcelain teeth is modelled (veneer). Metal-based frameworks are widely employed for the core, however they are known to induce delayed type hypersensitivity reactions and/or local toxic injuries in the oral tissues [3-5]. All-ceramic crowns, where the core is made with alumina (Al$_2$O$_3$) or zirconia (ZrO$_2$), have been developed in order to reduce the risks of such side effects. Concerns have been raised with regard to the potential radioactivity risk associated to the use of zirconia, since unpurified powders of this material are known to contain impurities of natural radionuclides of the secular chains of $^{235}\text{U}$, $^{238}\text{U}$ and $^{232}\text{Th}$ in non-negligible amounts [6-8].

This study presents measurements of beta dose and of gamma and alpha spectrometry in zirconia-based ceramics. The radioactivity content of these materials and the radiological hazard associated with their use are discussed, also in relation with the results of the previous studies on common dental porcelains.

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2. Materials and Methods

2.1 Samples

Several specimens of three different brands of zirconia-based ceramics commonly available on the European market were analyzed. One material was obtained in solid form, in the shape both of disk and of cylinder, the two other materials were obtained in powder form.

2.2 Alpha spectrometry

For alpha spectrometry, the samples were grinded and dissolved with concentrated hydrofluoric acid at 200 °C. Uranium and thorium were purified by anion exchange chromatography. \(^{235}\)U and \(^{232}\)Th were used as yield tracers. Prior to the radiochemical determination of \(^{230,232}\)Th and \(^{234,238}\)U the ceramic samples were grinded to a fine powder with a planetary mill. After the addition of \(^{232}\)U and \(^{229}\)Th tracers, 1.2 to 1.5 g of the powder were digested with 40% hydrofluorid acid at 220 °C for about two days. The residue was fumed at least three times with 70% perchloric acid to remove any fluoride. The residue was dissolved in 8 M nitric acid. The solution was passed through a Dowex 1X4 column. After washing with 8 M nitric acid, thorium isotopes were eluted with 9 M hydrochloric acid and uranium isotopes with 0.1 M hydrochloric acid/0.01 M hydrofluoric acid. After evaporation to dryness with nitric acid, thorium and uranium were electrodeposited from 0.15 M ammonium sulphate electrolyte (pH = 2.5). The alpha spectra were recorded with PIPS detector (600 mm\(^2\), Canberra, Rüsselsheim, Germany) and were evaluated with the software Interalpha (Canberra).

2.3 Beta dosimetry measurements

The powder samples were placed inside cylindrical polypropylene boxes. The dimensions of the boxes were chosen so that the powder layers were at least 3 mm thick, i.e. more than the range of beta particles with 1.3 MeV energy (the most energetic beta particles emitted by \(^{40}\)K). Three thermoluminescent detectors (TLDs) were positioned upon each sample. The TLDs used consisted of a thin layer of \(\alpha\)-Al\(_2\)O\(_3\):C grains arranged on a round aluminum backing with 6.5 mm diameter (Landauer Inc., USA). This experimental set-up guaranteed that the beta energy absorbed by the TL detectors was independent on the mass of the powder under investigation. The beta dose rates of the solid materials were determined placing the detectors directly upon the flat surfaces of the samples. The number of dosimeters used for each single specimen depended on its size and geometry.

Prior to their application, the dosimeters were annealed in an oven to a temperature of 400°C for approximately 15 minutes. Then the samples with the dosimeters were stored for approximately three months inside a lead–shielded cavity. A thin Mylar sheet (15 µm thickness) was put between sample and dosimeters in order to stop the alpha particles emitted by the sample surface. The contribution of the background gamma radiation inside the shield was evaluated by means of control measurements using pure (beta-free) quartz powder (Merck, Darmstadt, Germany) in the same configuration as that of the powder samples.

After storage, the glow curve of each detector was measured using a SOLARO dual channel TLD reader model 680 (Vinten Analytical Systems Ltd, Sandy, UK; heating rate 1°C/s, \(T_{\text{max}}\) 300 °C). The beta dose rate was calculated as described in [9].

2.4 Gamma spectrometry

Gamma spectrometry measurements were performed using a high-purity germanium detector (EG&G-Ortec Pop-Top HPGe). Powder samples were put into cylindrical containers of polypropylene (diameter 40 mm, height 30 mm), placed directly on the capsule of the detector and measured for approximately seven days. The environmental gamma contribution, including the one from the containers, was estimated by performing measurements of the empty boxes in the same geometry of the samples.
The quantification of the specific activity of the radionuclides inside the samples was obtained using IAEA-375 reference material [20] for the determination of the radionuclides of the uranium and thorium natural chains, and using KCl powder for the assessment of $^{40}$K activity concentration.

Gamma measurements were performed also for the solid samples. In this case, however, the samples had a different geometry than that of the standards, and therefore higher uncertainties were associated to the quantitative estimates of the specific activities. Nevertheless, the measurements in the solid samples provided qualitative information crucial for pointing out and identifying unusual levels of radioactivity.

3. Results

Table 1 reports the beta dose rates due to the different materials. The median estimates of the gross beta dose rates per unit area, measured at the surface of the zirconia samples, were in the range 0.011-0.026 mGy·y$^{-1}$·mm$^{-2}$, i.e. slightly higher than the natural background (0.0075±0.0009 mGy·y$^{-1}$·mm$^{-2}$) and lower than the typical values measured in feldspatic and glass porcelains (range 0.045-0.105 mGy·y$^{-1}$·mm$^{-2}$) [9]. However, the results varied widely among dosimeters placed side by side on the same sample, and in single cases differences of even nearly two order of magnitudes were observed. The ranges, mean and median values are given in Table 1. Figure 1 shows the frequency distribution of all the measurements with zirconia samples. It can be seen that the distribution was quite wide, with some very high results. This behaviour was typical only of zirconia specimens; the variations observed in other dental materials, including porcelains, alumina-based ceramics and resin-based composites, were less than 15% [9].

Figure 1: Frequency distributions of the beta dose rates per unit area measured at the surface of the zirconia samples.
Table 1: Gross beta dose rates per unit area measured at the surface of the zirconia samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Form</th>
<th>Range</th>
<th>Mean value</th>
<th>Median</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1a</td>
<td>Cylinder</td>
<td>0.01-0.06</td>
<td>0.021±0.018</td>
<td>0.014</td>
</tr>
<tr>
<td>Z1b</td>
<td>Disk</td>
<td>0.02-0.38</td>
<td>0.05±0.09</td>
<td>0.026</td>
</tr>
<tr>
<td>Z2</td>
<td>Powder</td>
<td>0.01-0.38</td>
<td>0.06±0.10</td>
<td>0.015</td>
</tr>
<tr>
<td>Z3</td>
<td>Powder</td>
<td>0.01-0.05</td>
<td>0.018±0.016</td>
<td>0.011</td>
</tr>
</tbody>
</table>

A tentative explanation of this behaviour was to assume an inhomogeneous distribution of beta emitters in the sample matrix, with the presence of localized clusters of radioactivity responsible for the high readings in selected detectors.

The beta dose in feldspathic and glass ceramics was shown to be mainly attributable to $^{40}$K, which is present in high concentrations in those materials (between 2 and $3\times10^3$ Bq·kg$^{-1}$); the content of $^{40}$K in zirconia samples was on the contrary not distinguishable from the background contribution. Therefore, the origin of the high doses should be attributed to other emitters.

As already mentioned before, high levels of radioactive impurities can be present in zirconia powders, but purified materials to be used in medical implants and dental prosthetics can reach specific activities lower than that of human bone [10]. If however some local highly active clusters have remained in the powder, their beta emissions could be the origin of the elevated doses measured (contribution due to alpha-particles were excluded on the basis of the experimental setup chosen). The concentrations of radionuclides of the U/Th series in the dental specimens are shown in Table 2.

Table 2: Natural radionuclides in the zirconia samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Form</th>
<th>$^{234}$U (Bq·kg$^{-1}$)</th>
<th>$^{238}$U (Bq·kg$^{-1}$)</th>
<th>$^{230}$Th (Bq·kg$^{-1}$)</th>
<th>$^{232}$Th (Bq·kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1b</td>
<td>Disk</td>
<td>6.2±1.5</td>
<td>5.7±1.4</td>
<td>7.3±2.5</td>
<td>1.7±1.1</td>
</tr>
<tr>
<td>Z2</td>
<td>Powder</td>
<td>8.8±1.7</td>
<td>9.9±1.8</td>
<td>1.0±2.9</td>
<td>2.6±1.4</td>
</tr>
<tr>
<td>Z3</td>
<td>Powder</td>
<td>6.3±1.3</td>
<td>6.2±1.3</td>
<td>8.5±3.7</td>
<td>6.0±4.2</td>
</tr>
</tbody>
</table>

The data confirm that the average content of these contaminants is well below the permitted levels. A limited number of smaller aliquots were taken from each sample, in order to check for possible inhomogeneous distributions of the contaminants. The results of the alpha spectrometry measurements conducted in these samples are shown in Figures 2 and 3. The variations between samples are moderate, and compatible with the experimental standard deviations.

Although no real systematic subsampling was conducted, and the number of specimens examined in this preliminary stage of the analysis was limited, the results gave no indication of possible formation of highly active clusters. The concentrations of the radionuclides of U/Th chains were lower than 15 Bq·kg$^{-1}$, comparable to those in other dental materials. It might be interesting to note that until the early 1980s it was common to add natural or depleted uranium to dental ceramics up to several thousands of Bq·kg$^{-1}$ in order to reproduce the colours and the fluorescence properties of the vital teeth [11, 12]. Although this practice has now been abandoned, nowadays dental porcelains still contain relevant amounts of $^{87}$Rb (about $1\times10^4$ Bq·kg$^{-1}$), in addition to the natural $^{40}$K, which is responsible for the elevated beta dose rates observed in those materials (approximately 10 times higher than those measured in natural teeth). In any cases all these concentrations are well below the recommended exclusion levels set by IAEA [13].
Figure 2: Variations of $^{234}$U concentration in several specimens of the same sample.

Figure 3: Variations of $^{238}$U concentration in several specimens of the same sample.
On the basis of the considerations above, it can be stated that persons with artificial teeth would not be exposed to a higher radiation risk from zirconia powders than from the current materials used. The controversial results of the beta dose evaluations require however a more specific investigation of their cause. A broader and more systematic investigation of the samples might help to confirm or deny the possible presence of locally concentrated radioactive clusters.

4. Conclusion

Zirconia ceramics do not seem to pose a greater radiological hazard than the more commonly used feldspatic and glass ceramics, and the radioactivity levels are well within the recommended exclusion levels. Anyway, patients with artificial teeth are in any case subject to higher dose levels than other members of the population, therefore further efforts should be taken to effectively reduce the content of natural radionuclides in dental ceramic materials.

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REFERENCES