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Elemental analysis of commercial zirconia dental implants - Is “metal-free” devoid of metals?

Christian Gross [a], Thomas Bergfeldt [b], Tobias Fretwurst [a], René Rothweiler [a], Katja Nelson [a], Andres Stricker [a,*]

[a] Department of Oral and Maxillofacial Surgery, University Medical Center Freiburg, Albert-Ludwigs-University of Freiburg, Hugstetter Str. 55, 79106, Freiburg im Breisgau, Germany

[b] Institute of Applied Materials, Applied Material Physics (IAM-AWP), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344, Eggenstein-Leopoldshafen, Germany

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ABSTRACT

Objectives: The interest in ceramic dental implants made of yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) or alumina toughened zirconia (ATZ) has increased in recent years. However, in the light of aging, corrosion, and potential impurities of zirconia ceramics, the material composition of these implants and the associated term “metal-free” is persistently questioned. Thus, the present study aimed to conduct an elemental analysis of commercial zirconia dental implants to specify their elemental composition and to identify contaminants.

Methods: Nine commercial zirconia dental implant systems and corresponding material samples were analyzed using inductively coupled plasma-mass spectrometry (ICP-MS) and optical emission spectrometry (ICP-OES).

Results: While the elemental composition was dominated by the main components Zr, Y and Al (in ATZ samples), all investigated samples contained impurities with Hf and contamination with alkali and alkali earth elements (Na, K, Mg, Ca), essential trace elements (e.g. Fe, Cu, Zn) but also potentially noxious metal elements (e.g. Ni, Cr). Furthermore, ultra-trace level contamination with the radionuclides U-238 and Th-232 was found in the majority of samples.

Significance: The results indicate that, although all the investigated Y-TZP and ATZ dental implants meet the currently relevant ISO standards and manufacturer’s specifications, from an elemental point of view, they are not devoid of metals. Due to the lack of a universal definition and thresholds for the term “metal-free”, the question of whether the examined zirconia dental implants can be holistically classified as “metal-free” or not remains a controversial, philosophical one.

1. Introduction

After decades of research and development, titanium dental implants are today a cornerstone of modern prosthetic restoration after tooth loss. Although titanium is still the material of choice for dental implants, it can trigger immunological reactions and, because of its greyish color, has aesthetic limitations, when the implant neck is exposed (Muller and Valentine-Thon, 2006; Sicilia et al., 2008; Osman and Swain, 2015; Cionca et al., 2017; Heydecke et al., 1999). Due to nascent demands for dental implant aesthetics and the request for metal-free restorations, the general interest in tooth-colored zirconia (zirconium dioxide, ZrO_2) ceramic dental implants has increased in recent years (Cionca et al., 2017). Numerous manufacturers now offer one- or two-piece zirconia implant systems, which are widely advertised as “metal-free”, as alternatives to titanium implants. Today’s zirconia dental implants commonly consist of yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) or aluminum oxide offset TZP (ATZ = Alumina Toughened Zirconia) ceramics (Osman and Swain, 2015; Cionca et al., 2017; Shenoy and Shenoy, 2010). In contrast to alumina (aluminum oxide, Al_2O_3) ceramics, which were used for the production of early ceramic dental implants and were associated with unsatisfactory survival rates (Steflik et al., 1995; Fartash and Arvidson, 1997), modern TZP ceramics feature

* Corresponding author.
E-mail addresses: christian.gross@uniklinik-freiburg.de (C. Gross), thomas.bergfeldt@kit.edu (T. Bergfeldt), tobias.fretwurst@uniklinik-freiburg.de (T. Fretwurst), rene.rothweiler@uniklinik-freiburg.de (R. Rothweiler), katja.nelson@uniklinik-freiburg.de (K. Nelson), andres.stricker@uniklinik-freiburg.de (A. Stricker).

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promising physico-mechanical properties, such as low thermal conductivity, improved flexural strength, and fracture toughness (Cionca et al., 2017; Chai et al., 2007; Yilmaz et al., 2007). Furthermore, it was shown that ceramic dental implants exhibit the same rate of osseointegration as titanium implants, good biocompatibility, and epithelial attachment, as well as low plaque accumulation (Depprich et al., 2008; Kohal et al., 2004; Roehling et al., 2018; Scarano et al., 2004). However, besides the widely advertised favorable properties of zirconia as a material for dental implants, there are increasing concerns about its material resistance and, above all, the hydrothermal aging with associated degradation (low-temperature degradation (LTD)) (Lughi and Sergo, 2010). As recent studies on LTD and corrosion of zirconia ceramics have shown that they are not 100% chemically stable (Lughi and Sergo, 2010; Thomas et al., 2016; Chevalier, 2006; Lawson, 1995; Lawson et al., 1995), questions arise about the composition of zirconia dental implants. Uncertainties are reinforced by discussions about the presence of elemental impurities in medical zirconia ceramics due to their natural origin (Bavbek et al., 2014; Porstendörfer et al., 1996; Piconi and Maccauro, 1999).

In nature, the element zirconium (Zr) occurs predominantly in the minerals zircon ($ZrSiO_4$) and baddeleyite (ZrO_2). Zircon is a by-product of titanium mining (ilmenite, rutile), whereas baddeleyite is a by-product of copper and uranium production (Piconi and Maccauro, 1999; Nielsen and Wilfing, 2010; Vagkopoulou et al., 2009). Thus, depending on the source, mining region, and subsequent processing of the zirconium-containing raw material, dental ceramics may be contaminated by various trace elements, such as heavy metals (metals with a specific density of more than 5 g/cm^3 (Järup, 2003)) and radionuclides (Nielsen and Wilfing, 2010; Vagkopoulou et al., 2009; Hurley and Fairbairn, 1957). As a consequence, dental zirconia ceramics are currently the subject of standardization, in particular by the International Organization for Standardization (ISO) standards ISO 13356 (Implants for surgery - Ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP)) (ISO, 2015) and ISO 6872 (Dentistry - Ceramic materials) (ISO, 2015).

The material composition of zirconia dental implants and the associated term “metal-free” are persistently questioned (Eckert, 2019). There is currently neither a standardized, universal definition nor thresholds for the term “metal-free”, but the term implies a quantifiable composition without metals. It is often argued that zirconia dental implants always contain oxide compounds of zirconium and its dopants and thus could be holistically considered non-metallic since metal oxides have predominantly non-metallic physical properties (Lughi and Sergo, 2010). However, while biomechanics, osseointegration, and survival rates of ceramic dental implants have been investigated (Cionca et al., 2017), little is known and published about the elemental composition and purity of zirconia dental implants (Beger et al., 2018).

Recently, the elemental composition of the surface of commercial zirconia implants have been investigated using non-destructive energy dispersive X-ray spectroscopy (EDX) (Beger et al., 2018). For a complete elemental and isotopic analysis of the implant body with high sensitivity and low detection limits down to the ultra-trace level ($<$0.0001 mass%, equivalent to $<$1 parts per million (ppm)), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) are currently the methods of choice (Limbeck et al., 2017). Thus, the present study aimed to conduct a state-of-the-art ICP-MS/OES analysis of commercial zirconia dental implants in order to specify their elemental composition and to identify contaminants.

2. Methods

2.1. Sample acquisition and interdisciplinary cooperation

In this study, nine commercial zirconia dental implants and corresponding material samples from eight manufacturers/vendors were examined (implants n = 9; material samples n = 9). The implants were purchased directly from the respective manufacturer/vendors. The corresponding material samples, which are commonly used for pre-implantation sensitivity testing, were supplied with the respective implants. After the documented receipt of goods, the implants and material samples were unpacked, transferred to threaded glass containers (AR-GLAS®, Schott AG, Mainz, Germany) and indexed by a three-digit code. An overview of all examined implants and material samples is given in Table 1.

The analytical methodology was provided and conducted by the Institute of Applied Materials - Applied Material Physics (IAM-AWP) of the Karlsruhe Institute of Technology (KIT) after the present study project had been approved and accepted by the Karlsruhe Nano Micro Facility (KNMF). During analysis, the IAM-AWP was blinded to the origin of the samples (index by three-digit code).

2.2. Preanalytical sample procession and digestion

For chemical digestion, the samples (analyzable weight per sample: 1–15 g) were crushed and milled to grain size, using a mortar mill made

Table 1
Investigated samples.

Manufacturer/ Vendor	S. No.	S.In.	LOT No.	Sample Name	Material
Straumann	1	P7A	RH923	PURE Ceramic Implant (Monotype)	ZrO_2 (Y-TZP)
	2	A9F	n/a	Material sample (disk)	
Axis biodental/ Camlog	3	U19	06717C2	CERALOG® Monobloc Implant	ZrO_2 (Y-TZP)
	4	Z6E	n/a	Material sample (implant-shaped)	
Bredent medical	5	L7G	450733	whiteSKY™ Zirconium Implant	ZrO_2 (Y-TZP)
	6	RT9	464492	Material sample (disk)	
Dentalpoint/ Zeramex	7	HT3	1009631	Zeramex® P6 Implant	ZrO2 (ATZ-HIP®)
	8	Y2X	1007997	Material sample (cylinder)	
	9	W31	1008824	Zeramex® T ZERALOCK Implant	ZrO2 (TZP-A-BIO-HIP®)
	10	P45	1007996	Material sample (cylinder)	
Z-Systems	11	T58	17405	Z5m(t) Implant	ZrO2 (TZP-A Bio-HIP®)
	12	M3N	n/a	Material sample Zirkolith® (disk)	
Moje KI/ Medentis	13	V8M	710047417/ 0496	ICX-Active WHITE Implant	ZrO_2 (Y-TZP)
	14	X1W	n/a	Material sample (disk)	
VITA Zahnfabrik/ vitaclinical	15	LM4	41340	ceramic.implant CI	ZrO_2 (Y-TZP)
	16	GK6	n/a	Material sample (disk)	
Moje KI/SDS Swiss Dental Solutions	17	C7N	429036218	SDS 1.1 Implant	ZrO_2 (Y-TZP)
	18	F92	409014918	Material sample (disk)	
n = 8	n = 18		implants n = 9; material samples n = 9		

S.No. = sample number; S.In. = sample index; LOT no. = LOT number/batch number; n/a = not available, not provided; (Y-) TZP=(yttria-stabilized) tetragonal zirconia polycrystals; ATZ = alumina toughened zirconia; ZrO2 = zirconium dioxide; HIP = hot isostatic postcompaction; Implant system names and materials according to manufacturer/vendor; L = length, Ø = diameter. ATZ-HIP® and TZP-A Bio-HIP® are registered trademarks of Metoxit AG, Thayngen, Switzerland.

of Si_3N_4 (SRS-2000, Analysen Geräte GmbH, Leutkirch, Germany). The samples were subsampled to three 150 mg replicates (weighing accuracy ± 0.05 mg; XP56, Mettler-Toledo, Gießen, Germany; sample HT3: only one 150 mg sample due to lack of material). Each subsample was melted in a mixture of 2 g lithium metaborate (EQF-ML-100; Equilab S. A., Madrid, Spain) and 25 mg LiBr (44199; Alfa Aesar, Thermo Fisher (Kandel) GmbH, Karlsruhe, Germany) in a platinum crucible (FLUXER F1, Equilab S.A., Madrid, Spain). After melting, with a temperature program up to 1200 °C, the flux was poured out automatically into a Teflon beaker, containing a mixture of 25 ml HNO_3 subb. 32% and 25 ml HCl subb. 17.5%. The fluid in the beaker was stirred with a Teflon coated magnetic bar until the melt dissolved. The clear sample solution was transferred to a Teflon vial, and the beaker was washed out with up to 100 ml ultrapure water (OmniaPure, Stakpure GmbH, Niederahr, Germany). The unmelted and undissolved Si_3N_4 residue, a contamination from the mortar mill, was filtrated and analyzed via X-ray fluorescence spectroscopy (XRF) (Pioneer S4, Bruker AXS, Karlsruhe, Germany), in order to ascertain that it was not sample material. Due to a large number of subsamples ($n = 52$), the quantitative measurements were performed in two measurement runs (see different limits of quantification (LOQ) in Table C.1/2 vs C.3/4).

2.3. Inductively coupled plasma optical emission spectrometry (ICP-OES)

To obtain an overview of the elemental concentration, each sample was diluted with nitric acid subb. (2%) by a factor of 10 and measured semiquantitatively via ICP-OES (iCAP 7600 ICP-OES Duo, Thermo Fisher Scientific Inc., Waltham, MA, USA). Each sample solution was diluted several times, depending on the concentration of the various elements. Instead of using volumetric dilution methods, the sample solution and ultra-pure water were weighed (XP 205, Mettler-Toledo, Gießen, Germany), as this is more accurate. Analysis of the elements was accomplished with four different calibration solutions and an internal standard (Sc) by ICP-OES (see above). For minor and trace elements, the solution was matrix adapted (Li, B, Y, Zr, Hf, acid). The range of the calibration solutions extended from zero to 0.2 mg/l and involved the area of the concentration of the samples. One to three wavelengths of each element were used for the calculations. Table A1 summarizes the ICP-OES instrument settings.

2.4. Inductively coupled plasma mass spectrometry (ICP-MS)

To measure the concentration of elements, which are less sensitive with ICP-OES, but are major trace elements in Y-doped ZrO_2, an ICP-MS (7500ce ICP-MS, Agilent Technologies Inc., Santa Clara, CA, USA) was used. The elemental analysis was accomplished with four different matrix adapted calibration solutions (Li, B, Y, Zr, Hf, acid) and an internal standard (In). The range of the calibration extended from 0.1-2.0 μg/l and 0.01–0.2 μg/l for Th and U and involved the range of concentration of the samples. One to three masses of the elements were used for calculation. Table A2 summarizes the ICP-MS instrument settings.

2.5. Quality control

For quality control of chemical digestion, measurements and result analysis, a BAM (Bundesanstalt für Materialforschung und -Prüfung/ Federal Institute for Materials Research and Testing) certified reference material (ERM® -ED105) was melted and analyzed in the same measurement run as the samples. Table B1 shows the certified values and the measurement results of the certified elements. The certified ICP calibration solutions (Alfa Aesar, Thermo Fisher (Kandel) GmbH, Karlsruhe, Germany) were controlled with another certified ICP solution from a different producer (Merck KGaA, Darmstadt, Germany). The recovery of these standards in matrix-adapted solutions was between 90 and 110%.

2.6. Calculations and descriptive statistics

Measurement results are reported as mean (of the respective subsamples), standard deviation (SD), and measurement uncertainty (±) (s. Table C1-4). For better data interpretation, the results were visualized in mg/kg (ppm) as well as in mass percent (mass%) (conversion factor: 10000, see Figs. 1–3). Furthermore, stoichiometric oxide compounds were calculated with the corresponding conversion factors (conversion factor = molar mass (oxide)/molar mass (elements present in the oxide)). Descriptive statistics were performed with IBM SPSS Statistics (version 25.0, released 2017, IBM Corp., Armonk, NY, USA). Cohort descriptive values (mean, SD) have been rounded for a better overview.

3. Results

All results of the ICP-MS and ICP-OES elemental analysis are shown in Table C1-4. Table 2 shows selected calculated, normalized stoichiometric oxides.

3.1. Zirconium (Zr), yttrium (Y) and aluminum (Al) fractions

The largest element fractions of the examined Y-TZP samples were represented by Zr and Y. On average, the Y-TZP samples ($n = 16$) consisted of 66.77 mass% Zr (SD: 0.61 mass%) and 4.05 mass% Y (SD: 0.19 mass%). In ATZ samples (HT3 and Y2X), both the Zr and Y fractions were smaller (Zr (mean): 52.50 mass%; Y(mean): 3.27 mass%). ATZ samples, as indicated by terminology, had large aluminum fractions (mean: 10.42 mass%). However, all examined Y-TZP samples also showed traces of Al (mean: 1317.63 mg/kg, SD: 516.23 mg/kg). Fig. 1 illustrates the Zr, Y, and Al fractions of each sample.

3.2. Hafnium (Hf) and other "heavy metals"

As is customary in the literature, the term "heavy metals" in the following refers to metals which, in the pure state, have a specific density of more than 5 g/cm^3 (Järup, 2003). Zirconium, a heavy metal itself, is considered separately in this study, as being the main component of the samples studied (see 3.1.).

In Y-TZP samples, the cumulative heavy metals fraction, which included the analyzed elements V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ge, As, Nb, Mo, Cd, Sn, Sb, Te, Hf, Ta, W, Tl, Pb, Bi, Th, and U, averaged 1.59 mass% (mean: 15903.76 mg/kg, SD: 319.31 mg/kg). However, hafnium (Hf) accounted for the largest share of this fraction (mean: 15768.75 mg/kg, SD: 257.47 mg/kg). ATZ samples had both a smaller cumulative heavy metal fraction (mean: 1.26 mass%, 12600 mg/kg) and lower hafnium contamination (mean: 12300.00 mg/kg).

In addition to hafnium, all samples showed contamination with iron (Fe) (mean: 106.17 mg/kg, SD: 65.85 mg/kg) as well. An outlier in terms of contamination with Fe was the ATZ sample Y2X (sample mean: 327.00 mg/kg). Furthermore, 16/18 samples showed traces of chromium (Cr) (mean: 10.13 mg/kg, SD: 7.20 mg/kg), 6/18 samples traces of nickel (Ni) (mean: 12.33 mg/kg, SD: 3.93 mg/kg) and 6/18 samples traces of zinc (Zn) (mean: 6.00 mg/kg, SD: 1.10 mg/kg). Sample F92 showed impurities with molybdenum (Mo) (sample mean: 437.00 mg/ kg), tin (Sn) (sample mean: 12.50 mg/kg), tellurium (Te) (sample mean: 1.50 mg/kg), tantalum (Ta) (sample mean: 53.10 mg/kg) and tungsten (W) (sample mean: 71.00 mg/kg). Fig. 2 visualizes the cumulative and specified trace contamination with heavy metals.

3.3. Ultra-trace level contamination with thorium (Th) and uranium (U)

The ICP-MS analysis revealed that 12/18 samples showed contaminations with Th-232 (mean: 0.29 mg/kg, SD: 0.14 mg/kg) and 10/18 samples contaminations with U-238 (mean: 0.37 mg/kg, SD: 0.11 mg/ kg) in the ultra-trace range above the limit of quantitation (LOQ). Fig. 3 visualizes the contamination with Th-232 and U-238 of all samples

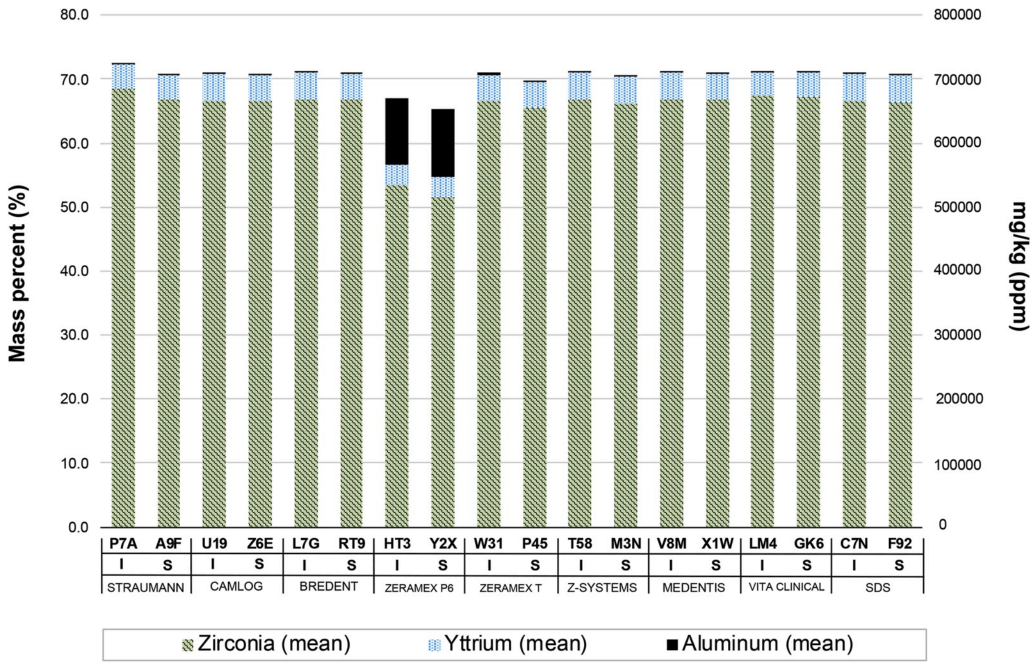

Fig. 1. Zirconium (Zr), yttrium (Y) and aluminum (Al) fractions.

investigated.

3.4. Other metals

Furthermore, all of the samples tested showed traces of the alkaline earth metal magnesium (Mg) (mean: 39.06 mg/kg, SD: 25.24 mg/kg) and 12/18 samples of the alkali metal sodium (Na) (mean: 78.33 mg/kg, SD: 31.19 mg/kg). Further individual impurities with other metals are shown in Table C1-4.

Fig. 1 shows the Zr, Y, and Al fractions of the samples examined. Note that while AL is a main component of ATZ samples (HT3 and Y2X), there is also low Al contamination of the TZP samples. Results are reported as mean in mass percent (mass%) and mg/kg (parts per million (ppm)). I=Implant; S = Material sample.

Fig. 2 A illustrates the cumulative contamination with the heavy metals Cr, Fe, Ni, Zn, Mo, Sn, Te, Ta, Th, U. Hafnium is given separately. Fig. 2B shows the specified contamination with Fe, Cr, Ni, Zn. Heavy metals = metal elements with a density greater than 5 g/cm^3 in their pure state. Results are given as mean in mass percent (mass%) and mg/kg (parts per million (ppm)). I=Implant; S = Material sample.

Fig. 3 gives an overview of the contamination with the actinides Th and U. Results are reported as mean +standard deviation in mass percent (mass%) and mg/kg (parts per million (ppm)). The red line indicates the limit of quantitation (LOQ). I=Implant; S = Material sample.

4. Discussion

In order to interpret the present data in a differentiated way, the material chemistry and physics of zirconia ceramics should be considered. In general, ceramics can be defined as crystalline solids consisting of an inorganic compound of metallic and non-metallic elements, which are predominantly held together by ionic and covalent bonds (Carter and Norton, 2013; Sudha et al., 2018). Pure zirconia (zirconium dioxide, ZrO_2), not to be confused with the metal element zirconium (Zr), is technically an advanced ceramic and chemically an allotropic metal oxide with predominantly non-metallic physical properties (Lughi and Sergo, 2010). It should be pointed out that it can be assumed that the metal elements detected by ICP-MS/OES are predominantly present as their corresponding oxide compounds in the native, final sintered implants (Lughi and Sergo, 2010; Carter and Norton, 2013; Sudha et al., 2018). The distinction between the metal elements and the corresponding metal oxides is crucial for the understanding of the present study.

4.1. Main components according to ISO 13356 – metal oxides

To provide high-purity medical zirconia ceramics, the raw zirconia powders and dopants generally undergo a complex purification process before being sintered (Burger et al., 1997). ISO 13356, frequently referred to by implant manufacturers and vendors in the European market, specifies the recommended chemical composition of Y-TZP ceramics used for implants for surgery based on the ZrO_2, HfO_2, Y_2O_3, and Al_2O_3 fractions, i.e., metal oxides (ISO, 2015). The element-to-stoichiometric oxides calculation of the present ICP-MS and ICP-OES data revealed that all Y-TZP samples investigated meet the requirements for ZrO_2, Y_2O_3, HfO_2, and Al_2O_3 fractions, according to ISO13356:2015 (see Tbl.2). The material composition of the investigated Y-TZP dental implants, with respect to the ZrO_2, HfO_2, and Y_2O_3 fractions, corresponds to that of commercial zirconia ceramics used for dental prosthetics (Bavbek et al., 2014).

ATZ dental implants are not subject to ISO 13356. However, it can be assumed that the major material composition of the examined ATZ samples is in accordance with the manufacturer's specifications (Zeramex® P6; 2019 product specifications according to Dentalpoint AG, Spreitenbach, Switzerland: 76 mass% ZrO_2, 20 mass% Al_2O_3 and 4 mass % Y_2O_3; compare to Tbl. 2).

4.2. Metal contaminants

It has already been shown that even commercial high-purity zirconia ceramics can still contain some contamination with other elements (Veronese et al., 2006; Ma and Li, 2006). However, a manufacturer-independent, quantified proof of impurities in commercial zirconia dental implants could not yet be provided. Recently, Beger et al. analyzed five commercial zirconia implants using energy-dispersive X-ray spectroscopy (EDX) and stated that they found no impurities or unexpected results (Beger et al., 2018). In contrast, the present study revealed some impurities, probably due to the higher

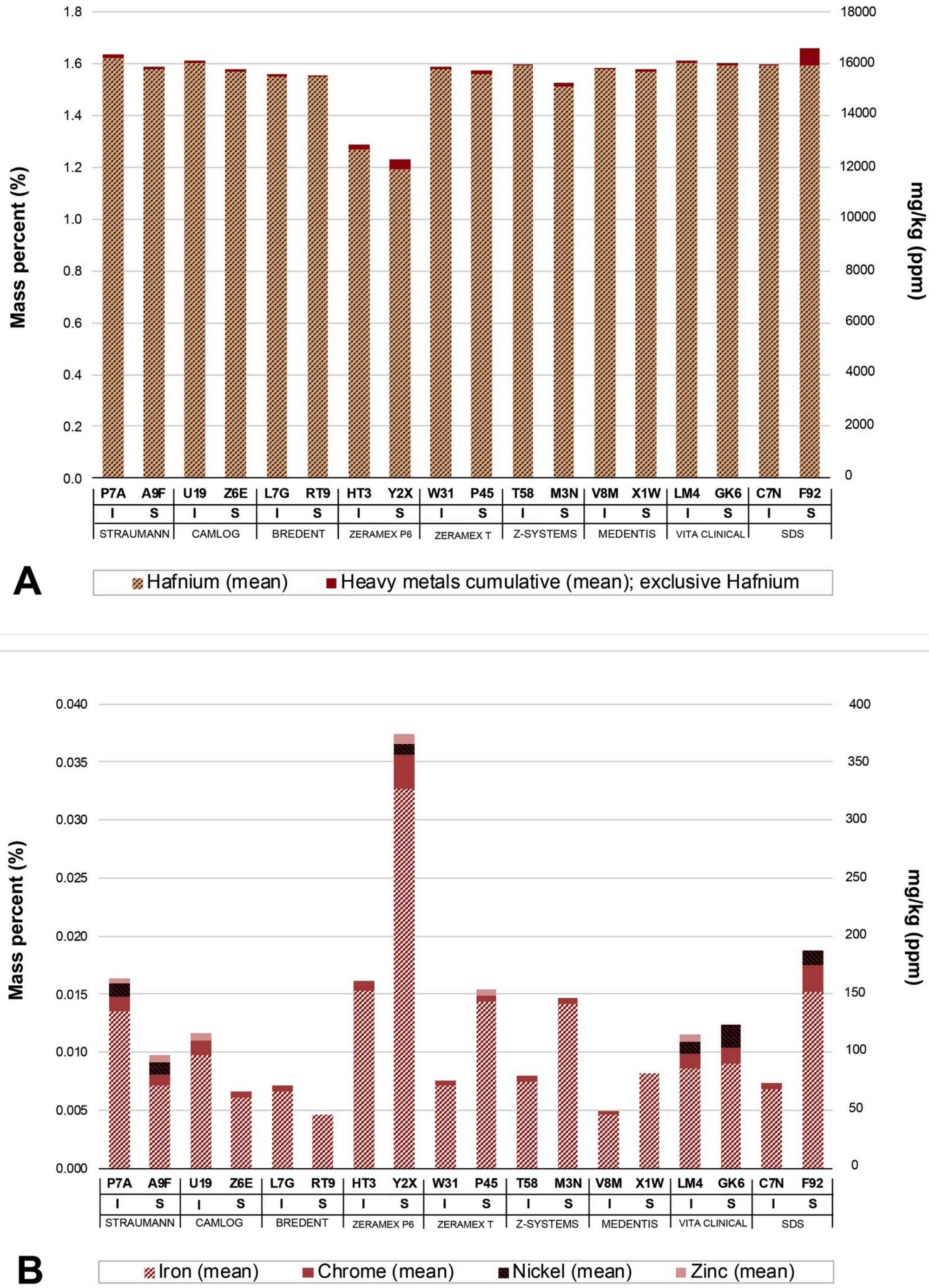

Fig. 2. Cumulative and specified trace contamination with selected heavy metals.

sensitivity and lower detection limits of ICP-MS and ICP-OES compared to EDX (Limbeck et al., 2017). The present study shows that, from an elemental point of view, the examined implants and corresponding material samples are not devoid of contamination with metal elements. The detected metal elements were mainly essential macro-minerals (e. g., Na, K, Mg, Ca) and trace elements (e.g., Fe, Cu, Zn) (Zoroddu et al., 2019).

Potentially noxious metal elements, such as Ni (nickel allergy) (Saito et al., 2016), Cr (Sun et al., 2015; Vincent, 2017), and the radionuclides U and Th (Keith et al., 2015; Porstendorfer et al., 1996), were also found in some samples. As shown in previous studies analyzing the composition of dental zirconia ceramics, hafnium, whose toxicity as an oxide compound (HfO_2) has been poorly investigated (Field et al., 2011), has been identified as the major contaminant (Bavbek et al., 2014; Beger et al., 2018). The hafnium contamination of zirconia ceramics is commonly explained by the pronounced similarity of the elements Zr and Hf and the consecutive difficult separation during the purification process (Cotton and Hart, 1975; Yang et al., 1999). In addition, although being a major constituent of ATZ samples, aluminum, whose neurotoxicity after chronic exposure is controversially discussed (Fulgenzi et al., 2014), was found as a contaminant in all Y-TZP samples as well. At this point, it should be noted that the results of this study do not provide information on the actual systemic or peri-implant exposure to contaminants or any resulting biological hazard. It can be expected that the detected metal contaminants are predominantly firmly fixed in compounds and therefore have little or no biological relevance (Carter and

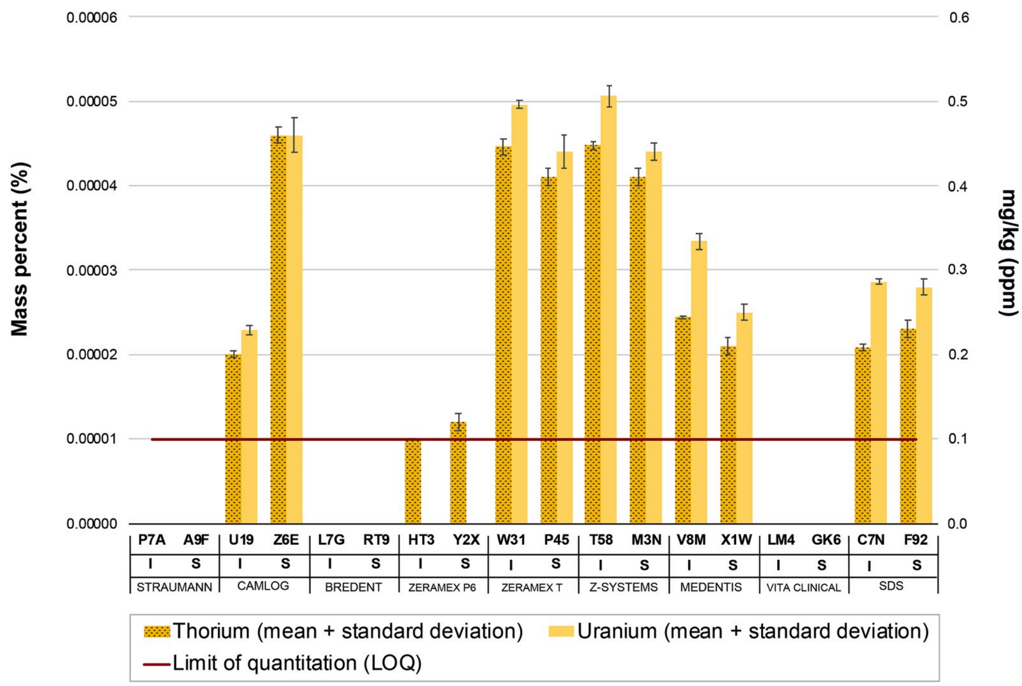

Fig. 3. Ultra-trace level contamination with thorium (Th-232) and uranium (U-238).

Table 2
Calculated, normalized stoichiometric oxides.

Oxide	Conversion factor (E-O)		Calculated results (mass%)			
			Y-TZP samples (n = 16)	ISO 13356	Meet criteria	ATZ samples (n = 2)
ZrO_2	1.3500	Mean	92.64	*	n = 16	73.7
		SD	0.31		(all)	0.42
Y_2O_3	1.2699	Mean	5.28	>4.5 to ≤6.0	n = 16	4.31
		SD	0.26		(all)	0.00
HfO_2	1.1793	Mean	1.91	≤5.0	n = 16	1.51
		SD	0.03		(all)	0.04
Al_2O_3	1.8895	Mean	0.26	≤0.5	n = 16	20.46
		SD	0.10		(all)	0.43
ZrO_2+Y_2O_3+HfO_2		Mean	99.84	> 99	n = 16	
		SD	0.06		(all)	

The stoichiometric oxide conversion factor was calculated as following: conversion factor = molar mass (oxide)/molar mass (elements present in the oxide). The calculation of stoichiometric oxides included 100% normalization. E-O = Element to oxide; SD = standard deviation; ISO 13356 (Implants for surgery - Ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP)) (ISO, 2015). * According to *ISO 13356: ZrO_2+HfO_2+Y_2O_3 > 99 mass%. ATZ samples are not standardized by ISO 13356.*

Norton, 2013; Sudha et al., 2018). However, this needs to be clarified by further investigations.

The metal contaminants found can be of different origin. The observed joint presence of Fe, Cr, and Ni (some samples) could be due to contamination by processing the blanks with instruments made of stainless steel (iron alloys, containing 12–30% Cr and 0–22% Ni) (Gooch and Gooch, 2011). Furthermore, some manufacturers sandblast (e.g., with aluminum-containing particles) and/or acid-etch (e.g., with hydrofluoric acid) the surface of their zirconia implants to promote osseointegration (Beger et al., 2018). Thus, incomplete purification of the raw zirconia powders (Burger et al., 1997), but also the potential subsequent contamination during processing of the sintered or pre-sintered zirconia blanks, may provide explanations for the impurity differences found between the implant systems as well as between the implants and their corresponding material samples.

The ICP-MS/OES analysis does not provide information about differences between the sample core and the sample surface with regard to impurities. Furthermore, the present study should be considered as a random sample survey, as a batch comparison was not performed, and the sample number was limited. Further research is needed to prove a generalization.

4.3. Impurities with uranium (U) and thorium (Th)

It is known that unpurified zirconia powders, but also purified medical zirconia ceramics, can be contaminated with the natural radionuclides U-238 and Th-232 (Piconi and Maccauro, 1999; Nielsen and Wilfing, 2010; Vagkopoulou et al., 2009; Hurley and Fairbairn, 1957). The presence of radionuclides could also be detected in dental zirconia ceramics (Bavbek et al., 2014; Veronese et al., 2006). Nevertheless, there has been no independent, published quantification of the radionuclide contamination for zirconia dental implants yet. The present study revealed ultra-trace contamination (<1 mg/kg) with U-238 and Th-232 in most of the studied implant systems and their corresponding material samples (see. Fig. 3). However, with such low contamination of the affected implants, it is to be expected that the resulting mass activity is well below the limits of ISO 13356 (200 Bq/kg) and ISO 6872 (max: 1, 0 Bq/g) (ISO, 2015; ISO, 2015). But, the quantification of radioactivity needs further investigation by radiochemical analysis.

4.4. "Metal-free" = devoid of metals?

Currently, manufacturers and vendors of zirconia dental implants strongly promote the term "metal-free" or "100% metal-free" and commonly refer to ISO 13356:2015, which specifies the chemical composition of zirconia dental implants only for oxide compounds and not for any metal elements (ISO, 2015). This is based on the assumption that the metals involved are predominantly present as metal oxides with non-metallic physical properties (Lughi and Sergo, 2010; Carter and Norton, 2013; Sudha et al., 2018). However, it is also known that the oxide bonds of crystalline ceramics can be broken by aqueous attack (e. g., in an aqueous environment such as in the oral cavity) and, thus, metal ions may be present temporarily (Thomas et al., 2016; Frankel et al., 2018). This should be especially considered in the light of LTD and the aging of zirconia ceramics reported in the literature (Lughi and Sergo, 2010). Even if the facts that zirconium itself is a metal element and zirconia is a metal oxide are neglected (Nielsen and Wilfing, 2010), the small but present metal impurities found in this study suggest that, from an elemental point of view, the investigated zirconia dental implants are not devoid of metals. Nevertheless, the question of whether the examined zirconia dental implants can be holistically classified as "metal-free" or not remains a controversial and philosophical one, since there is still neither a universal definition nor critical thresholds for the term "metal-free".

As an alternative to zirconia ceramics of natural origin, fiber-reinforced composites (FRCs) are increasingly being discussed and tested as a non-metal material for dental implants (Ballo et al., 2014). They can establish a titanium osseointegration-comparable close bone contact and, when combined with biostable glass, can present bioactivity, in contrast to the mainly bioinert zirconia ceramics (Ballo et al., 2014; Vallittu, 2017; Posti et al., 2016). However, it remains to be clarified how "metal-free" FRCs are.

5. Conclusion

Based on the results of the ICP-MS/OES elemental analysis, the following conclusions can be made:

1. The investigated zirconia dental implants meet the currently relevant ISO standards and the manufacturer's specifications,
2. The investigated zirconia dental implants and corresponding material samples are not devoid of metal elements, such as heavy metals and radionuclides (U-238 and Th-232).
3. Further studies must prove generalization and clarify whether the found impurities, which were to be expected due to the natural origin of the implant raw material, actually have biological relevance.
4. From an elemental point of view, the investigated zirconia dental implants are not devoid of metals.
5. The question of whether the examined zirconia dental implants can be holistically classified as "metal-free" or not remains a controversial, philosophical one.

Ethics approval and consent to participate

No ethics approval needed as no patients/animals were studied.

Consent for publication

No consent needed, as no patient data/material was used.

Availability of data and material

All data generated or analyzed during this study are included in this published article.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Christian Gross: Conceptualization, Data curation, Writing - original draft, Visualization, Funding acquisition. **Thomas Bergfeldt:** Methodology, Validation, Investigation, Resources, Data curation, Writing - review & editing, Visualization. **Tobias Fretwurst:** Supervision, Conceptualization, Writing - review & editing. **René Rothweiler:** Conceptualization, Writing - review & editing. **Katja Nelson:** Supervision, Conceptualization, Writing - review & editing. **Andres Stricker:** Conceptualization, Validation, Resources, Data curation, Writing - review & editing, Supervision, Project administration, Funding acquisition.

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Appendices

Appendix A

Table A.1
Instrument settings for ICP-OES (iCAP 7600 Duo, Thermo Fisher Scientific Inc.)

ICP	Peristaltic pump	
	Mira Mist Teflon nebulizer	Gas Flow 0,6 (L/min)
	Cyclon spray chamber	
	Quarztorch with ceramic injector tube	
	RF Power (W)	1150
	Auxiliary gas flow	0,5 (L/min) for main compounds 1,5 (L/min) for minor and trace elements
Wavelength (nm)	Na	589.592
	Mg	279.553; 280.270

(*continued on next page*)

Table A.1 (*continued*)

Al	167.079; 176.638; 308.215
P	177.495; 213.618
K	766.490; 769.896
Ca	184.006; 393.366
Ti	334.941; 338.376
V	290.646; 311.838: 326.769
Cr	205.560; 206.550; 267.716
Mn	257.610; 260.569; 293.930
Fe	238.204; 239.562; 259.940
Co	228.616; 230.786
Ni	216.556; 231.604
Cu	213.598; 224.700
Zn	206.200; 213.856
Ge	209.426; 303.906
As	189.042; 193.759; 197.262
Se	196.090
Sr	216.596; 407.771; 421.552
Y	324.228; 360.073; 371.030
Zr	348.115; 357.685; 383.676
Mo	202.030; 203.844; 204.598
Ba	230.424; 233.527; 493.409
Hf	251.303; 264.141; 277.336
W	202.998
Bi	223.061

Table A.2
Instrument settings for ICP-MS (7500ce, Agilent Technologies Inc.)

ICP	Nebulizer pump	0,1 rps
	Micro Mist Quartz nebulizer	
	Scot spray chamber	
	Quartztorch with Quartz injector tube	
	RF Power (W)	1400
	Carrier Gas	1,0 (L/min)
	Makeup Gas	0,2 (L/min)
MS	Dwell time/isotope	100 ms
Isotopes	Ga	69; 71
	Rb	85; 87
	Nb	93
	Cd	114
	Sn	116; 118; 120
	Sb	121; 123
	Te	130
	Ta	181
	Tl	203; 205
	Pb	207; 208
	Th	232
	U	238

Appendix B

Table B.1
ERM®-ED105 quality control – ICP-OES/ICP-MS

Element	Mass fraction		
	Certified value (mg/kg)	Uncertainty (mg/kg)	Measured value (mg/kg)
Mg	12.9	1.7	15
Al	660	15	674–676
Ca	242	9	233–242
Ti	497	11	472–487
Fe	95	9	94–95
Th	112	17	106–118
U	292	19	272–305
	Certified value (Mass %)	**Uncertainty (Mass %)**	**Measured value (Mass %)**
Y	6.11	0.09	5.87–5.88
Hf	1.535	0.024	1.51–1.52

Certified value and uncertainty as given in the ERM®-ED105 certification report – "The Certification of Mass Fractions of Al, Ca, Fe, Mg, Si, Th, Ti, U, Hf, and Yttrium Stabilized Zirconium Oxide"; BAM, Berlin, July 2015.

Appendix C

Table C.1
ICP-MS/ICP-OES results (given as mg/kg (ppm))

Sample index			P7A			U19			L7G			HT3			W31		
Sample name			PURE Ceramic Implant (Monotype)			CERALOG® Monobloc Implant			whiteSKY™ Zirconium Implant			Zeramex® P6 Implant			Zeramex® T ZERALOCK Implant		
Element	Unit	LOQ	Mean	SD	±	Mean	SD	±	Mean	SD	±	Mean	SD	±	Mean	SD	±
Na	mg/kg	20.00	<20.00		–	33.00	1.00	4.95	<20.00		–	55.00	*	5.50	125.00	2.00	12.50
Mg	mg/kg	11.00	35.00	4.00	3.50	31.00	2.00	3.10	28.00	2.00	4.20	54.00	*	5.40	28.00	2.00	4.20
Al	mg/kg	36.00	623.00	25.00	17.44	1370.00	20.00	38.36	1400.00	10.00	39.20	104000.00	*	2912.00	2610.00	60.00	73.08
P	mg/kg	20.00	<20.00		–	<20.00		–	<20.00		–	<20.00	*	–	<20.00		–
K	mg/kg	29.00	<29.00		–	<29.00		–	<29.00		–	<29.00	*	–	<29.00		–
Ca	mg/kg	26.00	<26.00		–	31.00	1.00	6.20	<26.00		–	55.00	*	5.50	<26.00		–
Ti	mg/kg	5.00	<5.00		–	5.00	1.00	1.00	<5.00		–	5.00	*	1.00	<5.00		–
V	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–	<7.00	*	–	<7.00		–
Cr	mg/kg	2.00	13.00	2.00	2.60	12.00	2.00	2.40	5.00	1.00	1.25	8.00	*	2.00	5.00	1.00	1.25
Mn	mg/kg	8.00	<8.00		–	<8.00		–	<8.00		–	<8.00	*	–	<8.00		–
Fe	mg/kg	28.00	135.00	6.00	6.75	98.00	5.00	4.90	66.00	1.00	6.60	153.00	*	7.65	71.00	3.00	7.10
Co	mg/kg	4.00	<4.00		–	<4.00		–	<4.00		–	<4.00	*	–	<4.00		–
Ni	mg/kg	8.00	11.00	1.00	2.20	<8.00		–	<8.00		–	<8.00	*	–	<8.00		–
Cu	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–	<7.00	*	–	<7.00		–
Zn	mg/kg	5.00	5.00	1.00	1.00	6.00	1.00	1.00	<5.00		–	<5.00	*	–	<5.00		–
Ga	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00	*	–	<1.00		–
Ge	mg/kg	28.00	<28.00		–	<28.00		–	<28.00		–	<28.00	*	–	<28.00		–
As	mg/kg	26.00	<26.00		–	<26.00		–	<26.00		–	<26.00	*	–	<26.00		–
Se	mg/kg	10.00	<10.00		–	<10.00		–	<10.00		–	<10.00	*	–	<10.00		–
Rb	mg/kg	1.60	2.00	0.20	–	1.70	0.10	–	<1.60		–	<1.60	*	–	<1.60		–
Sr	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00	*	–	<1.00		–
Y	mg/kg	1000.00	38200.00	800.00	764.00	41200.00	200.00	824.00	41700.00	100.00	834.00	33100.00	*	662.00	41700.00	100.00	834.00
Zr	mg/kg	10000.00	684000.00	15000.00	11628.00	666000.00	2000.00	11322.00	668000.00	1000.00	11356.00	534000.00	*	9078.00	665000.00	1000.00	11305.00
Nb	mg/kg	3.00	<3.00		–	<3.00		–	<3.00		–	<3.00	*	–	<3.00		–
Mo	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00	*	–	<5.00		–
Cd	mg/kg	0.70	<0.70		–	<0.70		–	<0.70		–	<0.70	*	–	<0.70		–
Sn	mg/kg	3.00	<3.00		–	<3.00		–	<3.00		–	<3.00	*	–	<3.00		–
Sb	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00	*	–	<1.00		–
Te	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80	*	–	<0.80		–
Ba	mg/kg	2.00	<2.00		–	<2.00		–	<2.00		–	<2.00	*	–	2.20	0.30	0.55
Hf	mg/kg	200.00	16200.00	400.00	–	16000.00	100.00	–	15500.00	100.00	–	12700.00	*	–	15800.00	100.00	–
Ta	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00	*	–	<1.00		–
W	mg/kg	35.00	<35.00		–	<35.00		–	<35.00		–	<35.00	*	–	<35.00		–
Tl	mg/kg	0.20	<0.20		–	<0.20		–	<0.20		–	<0.20	*	–	<0.20		–
Pb	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80	*	–	<0.80		–
Bi	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00	*	–	<5.00		–
Th	mg/kg	0.10	<0.10		–	0.201	0.004	–	<0.10		–	0.100	*	–	0.446	0.009	–
U	mg/kg	0.10	<0.10		–	0.229	0.005	–	<0.10		–	<0.10	*	–	0.496	0.005	–
Total	mg/kg		739224.00			724788.13			726699.00			684130.10			725342.14		

LOQ = limit of quantitation; SD = standard deviation; ±: measurement uncertainty; * The sample HT3 was measured only once.

Table C.2
ICP-MS/ICP-OES results (given as mg/kg (ppm))

Sample index			T58			V8M			LM4			C7N			A9F		
Sample name			Z5m(t) Implant			ICX-Active WHITE Implant			ceramic.implant CI			SDS 1.1 Implant			Straumann material sample (disk)		
Element	Unit	LOQ	Mean	SD	±	Mean	SD	±	Mean	SD	±	Mean	SD	±	Mean	SD	±
Na	mg/kg	20.00	108.00	3.00	10.80	78.00	2.00	11.70	<20.00		–	72.00	2.00	7.20	<20.00		–
Mg	mg/kg	11.00	31.00	1.00	4.65	18.00	3.00	3.60	37.00	2.00	3.70	36.00	2.00	5.40	38.00	1.00	3.80
Al	mg/kg	36.00	1560.00	30.00	43.68	1400.00	20.00	39.20	642.00	17.00	17.98	1380.00	20.00	38.64	628.00	14.00	17.58
P	mg/kg	20.00	<20.00		–	<20.00		–	<20.00		–	<20.00		–	<20.00		–
K	mg/kg	29.00	<29.00		–	<29.00		–	<29.00		–	<29.00		–	<29.00		–
Ca	mg/kg	26.00	<26.00		–	<26.00		–	<26.00		–	<26.00		–	<26.00		–
Ti	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00		–	<5.00		–
V	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–	<7.00		–	<7.00		–
Cr	mg/kg	2.00	6.00	2.00	1.50	3.00	1.00	0.75	13.00	2.00	2.60	5.00	1.00	1.25	10.00	2.00	2.50
Mn	mg/kg	8.00	<8.00		–	<8.00		–	<8.00		–	<8.00		–	<8.00		–
Fe	mg/kg	28.00	74.00	3.00	7.40	46.00	1.00	6.90	86.00	3.00	8.60	68.00	3.00	10.20	71.00	2.00	7.10
Co	mg/kg	4.00	<4.00		–	<4.00		–	<4.00		–	<4.00		–	<4.00		–
Ni	mg/kg	8.00	<8.00		–	<8.00		–	10.00	1.00	2.00	<8.00		–	10.00	1.00	2.00
Cu	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–	<7.00		–	<7.00		–
Zn	mg/kg	5.00	<5.00		–	<5.00		–	6.00	1.00	1.00	<5.00		–	6.00	1.00	1.00
Ga	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00		–	<1.00		–
Ge	mg/kg	28.00	<28.00		–	<28.00		–	<28.00		–	<28.00		–	<28.00		–
As	mg/kg	26.00	<26.00		–	<26.00		–	<26.00		–	<26.00		–	<26.00		–
Se	mg/kg	10.00	<10.00		–	<10.00		–	<10.00		–	<10.00		–	<10.00		–
Rb	mg/kg	1.60	<1.60		–	<1.60		–	<1.60		–	<1.60		–	<1.60		–
Sr	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00		–	<1.00		–
Y	mg/kg	1000.00	41900.00	200.00	838.00	41500.00	200.00	830.00	36300.00	200.00	726.00	41600.00	200.00	832.00	37300.00	200.00	746.00
Zr	mg/kg	10000.00	669000.00	2000.00	11373.00	669000.00	2000.00	11373.00	674000.00	1000.00	11458.00	666000.00	2000.00	11322.00	669000.00	2000.00	11373.00
Nb	mg/kg	3.00	<3.00		–	<3.00		–	<3.00		–	<3.00		–	<3.00		–
Mo	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00		–	<5.00		–
Cd	mg/kg	0.70	<0.70		–	<0.70		–	<0.70		–	<0.70		–	<0.70		–
Sn	mg/kg	3.00	<3.00		–	<3.00		–	<3.00		–	<3.00		–	<3.00		–
Sb	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00		–	<1.00		–
Te	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80		–	<0.80		–
Ba	mg/kg	2.00	2.60	0.50	0.65	<2.00		–	<2.00		–	<2.00		–	<2.00		–
Hf	mg/kg	200.00	15900.00	100.00	–	15800.00	100.00	–	16000.00	100.00	–	15900.00	100.00	–	15800.00	100.00	–
Ta	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00		–	<1.00		–
W	mg/kg	35.00	<35.00		–	<35.00		–	<35.00		–	<35.00		–	<35.00		–
Tl	mg/kg	0.20	<0.20		–	<0.20		–	<0.20		–	<0.20		–	<0.20		–
Pb	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80		–	<0.80		–
Bi	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00		–	<5.00		–
Th	mg/kg	0.10	0.448	0.005	–	0.244	0.002	–	<0.10		–	0.208	0.004	–	<0.10		–
U	mg/kg	0.10	0.506	0.013	–	0.334	0.010	–	<0.10		–	0.286	0.003	–	<0.10		–
Total	mg/kg		728582.55			727845.58			727094.00			725061.49			722863.00		

LOQ = limit of quantitation; SD = standard deviation; ±: measurement uncertainty.

Table C.3
ICP-MS/ICP-OES results (given as mg/kg (ppm))

Sample index			Z6E			RT9			Y2X			P45			M3N		
Sample name			Camlog material sample (impl.-shaped)			Material sample Brezirkon™			Zeramex material sample (cyl.) ATZ			Zeramex material sample (cyl.) TZP			Material sample Zirkolith® (disk)		
Element	Unit	LOQ	Mean	SD	±	Mean	SD	±	Mean	SD	±	Mean	SD	±	Mean	SD	±
Na	mg/kg	27.00	42.00	3.00	4.20	<27.00		–	52.00	3.00	5.20	126.00	4.00	4.28	103.00	2.00	3.50
Mg	mg/kg	4.00	25.00	2.00	2.50	15.00	1.00	1.50	118.00	5.00	5.55	30.00	5.00	3.00	77.00	1.00	3.62
Al	mg/kg	68.00	1370.00	40.00	38.36	1370.00	10.00	38.36	104300.00	900.00	2920.40	1350.00	40.00	37.80	1860.00	20.00	52.08
P	mg/kg	33.00	<33.00		–	<33.00		–	<33.00		–	<33.00		–	<33.00		–
K	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–	<7.00		–	<7.00		–
Ca	mg/kg	31.00	<31.00		–	<31.00		–	44.00	2.00	6.60	<31.00		–	<31.00		–
Ti	mg/kg	5.00	<5.00		–	<5.00		–	6.00	1.00	1.50	<5.00		–	<5.00		–
V	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00		–	<5.00		–
Cr	mg/kg	4.00	5.00	1.00	1.00	<4.00		–	29.00	3.00	2.90	5.00	1.00	1.25	6.00	1.00	1.50
Mn	mg/kg	8.00	<8.00		–	<8.00		–	<8.00		–	<8.00		–	<8.00		–
Fe	mg/kg	12.00	61.00	3.00	3.05	46.00	3.00	2.30	327.00	12.00	6.54	144.00	2.00	2.88	141.00	11.00	2.82
Co	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00		–	<5.00		–
Ni	mg/kg	8.00	<8.00		–	<8.00		–	10.00	1.00	2.50	<8.00		–	<8.00		–
Cu	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–	<7.00		–	<7.00		–
Zn	mg/kg	5.00	<5.00		–	<5.00		–	8.00	1.00	2.00	5.00	1.00	1.25	<5.00		–
Ga	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00		–	<1.00		–
Ge	mg/kg	56.00	<56.00		–	<56.00		–	<56.00		–	<56.00		–	<56.00		–
As	mg/kg	25.00	<25.00		–	<25.00		–	<25.00		–	<25.00		–	<25.00		–
Se	mg/kg	10.00	<10.00		–	<10.00		–	<10.00		–	<10.00		–	<10.00		–
Rb	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00		–	<1.00		–
Sr	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80		–	<0.80		–
Y	mg/kg	500.00	41100.00	100.00	822.00	41700.00	300.00	834.00	32200.00	200.00	644.00	41200.00	100.00	824.00	41600.00	100.00	832.00
Zr	mg/kg	7000.00	666000.00	1000.00	11322.00	667000.00	4000.00	11339.00	516000.00	3000.00	8772.00	655000.00	1000.00	11135.00	662000.00	1000.00	11254.00
Nb	mg/kg	2.00	<2.00		–	<2.00		–	<2.00		–	<2.00		–	<2.00		–
Mo	mg/kg	9.00	<9.00		–	<9.00		–	<9.00		–	<9.00		–	<9.00		–
Cd	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80		–	<0.80		–
Sn	mg/kg	3.00	<3.00		–	<3.00		–	<3.00		–	<3.00		–	<3.00		–
Sb	mg/kg	3.00	<3.00		–	<3.00		–	<3.00		–	<3.00		–	<3.00		–
Te	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–	<1.00		–	<1.00		–
Ba	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–	<5.00		–	<5.00		–
Hf	mg/kg	100.00	15700.00	100.00	–	15500.00	100.00	–	11900.00	100.00	–	15600.00	100.00	–	15100.00	100.00	–
Ta	mg/kg	1.00	<1.00		–	<1.00		–	1.40	0.20	–	1.00	0.10	–	<1.00		–
W	mg/kg	50.00	<50.00		–	<50.00		–	<50.00		–	<50.00		–	<50.00		–
Tl	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80		–	<0.80		–
Pb	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–	<0.80		–	<0.80		–
Bi	mg/kg	4.00	<4.00		–	<4.00		–	<4.00		–	<4.00		–	<4.00		–
Th	mg/kg	0.10	0.460	0.010	–	<0.10		–	0.120	0.010	–	0.410	0.010	–	0.410	0.010	–
U	mg/kg	0.10	0.460	0.020	–	<0.10		–	<0.10		–	0.440	0.020	–	0.440	0.010	–
Total	mg/kg		724303.92			725631.00		–	664995.52			713461.85			720887.85		

LOQ = limit of quantitation; SD = standard deviation; ±: measurement uncertainty.

Table C.4
ICP-MS/ICP-OES results (given as mg/kg (ppm))

Sample index			X1W			GK6			F92		
Sample name			Medentis material sample (disk)			vitaclinical material sample (disk)			SDS material sample (disk)		
Element	Unit	LOQ	Mean	SD	±	Mean	SD	±	Mean	SD	±
Na	mg/kg	27.00	68.00	1.00	6.80	<27.00		–	78.00	5.00	7.80
Mg	mg/kg	4.00	26.00	1.00	2.60	15.00	1.00	2.25	61.00	2.00	2.87
Al	mg/kg	68.00	1380.00	10.00	38.64	619.00	6.00	17.33	1520.00	10.00	42.56
P	mg/kg	33.00	<33.00		–	<33.00		–	<33.00		–
K	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–
Ca	mg/kg	31.00	<31.00		–	<31.00		–	<31.00		–
Ti	mg/kg	5.00	<5.00		–	71.00	2.00	3.55	<5.00		–
V	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–
Cr	mg/kg	4.00	<4.00		–	14.00	1.00	2.10	23.00	1.00	2.30
Mn	mg/kg	8.00	<8.00		–	<8.00		–	<8.00		–
Fe	mg/kg	12.00	82.00	2.00	1.64	90.00	5.00	1.80	152.00	2.00	3.04
Co	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–
Ni	mg/kg	8.00	<8.00		–	20.00	1.00	2.00	13.00	1.00	2.60
Cu	mg/kg	7.00	<7.00		–	<7.00		–	<7.00		–
Zn	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–
Ga	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–
Ge	mg/kg	56.00	<56.00		–	<56.00		–	<56.00		–
As	mg/kg	25.00	<25.00		–	<25.00		–	<25.00		–
Se	mg/kg	10.00	<10.00		–	<10.00		–	<10.00		–
Rb	mg/kg	1.00	<1.00		–	<1.00		–	<1.00		–
Sr	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–
Y	mg/kg	500.00	41400.00	100.00	828.00	37600.00	200.00	752.00	41500.00	200.00	830.00
Zr	mg/kg	7000.00	667000.00	1000.00	11339.00	672000.00	1000.00	11424.00	664000.00	3000.00	11288.00
Nb	mg/kg	2.00	<2.00		–	<2.00		–	<2.00		–
Mo	mg/kg	9.00	<9.00		–	<9.00		–	437.00	4.00	10.05
Cd	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–
Sn	mg/kg	3.00	<3.00		–	<3.00		–	12.50	0.40	–
Sb	mg/kg	3.00	<3.00		–	<3.00		–	<3.00		–
Te	mg/kg	1.00	<1.00		–	<1.00		–	1.50	0.10	–
Ba	mg/kg	5.00	<5.00		–	<5.00		–	<5.00		–
Hf	mg/kg	100.00	15700.00	100.00	–	15900.00	100.00	–	15900.00	100.00	–
Ta	mg/kg	1.00	<1.00		–	<1.00		–	53.10	0.40	–
W	mg/kg	50.00	<50.00		–	<50.00		–	71.00	6.00	–
Tl	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–
Pb	mg/kg	0.80	<0.80		–	<0.80		–	<0.80		–
Bi	mg/kg	4.00	<4.00		–	<4.00		–	<4.00		–
Th	mg/kg	0.10	0.210	0.010	–	<0.10		–	0.230	0.010	–
U	mg/kg	0.10	0.250	0.010	–	<0.10		–	0.280	0.010	–
Total	mg/kg		725656.46			726329.00			723822.61		

LOQ = limit of quantitation; SD = standard deviation; ±: measurement uncertainty.

List of abbreviations

Al	aluminum
As	arsenic
ATZ	Alumina Toughened Zirconia
Ba	barium
BAM	(Bundesanstalt für Materialforschung und -Prüfung/Federal Institute for Materials Research and Testing
Bi	bismuth
Ca	calcium
Cd	cadmium
Co	cobalt
Cr	chromium
Cu	copper
EDX	energy dispersive X-ray spectroscopy
Fe	iron
Ga	gallium
Ge	germanium
Hf	hafnium
IAM-AWP	Institute of Applied Materials - Applied Material Physics
ICP-MS	inductively coupled plasma mass spectrometry
ICP-OES	inductively coupled plasma optical emission spectrometry
K	potassium
KIT	Karlsruhe Institute of Technology
KNMF	Karlsruhe Nano Micro Facility
LTD	low temperature degradation

Mg	magnesium
Mn	manganese
Mo	molybdenum
Na	sodium
Nb	niobium
Ni	nickel
P	phosphorus
Pb	lead
Rb	rubidium
Sb	antimony
Se	selenium
Sn	tin
Sr	strontium
Ta	tantalum
Te	tellurium
Th	thorium
Ti	titanium
Tl	thallium
U	uranium
V	vanadium
W	tungsten
XRF	X-ray fluorescence spectroscopy
Y-TZP	yttria-stabilized tetragonal zirconia polycrystals
Y	yttrium
Zn	zinc
Zr	zirconium

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