UNIFORM CORROSIVE TEST
FOR DENTAL MATERIALS

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The aim of our study was to unify testing of both ceramic and alloy dental materials to one common extraction procedure based on hydrochloric acid for both material groups and find suitable accompanying analytical method. Dental materials typical for routine praxis (eleven dental ceramics and seven metal alloys) were step-wise leached with 0.1 mol l^{-1} HCl at 37 °C two times for one week and once for two weeks. After the immersion test, the ions released were analysed using the inductively coupled plasma emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS).

Detection limits for the ICP-MS method and the ICP-OES method were hundreds to tenths of ng cm^{-2} and units to tens μg cm^{-2}, respectively. Recoveries

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for the spiked sample were 94.8-105 % for ICP-OES method and 94.4-108 % for ICP-MS method. The repeatability of the whole analytical procedure including the leaching step, evaluated on the basis of five repetitive extractions of a randomly selected sample was found up to 15 %. In the case of four dental ceramics, significant visual changes of their surface connected with a loss of mass (about 5 %) were observed. The loss of mass was evaluated and compared to international standards and literary data. Multivariate statistical methods proved similarities and differences between materials relating to chemical composition. A uniform corrosion test for ceramic and alloy dental materials was designed. Extracts (0.1 mol l^{-1} HCl, 37 °C, 168 hours) of ceramics and metal alloys were analysed (ICP-OES).

Introduction

Dental restorative materials are diverse substances including metal alloys (Ni, Cr, Ti, etc.) up to various kinds of ceramics (feldspar, silica, alumina, spinell, leucite, ZrO_2, etc.) long-term located in an oral cavity [1-5]. They have to exhibit resistance to mechanical load and pressure as well as to be highly chemically durable. During ingestion, pH values of food and beverages can vary from 2 to 11 and mostly are below 7; their temperature changes from about 0 (ice cream) to 70 °C (hot drinks). A saliva composition, dental plaque and bacteria presence represent an extreme chemical stress and support corrosion of materials in the sense of displacing of metal ions and protons. Corrosion and released ions are closely connected with biocompatibility and cytotoxicity of the corroded material. In order to reduce risks of adverse effect to the organism, it is inevitable to test dental materials just from the view of the chemical resistance [3].

For corrosion studies, interior environment is often replaced with artificial saliva [6-9]. For chemical testing, standard methods are available separately for ceramics and alloys. The ČSN EN ISO 6872 "Dental ceramic" standard recommends measuring of a total loss of mass after immersion in 4 % acetic acid for 16 hours at 80 °C and does not specify any other chemical tests [10]. The ČSN EN ISO 10993-14 "Quantitative and qualitative determination of degradation products from ceramic materials" mentions two chemical tests. The first one simulates "extreme" conditions, i.e., extraction in citrate buffer (120 hours, 37 °C). The second one imitates "common" conditions, i.e., normal pH (pH 7.4 ± 0.1) using the mixture of tris(hydroxylmethyl)-aminomethan and HCl (120 hours, 37 °C). This standard recommends inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry as suitable detection methods [11]. The ČSN EN ISO 10271 "Dental metal materials — methods of corrosive tests" does not mention any analytical method for determination of degradation products, only suggests a mixture of lactic acid and NaCl (pH 2.3) as

a simulation of acidified artificial saliva for extraction (37 °C, 168 hours) [12].

The recommendations of the ISO standard 6872 were used in studies [5,13-15], of the ISO 10271 in [2,16-18]. Various artificial saliva [3,7-9,19-26], beverages [9,25-27], organic acids [20,25,26], hydrochloric acid [4,28] or demineralized water [25-27] and mouthwashes [29] were used for the corrosion tests.

The aim of our study was to unify testing of both ceramic and alloy dental materials, i.e., to use only one common extraction procedure based on HCl in order to simplify existing procedures and to gain comparable data for both material categories. Further, together with the unified leaching test, to find the suitable analytical method. Finally, to employ the optimized procedure and statistical methods for finding of similarities and differences between materials, and for studying of their corrosive behaviour.

Experimental

The samples in the study represent typical dental materials available for clinical applications (Table I). The samples were formed to targets, cores or casted into copings, washed (common dish washing-up liquid, then repeatedly deionised water), dried (laboratory oven, 37 °C, 4 hours) and weighed. The surface areas were estimated.

The samples were inserted with 3 ml 0.1 mol l^{-1} HCl into polyethylene test tubes (10 ml, pre-treated with 2 mol l^{-1} HNO_3) and put in a heating water bath (37 °C, 168 hours). Then the extract was transferred into a volumetric flask, filled up to 10 ml with deionised water. For repeated extractions, the sample was left in the tube; a new portion of HCL was added and treated as mentioned above. A procedural sample blank was prepared together with samples. Every dental material was leached in two replicates. For the method validation, a sample representing an average matrix and covering a material variety was prepared: 1 ml of every extract was mixed together and spiked (Table II).

All reagents were of an analytical-reagent grade. Deionised water was purified using the SG Ultra Clear system (SG Water, Nashua, USA). 35 % (w/v) HCl and 65 % (w/v) HNO_3 (both LachNer, Neratovice, the Czech Republic) were distilled in a sub-boiling distillation equipment (BSB 939 IR, Berghof, Eningen, Germany). Calibration standards were prepared from single-element stock standards (Al, As, Au, Ca, Cd, Co, Cr, Cu, Fe, La, Li, Mn, Mo, Na, Ni, Pb, Si, Ti, Y, Zn) 1 ± 0.002 g l^{-1} (SCP Science, Canada).

The elemental analysis of extracts was carried out with the ICP-OES spectrometer Integra XL 2 and the O-TOF ICP-MS spectrometer Optimass 8000 (both GBC Scientific Equipment Pty Ltd., Australia). The operation conditions of the ICP-MS analysis were adjusted to compromise the sensitivity and resolution

Table I   Dental materials used in the study

	Brand name	Composition	Producer	Preliminary qualitative XRF analysis*
1	Zircon-Zahn	ZrO_2	Upcera Dental, China	Zr, Y, Hf
2	Procera®	ZrO_2	Nobel Biocare™, Sweden	Zr, Y, Os, Hf
3	Noritake	ZrO_2	Katana, Japan	Zr, Y, Os, Hf
4	LAVA™	ZrO_2	3M ESPE, Germany	Zr, Y, Mo, Fe, Co, Hf
5	Cercon®	ZrO_2	DeguDent, Germany	Zr, Ca, Y, Os, Fe, Hf
6	Procera®	Al_2O_3	Nobel Biocare™, Sweden	Al, Ca, Fe
7	Procera® +veneering ceramic	Al_2O_3	Nobel Biocare™, Sweden	Al, K, Ca, Si, Pb, Sr, Rb, Cr, Zn, Fe, Y, Zr
8	In-Ceram® Alumina	Al_2O_3	Vita, Germany	Ca, La, Al, Pr, Ce, Si, Fe, Nb, Ni, Pd, Ga
9	In-Ceram® Zirconia	$Al_2O_3 + ZrO_2$	Vita, Germany	Ca, Zr, Al, La, Y, Ce, Si, Hf, Pd, Mo
10	In-Ceram® Spinell	$Al_2O_3 + MgO$	Vita, Germany	La, Ca, Y, Ti, Al, Si, Bi, Ba, Pb
11	Vitablocs® Mark II	CEREC (feldspatic: $KAlSi_3O_8$-$NaAlSi_3O_8$-$CaAl_2Si_2O_8$)	DeguDent, Germany	Si, Al, K
12	IPS e. max Press	lithium disilicate ($Li_2Si_2O_5$)	Ivoclar Vivadent Inc., U.S.A	Si, Ca, Zn, K, Ce, P, Mn, Zr, Fe
13	Titanniobium, ingot	Ti-Nb (Ti 86; Nb 7; Al 6, w/w%)	Orotig, Italy	Ti, Si, Nb, Hf, Os
14	Titanniobium, coping	Ti-Nb (Ti 86; Nb 7; Al 6, w/w%)	Orotig, Italy	Ti, Nb
15	Safibond	Au-Pt (Au 77; Pd 18; Ag 2, w/w%)	Safina, the Czech Republic	Au, Pt, Ag, Zn, Pd, Mo
16	Remanium G soft	Cr-Ni (66 Ni, 26.5 Cr, 5 Mo, w/w%)	Dentaurum, Germany	Ni, Cr, Mo, Al, Mn, Y, Zr, Pd
17	Wiron 99	Cr-Ni (65 Ni, 22.5 Cr, 9.5 Mo, w/w%)	Bego, Germany	Ni, Cr, Mo, Ng, Mn, Y, Pd
18	Wirolloy	Cr-Ni (63.2 Ni, 23 Cr, 3 Mo, w/w%)	Bego, Germany	Ni, Cr, Fe, Mo, W, Si, Y, Pd, Zr
19	Heraenium NA	Cr-Ni (59.3 Ni, 24 Cr, 10 Mo, w/w%)	Heraeus Kulzer, Germany	Ni, Cr, Mo, Co, Al, Fe, Ca, Y, Pd

* (ElvaX, Elvatech Ltd., Ukraine)

Table II   The analytical characteristics and results of analysis of spiked sample

ICP-OES	Line nm	LOD^1 µg l^{-1}	LOD$_A$[a] µg cm^{-2}	SB µg cm^{-2}	spike µg l^{-1}	R %	RSD %
Al	167.081	16	0.11	< 0.11	100	105	7.2
Au[b]	242.795	4.8	0.032	< 0.032	20	98.1	4.8
Ca	422.673	1.1	0.0073	< 0.0073	50	97.2	4.6
Cr	267.716	1.2	0.008	< 0.0080	10	101	4
Fe	259.941	2.0	0.013	< 0.013	20	98.3	5.1
K	769.896	200	1.3	< 1.3	5000	96.2	5.9
La	412.324	4.2	0.028	< 0.028	1000	97.3	3.2
Li	670.784	6.4	0.043	< 0.043	100	98.2	3.8
Mg	280.27	1.0	0.0067	< 0.0067	50	102	3.2
Mn	257.61	1.9	0.013	< 0.013	10	98.6	4.8
Na	589.592	8.2	0.055	< 0.055	5000	101	4.9
Ni	231.604	3.5	0.023	< 0.023	100	100	4
Si	251.612	17	0.11	< 0.11	1000	106	5.1
Ti	323.452	1.6	0.011	< 0.011	200	94.8	3.9
Y	371.030	1.6	0.011	< 0.011	10	96.8	5.2
Zn	213.856	1.6	0.011	< 0.011	500	97.9	4.5
Zr[b]	339.198	3.0	0.02	< 0.020	10	100	4.8

ICP-MS	Isotope amu	LOD^2 µg l^{-1}	LOD$_A$[a] ng cm^{-2}	SB ng cm^{-2}	spike µg l^{-1}	R %	RSD %
Ag	107	0.089	0.59	2.5	1	98.0	6.3
As	75	0.010	0.067	1.0	1	103	8.2
Au	197	0.056	0.38	2.1	1	108	9.6
Cd	114	0.080	0.53	3.1	1	102	7.5
Co	59	0.033	0.22	1.9	1	98.2	6.2
Cr	52	0.035	0.23	2.2	1	96.2	8.1
Cu	65	0.036	0.24	3.4	1	98.3	6.5
Mo	95	0.023	0.15	3.6	1	104	7.9
Ni	62	0.051	0.34	5.2	1	94.4	11
Pd	195	0.056	0.37	2.9	1	99.2	6.6
Pb	E[c]	0.073	0.48	3.1	1	97.0	7.6
Ti	49	0.029	0.19	1.9	1	103	8.2
Y	89	0.028	0.19	2.3	1	98.1	7.9
Zr	94	0.036	0.24	2.5	1	101	8.4

LOD – limit of detection, LOD^1 for ICP-OES – a concentrations corresponding to the triple of the standard deviation of background counts for the least concentrated calibration standard, LOD^2 for ICP-MS – a concentration corresponding to the standard deviation of ten repetitive measurements of the blank solution containing only acidified water, [a] the original extract volume 3 ml was diluted to the final volume 10 ml + the average area 1.50 cm^2, [b] only in the first part of experiment used, E[c] – the sum of Pb isotopes 206+207+208

of the instrument for ^{238}U as well as to obtain the minimal LaO^+/La^+ and UO^+/U^+ ratios: the sample flow rate 1 ml min^{-1}, plasma power 1200 W, plasma, auxiliary and nebulizer gas flow rate were 10, 0.8 and 0.75 1 min^{-1}, respectively, and multiplier gain 2400 V. The sensitivity of 20000 counts s^{-1} for 1 μg l^{-1} (mass integrated peak) and resolution of 1600 was reached for ^{238}U. The measurement conditions for ICP-OES were optimised based on signal-to-background ratios of the least concentrated elements. The operation conditions of the ICP-OES analysis were: the sample flow rate 0.4 ml min^{-1}, plasma power 1000 W, plasma, auxiliary and nebulizer gas flow rate were 10, 0.6 and 0.65 1 min^{-1}, respectively, photomultiplier voltage 600 V, view height 6.5 mm, ten replicated reading on-peak 3s, fixed point background correction. In case of Mg and Ca, it was necessary to reduce the photo-multiplier voltage to let down their signal intensities, and the real ICP-OES detection ability for Mg and Ca was far better. The external calibration standards acidified with hydrochloric acid were used for quantification. In the case of both methods, spectral interferences were not detected. Possible non-spectral interferences in both analytical methods were evaluated using the spiked sample of mixed single extracts and the standard addition method. These effects were not proved. The internal standard Rh was used for overcoming of instabilities given by plasma fluctuations.
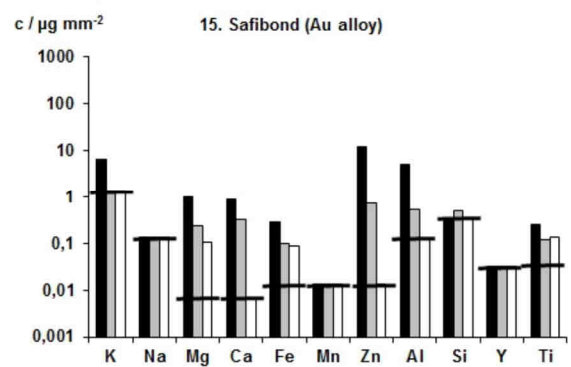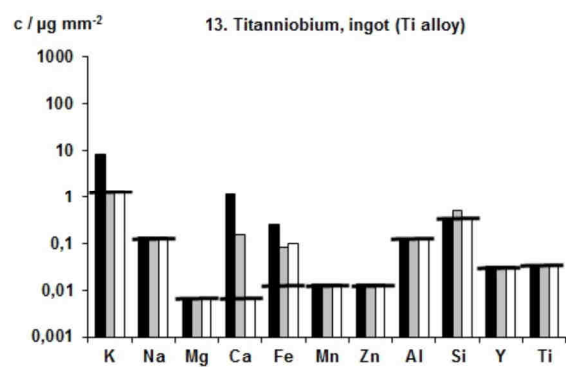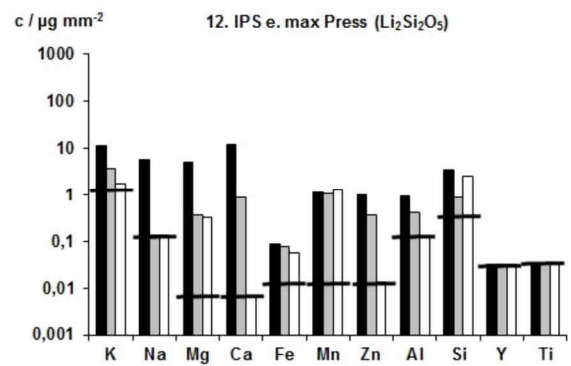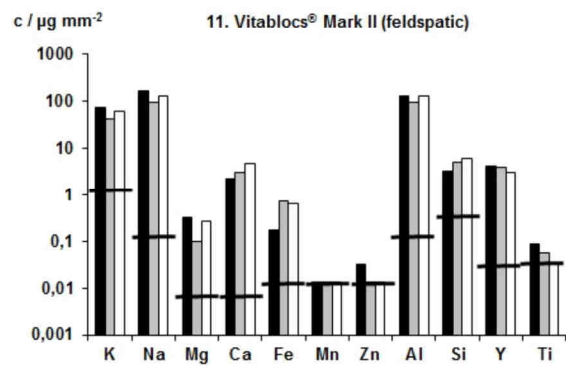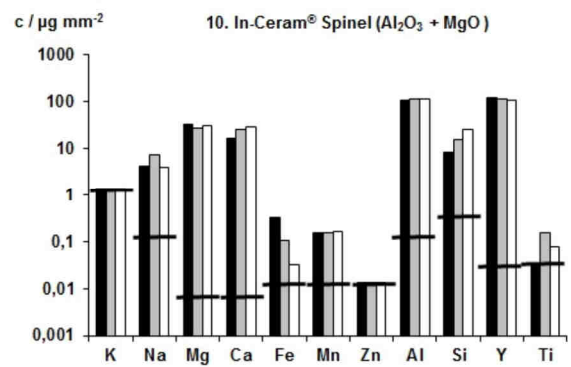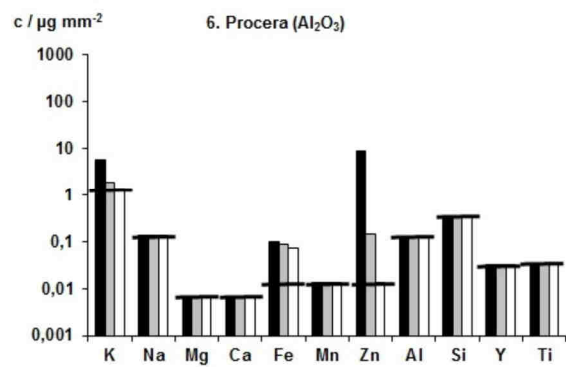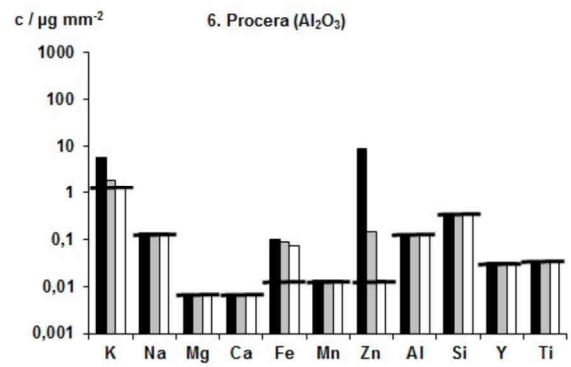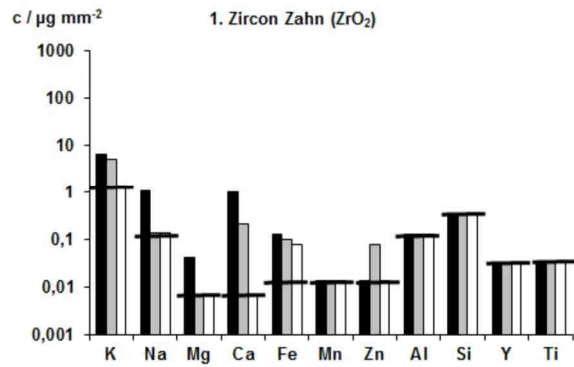
The emission lines, isotopes and analytical characteristics are listed in Table II. The method was validated using the mixed sample (5 replicated). Spiked amounts were 10-5000 (ICP-OES) and 1 μg l^{-1}(ICP-MS). Recoveries (R) were 94.8-105 % for the ICP-OES and 94.4-108 % for the ICP-MS. Repeatability (relative standard deviations, RSD) was 3.2-7.2 % (ICP-OES) and 6.2-11 % (ICP-MS). The repeatability of the whole analytical procedure including the leaching step based on five repetitive extraction of the random sample (IPS e. max Press) for elements detectable in the extract was 10-15 %.

Final volumes of extracted dental material were relatively low — ten millilitres but they were sufficient for both analytical methods. A consumption of the ICP-OES analysis was about five millilitres, for the ICP-MS it was necessary to have two millilitres.

Results and Discussion

The Leaching and Analytical Procedure

Looking through the ISO standards and corrosion studies, acid constituents and chlorides are mostly presented in the extraction media. HCl combines both of them and overcomes subsequent analytical problems with purity of chemicals used for testing mixtures reflected in sample blanks (easily distillable, accessible in a high quality).
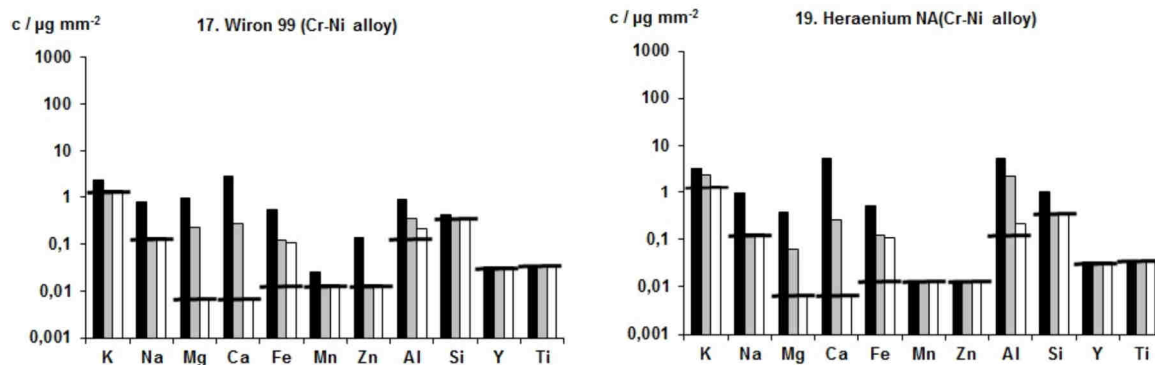
1. Zircon Zahn (ZrO₂)

6. Procera (Al₂O₃)

6. Procera (Al₂O₃)

10. In-Ceram® Spinel (Al₂O₃ + MgO)

11. Vitablocs® Mark II (feldspatic)

12. IPS e. max Press (Li₂Si₂O₅)

13. Titanniobium, ingot (Ti alloy)

15. Safibond (Au alloy)

Fig. 1   Sequential leaching of dental materials. 0.1 mol l^{-1} HCl used at 37 °C, 1st extract (□) – one week; 2nd extract (■) – after 1st week an original extraction agent was transferred, a new portion was added and let another week; 3rd extract (▨) – after 2nd week the original extraction agent transferred, a new portion was added and let another 2 weeks

In comparison with the ISO standards [10,12], our extraction procedure was changed. The HCl concentration was 0.1 mol l^{-1}, i.e., lower than given by the ISO 10271 [12]. Sample weights were smaller (weights 0.2-1.3 g) than recommend by the ISO standards (5-10 g). Always, one piece was taken for extraction with 3 ml 0.1 mol l^{-1} HCl for 168 hours at 37 °C. Leaching was consequently repeated. The first extract was transferred to a volumetric flask, another 3 ml HCl was added and the experiment continued next week. The second extracts were removed, new acid was added and leaching continued another two weeks in order to gain the third extracts. Results for some samples are displayed in Fig. 1. The amount of released element is expressed as μg cm^{-2} to be comparable with the ISO standards [10-12].

Released ions amounts (related to the sample area) were compared in three sequential extracts. Evidently from Fig. 1, ions release occurred mostly during the first week of the corrosion test. The multivariate statistical analysis (Statistica 10, StatSoft Cz, the Czech Republic) of the first extracts proved the effectiveness of the procedure. The principle component analysis based on the results of chemical analysis (elemental concentrations of Na, Mg, Fe, Mn, Si, Al, Y, Zr, Ti, Cr, Ni; Fig. 2) reveal mutual similarities and differentiations in chemical composition of the first extracts (e.g., materials 8-10 all Vita, Germany; 13 and 14 Titanniobium alloys, 16-19 Cr-Ni alloys). Similar materials belong together and behave similarly during the corrosion test. Ions released within one week procedure can give evidence of the tested material corrosion properties. The testing procedure was thus shortened to 7 days and only one extract was used in all next experiments.
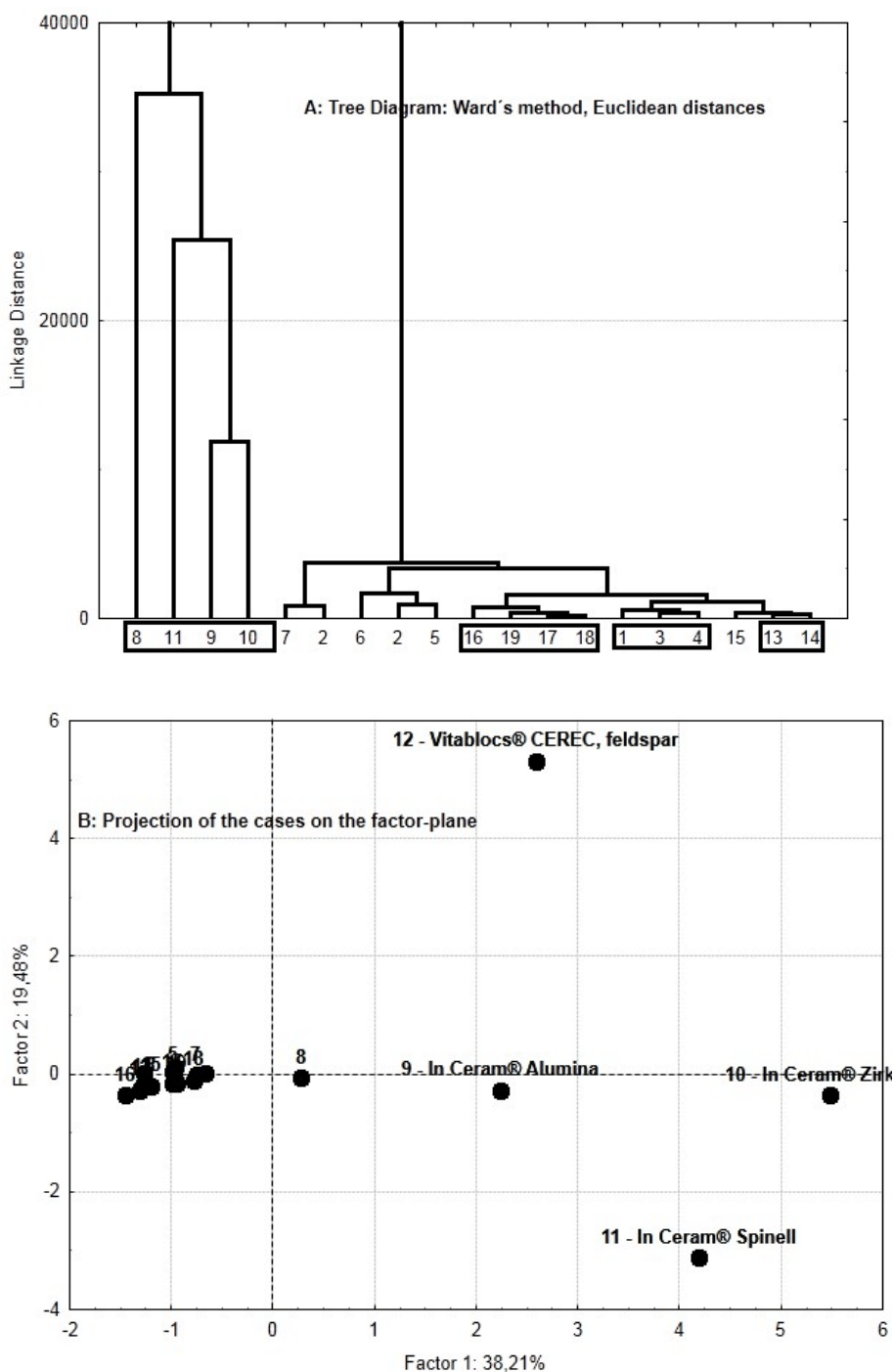
Fig. 2   The statistical evaluation of data for the ICP-OES analysis of first extracts; using multivariate methods: a – the tree diagram, b – the principal component analysis

Justification of Analytical Methods

In Fig. 1, the results for all three extracts obtained by the ICP-OES are presented (Al, Ca, Fe, K, Mg, Mn, Na, Si, Ti, Y, Zn) with exception of undetected, highly resistant Au and Zr. The ICP-MS analysis indicated As, Cr, Cu, Mo, Ni, Ti, Y, Zr,

Pb, Cd, Au, Ag, Pd mostly at the level of sample blank. Cr, Ni, Mo and Cu were provable in the Cr-Ni alloys: Cr 0.071-0.85, Cu 0.021-0.041, Mo 0.075-0.58, Ni 0.55-4.0 μg cm^{-2}. 0.31-560 μg cm^{-2} of Y was found in Al_2O_3 materials (In-Ceram® Alumina, Zirconia, Spinell) and in Vitablocs® Mark II. Ti was indicated in Ti-Nb alloys (1.4-4.1 μg cm^{-2}). These concentrations are easily detectable using the ICP- OES which is easier and for sample preparation and handling, more comfortable, less technically and economically demanding than the ICP-MS.

The ICP-OES LODs can be decreased using smaller final volumes of extracts (5 ml). The ions detectable by the ICP-OES give together about 99 % of all released ones. It seems to be reasonable to use only the ICP-OES as a detection technique.
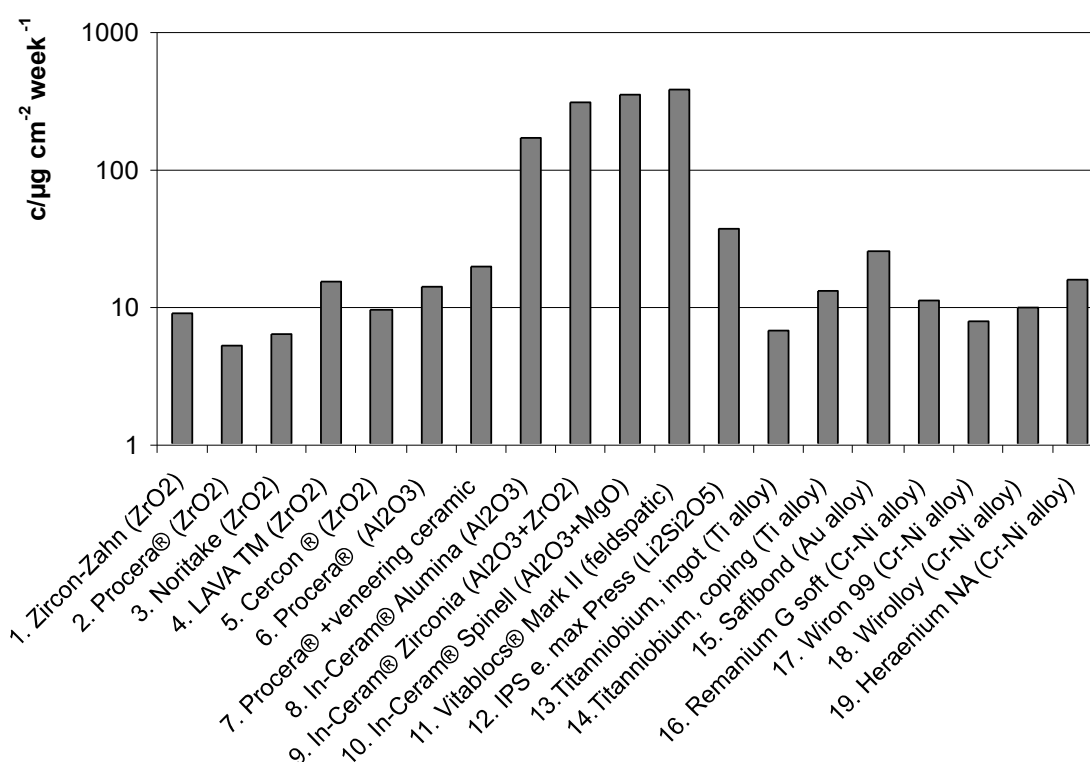

Fig. 3   The loss in mass for dental materials tested

Loss of Mass

Five ceramic materials (In-Ceram® Alumina, In-Ceram® Zirconia, In-Ceram® Spinell, Vitablocs® Mark II and IPS e. max Press) have lost 4-5% of the origin mass. The standard ISO 6872 gives the values for evaluation of chemical solubility of dental ceramics. The maximal loss of mass for core ceramics is 2000 μg cm^{-2}, for others 100 μg cm^{-2} [10]. For dental alloys, similar values are not available [12]. Manaranche and Hornberger [2] established the proposal to classify dental alloys according to their corrosion: class I release <1-10, class II 10-100 and not

acceptable class III 100-1000 $\mu g \, cm^{-2} \, week^{-1}$. Figure 3 reveals differences in the ions released from the tested materials. Similarly to the above mentioned classes [2], four of ZrO_2 ceramics (Zircon-Zahn, Procera, Noritake, Cercon), the Titanniobium ingot and two Cr-Ni alloys (Wiron 99 and Wirolloy) are included into the class I. According to these criteria, In-Ceram® Alumina, In-Ceram® Zirconia, In-Ceram® Spinell and Vitablocs® Mark II are in the class III with an unacceptably high ions release. However, these four samples meet the limit of the standard ISO 6872 [14] for core ceramics 2000 $\mu g \, cm^{-2}$. In this case it could be misleading and therefore it is impossible to compare our values with this limit, because various testing conditions based on different extraction ways were used. Different and a bit inconsistent results for the same extraction procedures and similar materials can be often found in the literature [4,15,17].

Evaluation of Tested Materials and Suitability of Choice of Analysed Elements

The results for consequent extracts (Fig. 1) revealed groups of samples with decreasing or increasing ions contents. In the case of decrease, some ions (Na, K, Mg, Ca) were noticed mostly only in the first extracts, which is likely given by a surface contamination and insufficient cleaning before the corrosion test. In the case of dental alloys, release of ions can be gradually restricted by a formation of passivating oxide layer. The second group, which is the same as statistically identified as the "In ceram" and "Vitablocs" cluster, exhibits a rising trend for most of elements. Probably, this fact is connected with dissolving of elements from the inner volume after surface erosion.

As expected and statistically proved, released ions are connected to the sample composition (Al in extracts of all Al_2O_3 samples, Cr and Ni leached from Cr-Ni alloys). Analysed elements were chosen according to the known or predicted composition ("matrix" Al, Si, Zr, Y Au, Cr, Ni, etc.), the preliminary X-ray analysis (Cu, Mn, Zn) and health risks (Pb, Cd, As). As was detected only in one extract (In-Ceram® Alumina; 0.12 $\mu g \, cm^{-2}$), Pb, Cd, Mn, Zn were detected at the sample blank levels. Cu accompanied the "matrix" elements Cr, Ni and Mo in the Cr-Ni alloys. Zr was detected only in one zirconium ceramic (Zircon-Zahn).

Conclusion

The unified corrosion test of both dental ceramics and alloys is discussed. Hydrochloric acid (0.1 mol l^{-1} HCl, 37 °C, 168 hours) represents an extremely simple connection of requirements to acidity and chloride matrix used frequently in corrosion studies and the ISO standards. Both analytical methods tested (the ICP-OES, ICP-MS) provide satisfactory limits of detection, recoveries and

repeatabilities. The less technically and economically demanding ICP-OES is able to reveal 99 % of the released elements.

Eleven dental ceramics and seven alloys were tested. Visual surface changes and a loss in mass (about 5 %) were noticed for four ceramics (mixtures of aluminium and other oxides). Noticeable amounts of metals related to the alloy composition (Cr-Ni based alloys) were observed. This corrosion test is useable for both ceramics and alloys. It has the potential to simplify existing procedures and to gain comparable data for both material categories.

Acknowledgement

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