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An innovative method for in-situ composition analysis of fixed metallic dental restorations

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ABSTRACT

Dental restorations made from alloys corrode during their service time. In cases of suspected toxic or allergic reactions to the corrosion products, the composition of the intraoral dental restorations has to be determined. The sample materials can be obtained intra-orally in a non-destructive manner using the chipping test. Metallic shavings are extracted with the aid of a dental stone and graphite carrier platelet, which is then transferred to an electron microscope for electro dispersive X-ray (EDX) analysis. The chipping test suffers from a rather complicated and error-prone procedure of obtaining and transferring the samples.
Objective. The objective of the present study was the validation of a simplified method for non-destructive in-situ extraction of dental alloy samples, using a newly developed dental bur made from carbon fiber reinforced polyether ether ketone (PEEK), which at the same time serves as an electrically conductive sample carrier for EDX analysis.
Methods. Fifteen burs for dental hand pieces were manufactured from carbon fiber reinforced PEEK, using two formulations. The burs were passed over precious and non-precious dental alloys with different rotation speeds. The alloy samples embedded in the burs were analyzed using EDX and compared to a control.
Results. The burs manufactured from PEEK containing 30% short carbon fibers proved sufficiently robust for sample extraction even from the harder non-precious metals. The results of EDX analysis were in accordance with the control,no statistical significant differences, free of contamination, and were not affected by rotation speed,higher as 20%.
Significance. The proposed method is valid, practical and constitutes an improvement over the traditional chipping test.

1. Introduction

Metal alloys are widely used at present for the production of dental restorations. Thanks to their intrinsic metallic properties, they can be manufactured into delicate structures that are able to withstand the considerable strains encountered in the oral cavity.

The processing of dental alloys as well as their customization to the particular application in the patient's mouth have been improved and refined over the last century.

Even though viable alternatives exist in the form of high-strength zirconium-dioxide-based ceramics, metallic restorations continue to be placed and can still be found in the mouths of innumerable patients, often having accumulated many years of service.

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A serious drawback of metallic components is their propensity towards corrosion, a process that is promoted by the particular conditions encountered within the oral cavity. Permanent moisture, fluctuating values of pH, varying electrolyte composition in the presence of chloride ions, as well as a wide range of temperatures add to intermittent mechanical stresses in creating a highly challenging environment.

The biocompatibility and longevity of metallic biomaterials are consequently directly tantamount to corrosion resistance [1].

Conclusive evidence exists that dental alloys – that is, metallic biomaterials – can adversely affect the physical condition of patients [2–8]. It has also been widely observed that changes of the oral mucosa can develop adjacent to dental alloys. Among those are oral lichenoid reactions (OLE) and oral lichen planus (OLP). In less severe cases, reddening of the buccal and lingual mucosa as well as metallic taste can occur [9]. Metallic ions released from dental alloys can trigger and sustain chronic inflammation [10].

The effect of metal ions released in the oral cavity is not completely understood yet. Furthermore, the impact of an alloy on the human organism differs from patient to patient. Consequently, for most alloy formulations, no reliable claims can be made regarding their risk potential, especially when under consideration for market approval. This fact merits closer attention.

Many metal ions are essential for biochemical reactions in the human organism. This however cannot lead to the conclusion that the corrosions products of these same metals, when released from dental alloys in the oral cavity, can be considered harmless. Even essential elements such as iron (Fe), Zink (Zn) and copper can unbalance homeostasis in certain doses, negatively affecting patient wellbeing, as described by Jomova et al. [11] and Lee et al. [12].

When describing the different modes of action of metal ions, a local effect can be distinguished from a systemic effect. The systemic effect can be either toxic or allergenic. A toxic effect exists when a dose-response-relationship is present. The allergenic effect is independent of concentration. An allergenic effect of type 4 can be diagnosed by the lymphocyte transformation test (LTT) [16].

Today, many chronic inflammatory diseases can be diagnosed and treated. When hunting for the causes of chronic inflammatory diseases, dental materials, especially dental alloys, are of particular interest, because they constantly release their degradation or corrosion products to the patient organism over long stretches of time [17,18].

To be able to perform a nondestructive elemental analysis in the case of a suspected dental material intolerance, the so-called chipping test (originally named “Splittertest” in German) was developed by Wirz et al. [13]. This test method allows the extraction of material samples from the surfaces of intraoral fixed prostheses in situ, without having to remove or damage the sound restorations.

In carrying out the chipping test, a silica oxide grinder or fresh diamond bur is passed over the metal restoration in consideration and the resulting shavings or chippings are transferred to a graphite-coated platelet. This electrically conductive platelet containing the metal shavings is glued to a metallic carrier in order to be inserted into an electron microscope for elemental analysis using energy dispersive X-ray analysis (EDX). Hereby the detection and analysis of characteristic X-ray radiation provides information on the specimen’s elemental composition.

This test has been most notably applied at the University of Basel over a period of more than ten years, comprising a number of more than 1600 patients. The resulting therapeutic decisions lead to treatment success in 90% of cases [14,15].

A drawback of the chipping test is the complexity involved in transferring the shavings from the grinder or bur to the graphite platelet. Usually, an assistant is required for holding the platelet, making an uncontaminated sample collection from hard to reach areas all but impossible. Furthermore, for each sample extraction a new, clean grinder or diamond bur has to be used to prevent falsification of the results due to contamination.

To that extent, a specialized bur that allows for sample collection of metallic shavings and at the same time serves as a carrier substrate for EDX analysis would be of great benefit, improving handling and sample quality.

Due to their electric conductivity, purity and inertness, carbon fibers are especially suitable for this application. A composite material of sufficient mechanical strength can be attained when utilizing carbon fibers as a reinforcement in a matrix of the high-performance polymer polyether ether ketone (PEEK).

Consequently, the aim of the current study was the development and testing of a dental bur made of carbon fiber reinforced (CFR-)PEEK to achieve simplified handling when conducting the “Wirz” Chipping Test and at the same time improving analytical precision.

2. Materials and methods

To begin with, a PEEK compound had to be identified that, when brought into the form of a conventional round bur for low speed dental hand pieces, would be able to meet the following requirements:

- Sufficient edge strength to allow chip removal from precious and non-precious metallic dental restorations
- Good adherence of the chippings to the surface of the bur
- Sufficient electrical conductivity to be employed in any conventional type of electron microscope

For this purpose, two different carbon fiber reinforced PEEK compounds were provided by the manufacturer Lehmann & Voss (Hamburg, Germany):

- Containing 10% short carbon fibers (hereafter designated PEEK-1)
- Containing 30% short carbon fibers (hereafter designated PEEK-2)

These PEEK compounds were injection molded into the form of a commercially available PEEK-based round bur (Polybur, Brassler, Lemgo, Deutschland), suitable for the standard chuck of a dental low speed hand piece (Fig. 1)

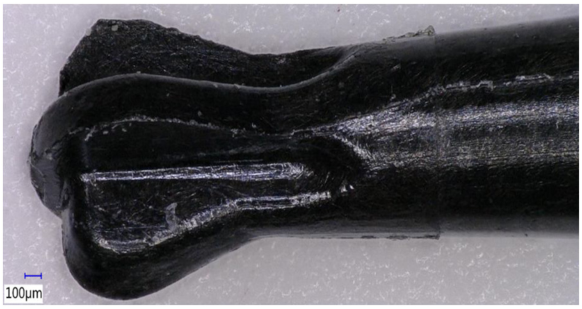

Fig. 1 – Head of the round bur prototype manufactured from CFR-PEEK.

Fig. 2 – CFR-PEEK sample carrier enclosed in resealable sleeve for transportation.

15 round burs each manufactured from PEEK-1 and PEEK-2 were chucked into the low speed hand piece of a dental chair delivery system (M1, Siemens Sirona, Bensheim, Germany). The burs where applied against precious and non-precious metal surfaces of a model cast prosthesis for 15 seconds each under manual pressure. Different revolution speeds of 10.000 rpm, 30.000 rpm, 50.000 rpm, 70.000 rpm and 100.000 rpm were employed.

Subsequently, the round burs were individually placed into resealable plastic sleeves to prevent contamination during the transport to the scanning electron microscope (Fig. 2).

The burs were placed into the electron microscope and the surfaces containing the impacted metal chippings were analyzed as to their elemental composition with the aid of energy dispersive X-Ray spectroscopy (EDX) (Quantax 6, Bruker, Berlin, Germany). The composition analysis was performed by the EDX system manufacturer's software (Esprit 2.0, Bruker, Berlin, Germany). Hereby at least three different impacted particles per bur were evaluated, as well as an additional sample of the metallic source material as control.

Furthermore, the edge stability of the burs was examined by scanning electron microscopy (CamScan Maxim, CamScan Electron Optics, Cambridge, UK).

The obtained data were statistically analyzed and compared by ANOVA.

3. Results

Optical microscopic inspection revealed that burs made from PEEK-1 compound showed considerable deterioration of the

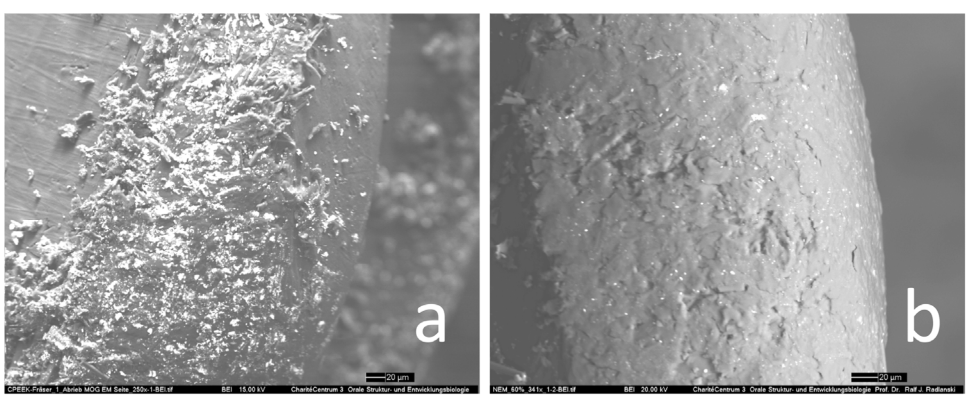

Fig. 3 – Backscatter electron (BSE) image of CFR-PEEK sample carrier head. CFR-PEEK surface appears in tones of grey, embedded metal particles appear white. Left (a): after sample extraction from precious metal; Right (b): after sample extraction from non-precious metal.

Table 1 – Results of elemental composition analysis of precious metal alloy as a function of rotation speed, with base material composition as control.

Rotation speed [%]	Cu [wt%]	Zn [wt%]	Ag [wt%]	In [wt%]	Pt [wt%]	Au [wt%]
20	4,25 ± 0,49	1,2 ± 1,04	3,99 ± 3,41	0,83 ± 0,73	17,02 ± 12,75	72,72 ± 14,89
40	5,29 ± 1,35	2,17 ± 0,75	6,37 ± 0,79	0,71 ± 0,39	8,47 ± 1,43	76,99 ± 1,47
60	5,64 ± 1,20	1,92 ± 0,17	5,09 ± 2,59	0,56 ± 0,40	7,95 ± 0,69	78,83 ± 2,18
80	4,52 ± 0,30	2,02 ± 0,26	5,53 ± 2,84	1,12 ± 0,20	10,24 ± 0,71	76,95 ± 4,23
100	6,14 ± 2,91	2,69 ± 1,46	9,91 ± 4,59	1,28 ± 0,32	6,44 ± 4,89	73,54 ± 4,38
Average	5,17 ± 0,78	2 ± 0,54	6,18 ± 2,26	0,9 ± 0,30	10,02 ± 4,14	75,81 ± 2,57
Control	4,08 ± 0,23	2,18 ± 0,27	6,49 ± 0,43	1,01 ± 0,25	11,69 ± 1,57	74,55 ± 1,49

Table 2 – Results of elemental composition analysis of non-precious metal alloy as a function of rotation speed, with base material composition as control.

Rotation speed [%]	Co [wt%]	Cr [wt%]	Mo [wt%]
20	64,64 ± 0,26	29,95 ± 1,28	5,5 ± 1,21
40	60,89 ± 3,60	31,94 ± 1,81	7,17 ± 2,52
60	61,34 ± 1,77	26,9 ± 5,04	11,76 ± 6,36
80	55,13 ± 3,12	36,98 ± 1,2	97,89 ± 1,84
100	57,23 ± 3,07	35,86 ± 3,79	6,92 ± 0,72
Average	59,85 ± 3,72	32,33 ± 4,16	7,85 ± 2,35
Control	58,00 ± 5,17	34,16 ± 3,36	7,84 ± 1,98

cutting edges and an absence of embedded particles when applied on the harder non-precious metal. The burs made from PEEK-2 compound on the other hand proved to be sufficiently resistant for sample extraction even from the harder non-precious metal (Fig. 3).

The shavings were securely embedded in the polymer matrix even though the bur had been handled and transported in the resealable plastic sleeve without particular caution.

The comparison of the elemental analysis results obtained from the PEEK-2 burs showed no significant difference in composition as a function of the rotation speed (Tables 1 and 2). Apart from oxygen and carbon, no foreign contamination could be found.

4. Discussion

The requirements set forth at the beginning of the study, which are simple handling and analytical precision when conducting the "Wirz" chipping test, were met in the case of the PEEK-2 compound reinforced with 30% short carbon fibers. The achieved edge hardness permitted the necessary amount of metal to be extracted and the conductivity of the substrate material proved to be sufficient for EDX analysis without having to resort to graphite coating.

Therefore, the described method is helpful as a diagnostic aid and provides answers to the following questions:

a) Which alloying elements are present in the patients' oral cavity?
b) In which part of the present metallic restorations can they be found?
c) Where is the source of elements detected through saliva tests?

The simple handling made possible by the presented technique prevents the introduction of contaminations that might act as confounding factors. Thus, a very accurate analysis of the alloy composition is made possible without having to destroy or remove the prosthetic restoration in question from the patient's mouth.

5. Conclusions

The non-destructive in-situ elemental analysis of metallic dental prostheses in cases of suspected dental alloy intolerance can be conducted in a simple and accurate manner using the newly developed carbon fiber reinforced PEEK bur as a sample carrier.

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