Identification of Cobalt and Chromium in Prosthetic Restorations by thin Layer Chromatography

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Acta Stomatol Croat
2000; 47-50

PRELIMINARY REPORT
Received: January 17, 2000

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Summary

Owing to the ample dental market supply, more than a thousand different systems and alloys for prosthetic use are presently available. The aim of the study was to identify the basic components of the existent prosthetic constructions in patients requiring additional prosthetic therapy. Anodic sampling of eight prosthetic restorations of unknown composition was performed using a minielectrode with a graphite handpiece, aqueous NaCl solution as electrolyte, and a 4.5 V battery as a source of electric current. The samples were analyzed by quantitative thin-layer chromatography (QTLC). Sample chromatograms were developed by use of the acetone and 2 M HCl solvent system. Cobalt was visualized using aqueous solution of sodium -diethyldithiocarbonate, and chromium by ethanol solution of dimethylglyoxime. The percentage proportion of the elements identified was determined on an image analyzer, previously gauged according to the known standards.

Key words: *dental alloys, anodic sampling, quantitative thin-layer chromatography (QTLC)*

Introduction

More than a thousand different types of dental alloys for prosthetic reconstruction are presently available on the market (1). The choice of casting dental alloys generally depends on the vicinity and impact of the market, economic factors, and possibilities of a particular dental laboratory. However, the mouth is sometimes a very aggressive corrosive medium, which requires the use of alloys of the same or at least similar composition. The human body is very sensitive, and sensitization or allergy to certain metal components may occur (2,3). Pierce and Goodkind point to the still inadequate knowledge about the effect of dental alloys containing nickel, beryllium and chromium on the human body, and recommend long-term biocorrosion studies in animals and humans to characterize the acute or chronic toxic effects of base alloys on the human body (4). Furthermore, palladium, although a precious metal, may also have toxic and/or allergic effects on the biological system, when used in the ionic form and at high concentrations (5). Wirz et al. report on inadequate biocompatibility and limited stability of palladium-based alloys in the oral cavity as well as on the resulting local or systemic reactions (6).

As the composition of the alloy used usually remains unknown to the therapist, the reason for possible adverse reactions can only be explained by subsequent identification of the composition of the prosthetic restoration. Laboratory analyses such as X-ray emission spectroscopy (XES), proton induced X-ray emission spectroscopy (PIXE), atomic absorption spectroscopy (AAS), and others are quite inappropriate for this purpose, as they require removal of the prosthetic restoration from the patient's mouth as well as samples of specific dimensions and preparation (7-11).

Therefore, the possibility of alloy sampling in the patient's mouth without changing the state and appearance of the prosthetic restoration is more attractive. This group of sampling and identification methods include abrasive stripping voltammetry, 'splitter test' with EDX analysis, and anodic sampling combined with quantitative thin-layer chromatography (QLTC). Abrasive stripping voltammetry is based on the abrasive transfer of alloy traces onto the surface of a graphite electrode, and electrochemical removal of these traces with the recording of current-voltage curves. Scholz et al. prefer this method for the analysis of amalgams or a particular metal (12), whereas Živko-Babić et al. use this method for demonstration of silver and palladium in silver-based alloys as well as of nickel, cobalt and chromium in base alloys (13). 'Splitter test' was introduced by Wirz (14,15). This type of sampling includes grinding of the metal powder from the crown or body of the bridge. The powder is spread onto a self-adhesive graphite foil, which then becomes conductive. The metal powder thus spread is determined by EDX analysis. The method has been accepted as a diagnostic tool to explain intolerability of the metal in the mouth (1,14-16). Rozylo used QTLC to determine the level of formaldehyde in hard tissues of human teeth (17). The results obtained by Šoljić and Jurlina proved the method to be sufficiently accurate and appropriate for simultaneous quantitative determination of platinum and rhodium in catalysts (18). Thin-layer chromatography is ever increasingly used for the analysis of high-alloy steel (19). The use of anodic sampling with QTLC for the identification of dental alloy composition was not described in dental literature until the study of Živko-Babić et al., who determined the proportion of cobalt in dental alloys containing cobalt as the main component, by use of anodic sampling and chromatographic method (20). Ivanković et al. have attempted to optimize the conditions of cobalt sampling and identification in dental alloys from different manufacturers (21).

Material and methods

Anodic sampling of the existing prosthetic restorations in the oral cavity was performed in eight patients who needed additional prosthetic therapy. The principle of anodic sampling involves anodic dissolution of the material by means of a special minielectrode. The device is schematically pre-sented in Fig. 1. The minielectrode consists of a metal handpiece covered with graphite, which contains a nylon fiber soaked in aqueous NaCl solution (1 g/100 mL). A 4.5 V battery serves as a source of electric current. During sampling the minielectrode, connected to the battery positive pole is attached to the metal part of the crown or base plate of the denture to be sampled, while the other electrode, connected to the battery negative pole, is attached to another metal in the mouth or to a copper plate outside the patient's mouth (Figs. 2 and 3). The sampling takes 20 s at room temperature (≈23°C). A new nylon fiber soaked in aqueous NaCl solution is used for each sampling. By closing the electric circuit, the anodic sample is dissolved, and the dissolved metal ions are transferred to the nylon fiber. This is followed by QTLC analysis of the dissolved metal ions using 200x200 mm glass-backed TLC plates (Merck, Darmstadt, Germany) coated with a 0.1-mm layer of microcrystalline cellulose. Immediately upon anodic sampling, the tip of the nylon fiber with dissolved metals is attached to the chromatographic plate, 20 mm from the lower edge of the plate, and is kept in this position for exactly 10 s. Thus, part of the electrolyte and the total mass of dissolved metals obtained by anodic sampling are transferred by capillary forces from the nylon fiber to the dry microcrystalline cellulose layer. The transfer is performed at eight points of the plate, 10 mm apart. The ninth point is left blank to show surface response. The plates are dried in a stream of hot air to remove the traces of electrolyte, and then placed into a chromatographic chamber containing the following solvent: acetone - HCl (conc.) - H_2O (86:8:6 v/v). The migration distance is 120 mm. Upon development, the plates are dried and the spots of cobalt are visualized by spraying with aqueous solution of sodium diethylth-iocarbonate (5 g/100 mL). Chromium is identified by use of ethanol solution of dimethylglyoxime (1 g/100 mL). A sample with negative cobalt and chromium response is presumed to be a silver-based alloy. This metal requires quite different conditions of sampling and identification. The percentage of the elements identified is determined on an image analyzer, Leco 2001 (Leco, St. Joseph, Canada), previously gauged according to the known standards.

Results

Chromatographic spots of the identified elements are shown in Figs. 4 and 5. The color and intensity of particular chromatographic spots identified the green and red spot to be produced by cobalt and chromium, respectively. The detection was confirmed by RF values of each of the elements, i.e. the ratio between the element migration distance and distance of the solvent front. The percentage of the mentioned metals in each sample analyzed was calculated by scanning the spots and comparing them with standard values (Table 2). Reproducibility of the results, as determined by use of relative standard deviation (RSD), was 2.6%. Cobalt was demonstrated in three samples, with the percentage proportion ranging between 55.8% and 65.5%. Such a high proportion of cobalt suggested it to be the main component of the alloy analyzed. Chromium was identified in seven samples, with a percentage varying from 16.3% to 25.7%. It is an alloy element. Neither of the elemets was found in the eighth sample.

Discussion

Knowledge of the composition of dental alloys before their incorporation into a biological medium is a precondition for successful prosthetic therapy. Identification of an alloy in the patient's mouth is limited by the impossibility of obtaining samples of specific dimensions, required for some analytical procedures. Therefore, the number of tests is limited in the case of cemented prosthetic restorations. Abrasive stripping voltammetry is a quantitative and unreliable method with possible failure or overlapping of particular metal peaks, whereas 'splitter test' requires grinding, slight though, of the crown in the patient's mouth. Elements making less than 2% of an alloy sample cannot be accurately identified by EDX analysis.

On the other hand, anodic sampling is rapid, simple, and nondestructive, provided the sample is conductive, which applies to all metal components of prosthetic alloys. The choice of electrolytes for sampling depends on the alloy composition, since an electrolyte that does not allow adequate oxidation will decrease the value of the results. Therefore, the elements potentially expected to be found should be determined before the sampling, and then an electrolyte which will produce soluble salts in the ionic form with the presumed element should be chosen accordingly. Also, inadequate concentration and low voltage will make the results unreliable.

In this study, only detection of the elements presumed to be found in a large proportion was carried out. Reproducibility of the results yielded value dispersion of up to 2.6%. As not all measurements were performed at the same time, a change must have occurred in the battery voltage, which was demonstrated by Ivanković et al. to substantially interfere with the measurement results (21). However, when the alloy composition, i.e. the presence of a potential allergen, is to be verified, the numerical figure plays only a minor role. In their pilot study, Živko et al. used an electrolyte of 0.9% NaCl and voltage of 4.5 V for cobalt sampling (20). Results of cobalt spot identification on the image analyzer deviated by up to 2.9% from the declared values, while identification of cobalt spots by video scanning in the study of Ivanković et al. showed deviation of up to 5.47% from the declared values. Using EDX analysis, Wirz reports on a 2% measurement error. Anodic sampling is inappropriate for the detection of nonmetals, which are frequently found as adjuvant elements in dental alloys.

For identification of a great number of metals in alloys, the question is how to separate particular elements, i.e. how to select and identify them to the greatest possible extent. Generally, no interferences are expected, because elements with identical RF values are rarely found in the same alloy. Until an act is passed in Croatia obliging the therapists to know and record the composition of an alloy incorporated into a biological medium, additional standardization of the use of this method in prosthetic dentistry should be encouraged.

Conclusion

The success of prosthetic therapy depends, among other factors, on the knowledge of the composition of the prosthetic restoration incorporated into the biological medium. By optimizing the conditions of anodic sampling and chromotographic analysis, the proportion of one or more alloy components can be determined in a rapid, simple and, most important, nondestructive way. This provides the basis for appropriate choice of alloy to be used for subsequent prosthetic therapy, at the same time showing whether the possible symptoms of a patient's sensitization or allergy are due to the composition of the existing prosthetic restoration.