The significance of pH for the inhibiting effect of phosphate buffer on the corrosion processes

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The influence of pH on the protective effect of phosphate buffer on the corrosion processes was studied by measuring the amounts of elements released from a dental amalgam. The analyses were conducted by means of atomic absorption spectrophotometry. The protective effect of phosphate buffer was reduced in solutions with low pH, and mercury could be detected in the solutions. Phosphate buffer maintained its aftereffect in the pH region 6.8–5.5. The flow rate of the solution did not influence the inhibiting effect of phosphate buffer.
□ *Aftereffect; amalgam; dissolution; flow rate; oral lichen planus; passivation*

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During the last few years the interest of many scientists in dental materials has been concentrated on the corrosion behavior of different types of dental amalgam and on the changes taking place in the microstructure of amalgam after exposure to aggressive agents (1, 2). Investigations have also been undertaken to assess the various corrosive factors operating in the oral cavity (3–8). Recently, some components of human saliva were found to inhibit the corrosion processes of dental amalgam (9). Thus, the corrosion process in the oral cavity can be described as a developing process between two contradictory systems: the corrosive and the protective systems. The outcome of this developing process will be corrosion or corrosion inhibition (9).

One of the salivary components that exhibit a protective effect on dental amalgam is phosphate buffer, and it has been shown that its effect is concentration-dependent. The purpose of the present study was to examine whether there are any other factors that may alter the inhibiting effect of phosphate buffer. Thus, it was decided to study the influence of pH on the protective effect of phosphate buffer on dental amalgam, the influence of stirring on the protective effect of phosphate buffer on dental amalgam, and whether phosphate buffer maintains its aftereffect in the pH region 6.8–4.5.

Materials and methods

Preparation of specimens

Amalgam specimens were prepared from a conventional amalgam (Table 1). The amalgam alloy was mechanically mixed with mercury in accordance with the manufacturer's instructions. The condensation of the amalgam mix was performed manually in a steel matrix with a diameter of 5 mm and a depth of 4 mm. After 24 h the specimens were ground on polishing paper no. 600 grit (grain size, 28 μm) and washed in distilled

Table 1. The composition of the dental amalgam used, in percentage by weight, and recommended mercury to alloy ratios according to the manufacturer

ANA 68* (batch no. 7903)					
Mercury	Silver	Tin	Zinc	Copper	Mercury to alloy ratio
1.5	68	26	0.5	5.5	1/1

* Nordiska Affinariet ANA, Box 911, S-251 09 Helsingborg, Sweden.

water and acetone. Seventy-two specimens were prepared totally.

Experimental set-up

Glass vessels containing 200 ml of each of the following solutions were prepared, and four amalgam specimens were suspended in each glass vessel by means of a silk string.

a) Solutions containing 15 mM phosphate buffer (50% NaH_3PO_4 and 50% Na_2HPO_4) and 85 mM sodium chloride were prepared with the following pH values: 6.8, 6.0, 5.5, 4.5, 4.0, 3.5, and 3.0. The specimens were maintained in the solutions for 15 days without stirring.

b) Solutions containing 15 mM phosphate buffer (without sodium chloride) were prepared with pH values of 6.8, 6.0, 5.5, 4.5, 4.0, 3.5, and 3.0. The specimens were maintained in these solutions for 15 days. On the 15th day the specimens were transferred to respective glass vessels containing 200 ml of an 85 mM sodium chloride solution. The specimens remained in sodium chloride solutions for 10 days. No stirring was carried out.

c) Solutions containing 15 mM phosphate buffer (without sodium chloride) were prepared with pH values of 6.8, 6.0, and 5.5. The specimens were maintained in these solutions for 15 days. On the 15th day the specimens were transferred to respective glass vessels containing 200 ml of an 85 mM sodium chloride solution. The specimens were immersed in sodium chloride solutions for 10 days. Stirring was carried out during these experiments.

d) Finally, four specimens were suspended in a glass vessel containing 200 ml of an 85 mM sodium chloride solution (pH 6.5). The duration of this experiment was 10 days.

Twenty-four hours after specimen immersion, samples (25 ml) were taken from all solutions. At the end of each experimental period the solutions were analyzed by an atomic absorption spectrophotometer (Pye Unicam SP 190, Pye Unicam Ltd, Cambridge, England) to measure the amounts of metal ions dissolved from the amalgam specimens. Air-acetylene flame was used in the analyses for silver, copper, and zinc and nitrous oxide-acetylene flame for tin. The amount of mercury was determined by the cold vapor method. The detection limits for the different elements were for silver, 0.03 μg/ml; copper, 0.03 μg/ml; mercury, 0.01 μg/ml; tin, 0.8 μg/ml; and zinc, 0.01 μg/ml.

Results

a) In solutions containing phosphate buffer and sodium chloride, an increasing zinc dissolution from amalgam specimens could be observed with decreasing pH in the pH range 6.8–4.0 (Table 2). Mercury could only be detected in the pH range 4.0–3.0.

b) Amalgam specimens immersed in phosphate buffer solutions that were not stirred showed an increasing zinc release with decreasing pH (Table 3). Mercury could not be detected in these solutions. In sodium chloride solutions, into which the amalgam specimens were transferred, no elements could be detected.

c) Amalgam specimens suspended in phosphate buffer solutions that were stirred showed almost the same dissolution pattern as those immersed in unstirred solutions (Table 4). Once again, no elements could be found in sodium chloride solutions.

d) The four amalgam specimens that remained suspended in the control sodium chloride solution for 10 days released small amounts of copper (0.12 μg/ml) and zinc (0.42 μg/ml).

Discussion

In a previous study (9) it could be demonstrated that the protective effect of phosphate buffer on the corrosion processes was concentration-dependent. The results of the present study show that the same effect can also be affected by pH changes in the environment. Furthermore, stirring does not seem to exert any influence on these processes.

In solutions containing phosphate buffer and sodium chloride small amounts of copper and an increasing dissolution of zinc

Table 2. Dissolution of elements (in μg/ml) from four amalgam specimens in phosphate buffer solutions containing sodium chloride and with different pH

	Zn		Cu		Hg	
pH	24 h	15 days	24 h	15 days	24 h	15 days
6.8	<0.01	0.05	<0.03	<0.03	<0.01	<0.01
6.0	<0.01	0.08	<0.03	0.04	<0.01	<0.01
5.5	0.06	0.25	<0.03	0.04	<0.01	<0.01
4.5	0.06	0.39	0.05	0.06	<0.01	<0.01
4.0	0.21	0.48	<0.03	<0.03	<0.01	0.02
3.5	0.23	0.45	<0.03	<0.03	<0.01	0.11
3.0	0.28	0.52	<0.03	<0.03	<0.01	0.07

could be observed in the pH range 6.8–4.0. In the same solutions with lower pH, the protective effect of phosphate buffer was reduced, and mercury release from the amalgam specimens could not be prevented completely. Copper seemed to be protected by phosphate buffer in the pH range tested. Insoluble copper phosphate was probably precipitated on the specimen surface. The results obtained in phosphate buffer solutions did not differ from the above-mentioned in the pH range 6.8–4.5.

Table 3. Dissolution of elements (in μg/ml) from four amalgam specimens in phosphate solutions with different pH

	Zn		Cu	
pH	24 h	15 days	24 h	15 days
6.8	0.03	0.07	<0.03	<0.03
6.0	0.04	0.06	<0.03	0.05
5.5	0.05	0.15	0.06	0.04
4.5	0.05	0.36	<0.03	<0.03
4.0	0.14	0.66	0.04	0.05
3.5	0.18	0.42	<0.03	<0.03
3.0	0.20	0.61	0.05	0.05

Table 4. Dissolution of zinc (in μg/ml) from four amalgam specimens in phosphate buffer solutions. Stirring was carried out during these experiments

pH	24 h	15 days
6.8	0.03	0.05
6.0	0.04	0.08
5.5	0.05	0.18

The dissolution rates of zinc measured in this study are low compared with those obtained by other workers (10, 11) in solutions containing more corrosive factors.

Several hypotheses have been proposed with regard to the protective mechanism of phosphate buffer on dental amalgam (9, 12) and tin (13). Analysis of the passivating layer in a scanning electron microscope equipped with EDAX showed the presence of tin and phosphorus. In addition, the dental amalgam tested showed good corrosion resistance at pH values as low as 3. According to the empirical potential/pH diagram of tin (14), the tin protective film should not deteriorate in the pH region tested in this study. Thus, the results of the present study imply that the passivation of dental amalgam is accomplished through the formation of a protective film consisting of tin phosphates, tin hydroxide, and tin oxide.

In a previous study (9) it was shown that phosphate buffer exercises an aftereffect on dental amalgam at pH 6.8. The results of this study could confirm and extend those findings to pH values of 6.8–4.5. The demonstration of an aftereffect by phosphate buffer on dental amalgam is probably due to the protective film mentioned above. This film of tin phosphates, tin hydroxides, and tin oxides is apparently stable enough to resist the aggression of sodium chloride for 10 days. Similar experiments conducted with organic inhibitors did not show the same effect on dental amalgam.

In the experimental model used in this study oxygen was present both in the solutions that were stirred and those that were

not, but its concentration was different in the two solutions. Owing to the short immersion of the amalgam specimens in the solutions it can be assumed that oxygen was not completely utilized by the various reactions in solutions without stirring. Thus, stirring represents only a higher flow rate of the solution. According to this study, the protective effect of phosphate buffer is independent of the solution's flow rate. In the in vivo situation, however, the flow rate of saliva affects the protective properties of phosphate buffer indirectly; that is, the saliva of slow secretors contains less orthophosphate per hour than that of rapid secretors (9). Copper was dissolved readily from dental amalgams in organic acid solutions with low pH (6). In the present study copper release from dental amalgam was low, although the pH of the solutions was almost the same as that of the organic acids. Consequently, the nature of the electrolyte is an important factor in metal release from dental amalgam.

The comparison between the dissolution rates measured after 24 h and those obtained after 15 days implies that amalgam protection against corrosion by phosphate buffer is not a process that can be completed during a certain period of time and thereafter remains inactive. It is a developing process that requires sufficient phosphate concentrations and appropriate pH to exert its inhibiting effect. Failure to satisfy these prerequisites can lead to the control of the developing processes of corrosion and corrosion inhibition by the corrosive factors.

Clinical studies (15, 16) have shown that many patients with oral lichen planus are sensitive to mercury. The number of oral lichen planus patients who reacted to mercury testing varied between 26% and 62%, according to the results of different studies. The disagreement in the percentage of sensitive patients is probably due to the different methods used in the various studies. Removal of restorations containing the irritant caused a noticeable regression of the mucosal lesion and, in a few cases, disappearance of the lesion (16, 17).

In addition, it has been demonstrated that most patients with oral lichen planus (87%) had low or very low secretion rates of unstimulated saliva, and a considerable number of these patients (42%) had low or very low pH of unstimulated saliva (18, 19).

Phosphate buffer exercises an inhibiting effect on the corrosion process of dental amalgam (9, 12). However, the protective effect of phosphate buffer is concentration-dependent (9, 13). This fact implies that the unstimulated saliva of slow secretors impairs the protection of dental alloys against corrosion. The present study has shown that the inhibiting effect of phosphate buffer can also be reduced by a low pH. In such a case the dissolution of mercury, which is a common irritant among oral lichen planus patients, increases from dental amalgam. Thus, the findings of these studies showed some of the etiological factors of oral lichen planus lesions. However, further clinical investigations are needed to confirm these in vitro findings.

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