The release of fluoride from two products of alginate impression materials

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The purpose of this study was to determine the fluoride content of two products of alginate and the possible fluoride transfer to the teeth, saliva and blood.

The total fluoride content of Zelgan normal-set® and Kerr alginate fast-set® powder was assayed by direct diffusion and diffusion of the ash. The soluble fluoride leaching out in water over 24 hour was also determined.

The results show that the fluoride contents of Zelgan and Kerr alginate powders are about 1.9 % and 1.5 % fluoride, respectively. Of the fluoride present in Zelgan and Kerr approximately 6.5 % and 5.8 %, respectively, leached out in 400 ml deionized water. The fluoride uptake was estimated in two adjacent enamel layers each approximately 7 µm thick, using 10 teeth exposed for 5 minutes and 18 h to the alginate gel (Zelgan). The results of acid etch microsamplings indicate a significant increase in the fluoride concentration of the first enamel layer after both 5 min and 18 h exposure. Fluoride uptake within the second enamel layer was insignificant, however. Fluoride transfer to the oral saliva and to the blood was evident after impression taking.

Key-words: Dental materials, enamel; caries prophylaxis; orthodontics

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The chief ingredient of irreversible hydrocolloid impression materials is a soluble alginate salt. This soluble salt reacts with a calcium salt to produce an insoluble alginate gel as follows:

Potassium alginate + calcium sulfate $\xrightarrow{(+\text{ water})}$ calcium alginate gel + potassium sulfate (16). Fluoride salts such as sodium silicofluoride, potassium zinc fluoride and potassium titanium fluoride are added to ensure a casting with a hard, dense surface. In proper concentrations these fluoride salts also act as accelerators during setting of the gypsum products (19). Information regarding the amount of fluoride present in alginate is not readily available. Due to the wide use of alginate impression materials in dentistry, it was decided to measure the release of fluoride from commercially available materials and examine its transfer to the teeth, saliva and blood after taking an impression.

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MATERIALS AND METHODS

Determination of fluoride in alginate

Two well-known products of alginate material were chosen; De Trey's Zelgan normal-set® and Kerr alginate fast-set® impression material. The fluoride content of these materials was deter-

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mined as follows:

Total fluoride content

A. Direct diffusion of alginate powder

Analysis of 25–400 mg alginate powder was performed. The fluoride content was determined using a modified Taves method (22). A trapping solution consisting of 0.3 ml of 4 M NaOH was used. Extra hexamethyldisiloxane (HMDS) was inroduced directly into the acidified solution in order to enhance the rate of diffusion. This resulted in trapping of larger amounts of fluoride by the alkaline solution. The diffusion procedure was continued for 6 h under rotary motion.

The capsule containing the trapping solution was then transferred to a polystyrene container. The solution was neutralized and buffered by addition of 0.3 ml 4 N HCl and 100 ml 0.5 M acetate buffer at pH 5.

Aliquots of the solution were analysed for fluoride using a fluoride sensitive electrode (Orion Model 96.09) and a digital pH/mV meter (Orion Model 801). Calibration of the apparatus was carried out with standard solutions containing 0.5, 1, 3, 5 and 10 ppm F.

B. Diffusion after ashing of alginate powder

A sample of 255–285 mg alginate powder (Zelgan) was weighed to the nearest ± 0.2 mg. One gram of calcium phosphate (containing 20 ppm F) was added to the sample to fix the fluoride and prevent its loss by volatilization during ashing procedures (23). The sample was ashed in an platinum crucible placed in an open furnace at 550°C for about 40 min. The ash was then cooled to room temperature, weighed and transferred to a stoppered polystyrene container. The diffusion procedure and fluoride determination were subsequently performed as described above.

Fluoride determination after leaching

A sample of 15 g alginate powder (Zelgan and Kerr) was mixed with 41 g tap water. The gel was loaded onto a perforated plastic tray and submerged in a separate plastic jar containing 400 ml deionized water at room temperature.

Aliquots were taken at intervals over 24 h to assay the fluoride leaching out of the impression. These were diluted with 10% by volume of acetate buffer (7.5 M, pH 5.2) containing 2% CDTA (1,2-diaminocyclohexane N, N, N', N'-tetraacetic acid). The fluoride concentration was then determined using a fluoride sensitive electrode.

Fluoride transfer to the teeth, saliva and blood

Fluoride content of human enamel exposed to an alginate gel (Zelgan) for 18 h

A random sample of four intact premolars extracted for orthodontic reasons was selected. The teeth were cleaned in deinozied water and the buccal enamel surface degreased by briefly washing with acetone. This improved adhesion of a round disc, 4 mm in diameter, made from Scotch tape (3 M Scotch pressure sensitive tape) on the mesial and distal aspect of each buccal surface. The tooth was then covered with nail-varnish and dried with air. The disc was removed

from the control side of each tooth leaving behind a varnish free area equivalent to 12.57 mm^2, ready for acid-etch procedure.

The control area was then covered with nail-varnish and dried with air. Thereafter the second disc was removed from the test side of each experimental tooth and exposed to the alginate gel (Zelgan). In this way each tooth served as its own control.

Each tooth was put in a plastic cup, 20 mm in diameter, and filled with alginate gel in such a way that the crown was completely covered by the gel. The teeth were exposed to the alginate for 18 h. After treatment they were briefly rinsed under running water. From the isolated areas on the buccal surfaces, two consecutive layers of enamel were removed by etching with 5µl of 1 N $HClO_4$ pipetted onto the exposed area for 2 periods of 30 sec.

Immediately after etching the solution was buffered by directly pipetting onto the test area 0.5 ml of 1 M citrate buffer (25 % 1 M citric acid and 75 % 1 M trisodium citrate) followed by 0.5 ml of deionized water. Residual solution left on the tooth surface was aspirated by means of a microsampling pipette and small fluoride free pieces of filter paper (Munktell No. 00). The aspirated residual solution and filterpapers were then added to the demineralizing solution left in the plastic cup. The final pH of the solution was 5.2.

Fluoride content of human enamel exposed to alginate gel (Zelgan) for 5 min

A sample of three pairs of intact homologous contralateral premolars was employed. The teeth had been extracted for orthodontic reasons from children aged 12–14 years and living in Stockholm (F^- content in the drinking water 0.25 ppm). The teeth were prepared for acid etching as described above.

Acid etch microsampling was performed using cotton pellets rendered free from fluoride by successive washing in distilled water followed by drying. A cotton pellet was saturated with 0.1. ml of 1 N_2HClO_4 and then held in forceps against the exposed area (12.57 mm^2) for 2 periods of 15 sec. (21). The cotton pellet was then placed in a plastic cup. Buffering and blotting of the enamel was carried out as previously described. The final pH of the solution was 4,9.

Determination of fluoride concentration

The fluoride content of the acid etch solutions was determined using the Orion fluoride electrode and digital electrometer. Fluoride standards were added to a solution of 1 M $HClO_4$ and 1 M citrate buffer in the same proportion as in the samples. A standard curve was made up from a series of solutions containing 0.1, 0.25, 0.5 and 1.0 ppm F. The fluoride concentration of the acid etch solutions was subsequently determined.

Determination of calcium and phosphorus concentration

The calcium concentration was determined by atomic absorption spectrophotometry (Pye Unicam SP 190). Aliquots, (0.1 ml) of the dissolved and buffered enamel sample, were diluted with 3.9 ml of deionized water. In addition, 1 ml of 5 % $LaCl_3$ solution was added to eliminate phosphorus and aluminium interference (18). The phosphorus concentration was determined by a single-step malachite-green method (11) using a spectrophotometer (Beckman Model 24).

To 0.02 ml of the demineralizing solution was simultaneously added 2.0 ml of malachite-green and 0.5 ml of urea solution. After 60 minutes the absorbance

was read against a reagent blank at 630 nm. All phosphorus values were obtained using duplicate determinations.

The average thickness and fluoride concentration of the enamel surface removed by acid etching was estimated. The total quantity of enamel in each sample was calculated on the assumption that the calcium content and the density of enamel are 37.4 wt % (20) and 2.95 g/cm^3 (13) respectively. The thickness of the etched layer was estimated from the following formula:

$$d = \frac{\mu g\ Ca \times 10^2}{37.4 \times 12.57 \times 2.95}\ \mu m$$

The fluoride concentration (ppm) in each enamel layer was calculated as follows:

$$ppm\ F = 10^6 \frac{\text{weight of dissolved fluoride } (\mu g)}{\text{weight of dissolved enamel } (\mu g)}$$

In experiment II, carried out on homologous teeth exposed to an alginate gel for 5 min., calcium and phosphorus were used for estimation of the enamel thickness assuming a content of 36 % calcium and 17.5 % phoshorus (3).

$$\mu g\ enamel = \frac{(\mu g\ Ca + \mu g\ P) \times 10^2}{53.5}$$

Statistical analysis

The average fluoride concentrations and enamel depths were analysed using Student's t-test to determine significant differences between the test and control groups. The S.D. for phosphorus was calculated from the following formula:

$$S.D. = \sqrt{\frac{\Sigma d^2}{2N}}$$

where d is the difference between duplicates of the same sample and N is the number of double determinations.

Fluoride concentration in whole saliva after impression taking with alginate

Four healthy volunteers 26 to 35 years of age took part in the study. The subjects were asked to refrain from eating and drinking fluoride rich items or using fluoridated dentifrice on the day before and the day of the experiment.

15 g of alginate powder (Zelgan), was mixed with 41 g of tap water ($F^- = 0.25$ ppm) for 45 sec. The gel was then loaded into a perforated impression tray and held against the upper arch for 5 min. During and after removal of the impression mixed saliva was collected in a graduated tube. The saliva was allowed to reach room temperature and a 0.9 ml sample transferred into a plastic cup. The sample was diluted 10 % by volume with acetate buffer (7.5 M, pH 5.2.) containing 2 % CDTA. Finally, the fluoride concentration was determined using a fluoride ion electrode.

Fluoride concentration in plasma after impression taking with alginate

A healthy male aged 34 took part in the study. The plasma fluoride level was determined prior to initiation of the experiment.

15 g alginate powder (Zelgan), was mixed with 41 g of tap water. The gel was loaded into a perforated plastic tray and held against the upper arch for 5 min. Saliva was stimulated by placing a few drops of citric acid on the tip of the tongue. After removal of the impression pooled saliva was swallowed together with a cup of tap water. Blood samples were taken 15, 30, 45, 75, 180 and 270 minutes after removal of the alginate impression from the mouth. Samples were drawn from the fingertip using polyethylene tubing, with a diameter of 2 mm (Intramedic PE 200) and transferred to heparinized microcentrifuge tubes (7).

Plasma aliquots were analysed in duplicate after the addition of a 10 % acetate buffer (7.5 M, pH 5.2) containing 2 % CDTA. The same subjects also volunteered for double impressions (upper and lower arches) and 4 impressions with about one month's interval between each study. The 4 impressions were taken consecutively at the following intervals: 5, 15, 25 and 40 minutes after the beginning of the experiment. The same procedure was followed as in the first experiment with the exception that this time the saliva was not stimulated. Fluoride was determined from separated plasma using a fluoride ion electrode. On another occasion the same subject ingested 3 mg F in aqueous solution as a reference.

RESULTS

Total fluoride determination

The results following direct diffusion are given in Table 1, and they show that the average fluoride concentration of Zelgan alginate was about 1.9 % F. Kerr contained less fluoride, approximately 1.5 % F.

The results of diffusion after ashing of the alginate powder (Zelgan) are shown in Table 2. The mean weight of the ash was found to be 70.8 % of the total weight of the sample.

Fluoride determination after leaching

The results given in Table 3 show that some of the fluoride present in the alginate impression material leached out during immersion in water. This concentration continued to increase for several hours. In some of the repeated experiments, however, most of the fluoride leached out during the first 3 h.

The results indicate that approximately 6.5 % and 5.8 % of the fluoride present in Zelgan and Kerr, respectively, leached out.

Table 1. *Fluoride concentration in different weights of alginate powder*

	Weight of the sample (mg)	Fluoride concentration (ppm)
Zelgan	90.5	19 890
	67.0	17 612
	53.4	17 978
	28.0	19 286
$\bar{x} \pm$ S.D.		18 692 ± 1075
Kerr	97.3	13 690
	60.5	14 546
	33.8	15 385
	32.9	14 894
$\bar{x} \pm$ S. D.		14 629 ± 714

Table 2. *Fluoride concentration in different weights of alginate powder (Zelgan) after diffusion of the ash*

Weight of the sample (mg)	Fluoride concentration (ppm)
280	17 838
255	16 503
285	19 629
$\bar{x} \pm$S.D. 273	17 990 ± 156g

Table 3. *Fluoride leached (mg F/400 ml H_2O) from 15 g of alginate soaked in 400 ml deionized water*

Interval	Zelgan	Kerr
5 min	4.0	4.6
10 min	5.0	8.4
60 min	13.0	11.0
75 min	17.0	11.6
2 h	17.2	12.2
3 h	18.2	13.0
24 h	18.4	13.2

This comparison was made using the total fluoride content determined by the diffusion method (Table 1).

The continuous leaching out of fluoride into the water occurred even after the complete gelation of the alginate. To confirm this a perforated tray loaded with alginate gel (Zelgan) was left for 30

Table 4. *Fluoride concentration (ppm) of two successive enamel surface layers after exposure to an alginate gel (Zelgan) for 18 hours*

Layer number	N	Enamel layer thickness (μm)				Fluoride concentration (ppm)				F-uptake (ppm)		P
		Test		Control		Test		Control				
		Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.	
I	4	6.8	0.26	7.3	0.23	1349	56	729	72	620	25	<0.01
II	4	7.5	0.15	7.5	0.35	654	80	531	92	123	20	> 0.3

S.E. = standard error of the mean
N = number of teeth
P = probability based on t-test

Table 5. *Fluoride concentration (ppm) in buccal surfaces of homologous contralateral premolars after exposure to alginate gel (Zelgan) for 5 min*

Layer number	Pairs of teeth	Enamel layer thickness (μm)				Fluoride concentration (ppm)				F-uptake (ppm)		P
		Test		Control		Test		Control				
		Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.	
I	3	5.2	0.43	6.9	0.16	1421	167	807	57	614	178	<0.02
II	3	6.3	0.42	6.7	0.20	748	64	608	47	140	60	>0.1

min. The tray was then soaked in 400 ml deionized water at room temperature. After 24 h the fluoride concentration was 16 000 μg/400 ml H_2O and the pH of the leaching solution rose to more than 9.

Fluoride uptake in human enamel

The fluoride concentration of the surface layers following isolation, etching and analysis is shown in Table 4.

The uptake of fluoride by sound enamel was assessed by comparing the fluoride concentrations measured in biopsies taken from the control and test areas of the same tooth before and after exposure to the alginate. The fluoride uptake in the first layer was 5 times greater than that in the second layer. The difference in fluoride levels between the test and control areas was found to be statistically significant for the first enamel layer ($P < 0.01$), but not significant for the second layer ($P > 0.3$).

The enamel was removed at an average rate of about 0.24 μm sec^{-1} for the first layer and 0.25 μm sec^{-1} for the second layer.

Table 5 shows the mean fluoride concentrations in enamel biopsies from 3 pairs of homologous contralateral premolars exposed to an alginate gel for 5 minutes and etched with 0.1 ml of 1 N $HClO_4$ for 15 sec. The demineralization rate was about 0.40 μ sec^{-1} for the first layer and 0.43 μm sec^{-1} for the second layer.

The amount of phosphorus, calcium and fluoride dissolved during the first and second demineralization is presented in Tables 6 and 7, respectively.

The Ca/P ratio was the same for both layers, 2.14 ± 0.08 (Mean ± S. D.; n = 12). The S.D. for phosphorus was 0.02. The coefficient of variance for 24 double determinations was 2 %.

In Table 6 the amount of biopsied enamel and fluoride in the control group is 254 ± 14 μg and 0.21 ± 0.04 μg, respec-

Table 6. *Phosphorus, calcium and fluoride found in buffered demineralizing solution (1.1 ml) from three pairs of homologous contralateral premolars after exposure to alginate gel (Zelgan) for 5 min. 1st demineralization*

Tooth	Side left/ right	Test group P,μg	Ca,μg	Ca/P	Enamel, μg	F,μg	Control group P,μg	Ca,μg	Ca/P	Enamel, μg	F,μg
1	L	35.00	77.00	2.20	209.35	0.42	41.77	88.00	2.11	242.56	0.24
1	R	29.16	57.20	1.96	161.42	0.30	43.48	93.50	2.15	256.04	0.15
2	L	41.94	88.00	2.10	242.88	0.28	46.72	101.20	2.16	276.49	0.23
2	R	28.47	61.05	2.14	167.33	0.20	40.41	86.35	2.14	236.93	0.17
3	L	37.34	83.60	2.24	226.06	0.23	43.48	96.25	2.21	261.18	0.23
3	R	24.55	53.90	2.20	146.64	0.19	44.16	90.20	2.04	251.14	0.21

Table 7. *Phosphorus, calcium and fluoride found in buffered demineralizing solution (1.1 ml) from three pairs of homologous contralateral premolars after exposure to alginate gel (Zelgan) for 5 min. 2nd demineralization*

Tooth	Side left/ right	Test group P,μg	Ca,μg	Ca/P	Enamel, μg	F,μg	Control group P,μg	Ca,μg	Ca/P	Enamel, μg	Fμg
1	L	40.00	88.00	2.00	239.25	0.21	38.87	79.75	2.05	221.72	0.18
1	R	42.28	90.20	2.13	247.63	0.19	41.09	93.50	2.28	251.57	0.12
2	L	46.38	101.20	2.18	275.85	0.22	39.22	85.25	2.17	232.65	0.14
2	R	38.87	86.35	2.22	186.77	0.17	42.11	88.00	2.09	243.20	0.14
3	L	44.84	97.35	2.17	265.78	0.13	46.89	97.90	2.07	270.64	0.14
3	R	31.71	68.20	2.15	186.75	0.12	44.46	94.05	2.12	258.90	0.17

tively (Mean ± S.D.). The corresponding data from the control group (Table 7) were 246 ± 18 μg enamel and 0.15 ± 0.02 μg fluoride. This indicates that doubling of the biopsy weight results in a reduction of fluoride concentration of about 29 %.

Fluoride concentration in saliva

The average fluoride concentration of the whole saliva collected from the participants during and at the end of impression taking of the upper teeth was 74 ± 15 (S.D.) ppm. Subsequent saliva samples were taken after 5, 10, 15, 30 and 60 minutes. The average fluoride level was 48 ± 10, 21 ± 6, 11.5 ± 1.5, 2.7 ± 1.2 and 0.66 ± 0.25 ppm, resepctively. The initial fluoride concentration was 0.015 ± 0.005.

Fluoride concentration in plasma

Fig. 1 shows that fluoride plasma peaks following 1, 2 and 4 impressions were 119, 200 and 224 ng/ml, respectively.

Systemic absorption of fluoride from alginate impression material was rapid, 119, 200 and 224 ng/ml, respectively.

Systemic absorption of fluoride from alginate impression material was rapid, leading to fairly high plasma fluoride values and reaching a peak within 30 minutes after single and double impressions and 90 minutes after 4 impressions (Fig. 1). The highest plasma fluoride level found the intake of 3 mg F as NaF aqueous solution was 150 ng/ml (Fig. 1).

DISCUSSION

Although alginate impression materials have been widely used in dentistry for about 40 years, no reports are available regarding their dental and systemic effects as far as fluoride is concerned. The striking observation made in this study was the high fluoride concentration in the materials and the transfer of fluoride to the teeth, saliva and blood.

The total fluoride present in the sample was determined by diffusion. Our preliminary results showed that analysis of more than 100 mg of alginate powder resulted in incomplete fluoride diffusion. Furthermore, some of the powder reacted with the acidic solution to form a gel.

Taves (22) demonstrated that agitation and concentration of the acidic and alkaline solutions affect the rate of diffusion. It was clear from our findings that the addition of 4 M NaOH and hexamethyldisiloxane increased the diffusion rate. Ashing of the alginate powder was performed to ensure that bound fluoride was made available for diffusion.

We found that addition to the samples of 33 % by weight calcium phosphate as a fixative rendered about 89 % of the total fluoride as determined by direct diffusion. In the second series ten times more fixative was added to the samples prepared for ashing. The results presented in Table 2 show that about 95 % of the total fluoride was recovered in this way.

Similar amounts of fixative were added to the standard solutions. Fluoride recovery, either by diffusing the ash or by direct diffusion, was 99 %. This indicates that under both circumstances recovery of fluoride added to the standards was virtually complete thus validating the analytical method.

In the first series of experiments the teeth were exposed for 18 h to the alginate, whereas in the second series the exposure time was limited to 5 min. The results indicated that no distinct increase in the F concentration in surface enamel occurred after 18 h exposure as compared to 5 min exposure. Many workers have demonstrated that prolonged contact with fluoride increases this uptake (3, 14). This was not the case in our findings; perhaps due to the complex state of part of the available F and the limited diffusion of F^- through the dense alginate set.

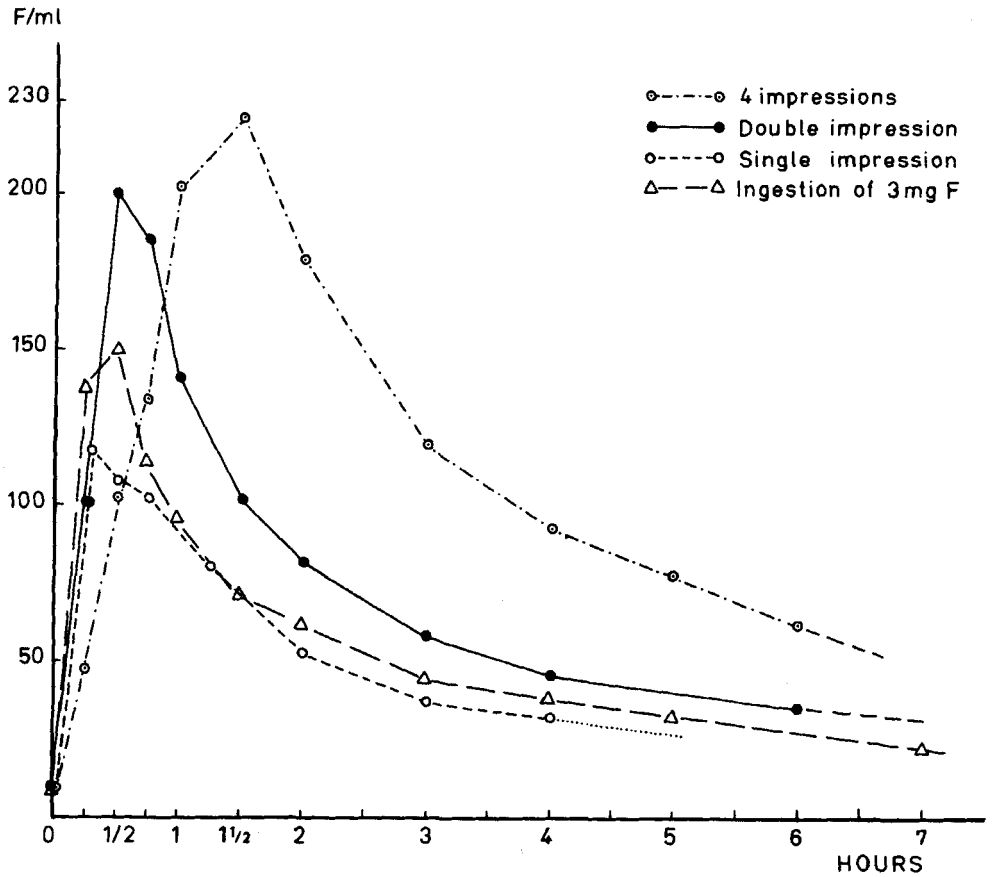

Fig. 1. Blood plasma fluoride levels after taking alginate impressions and ingestion of 3 mg F as NaF in aqueous solution.

Furthermore, F^- will have a strong affinity to the calcium present in the alginate as calcium sulfate to the extent of 16 % by weight (17). Due to a steep decrease in the fluoride concentration gradient toward the inner layers of enamel (3), comparisons of the F^- concentration in enamel biopsies are valid only if all samples are taken from a uniform depth. No enamel sampling methods can as yet provide repeated layers of exactly the same thickness (16). The thickness variation was, however, small enough to allow a comparison of F^- levels based on group mean values (10). Tinanoff, Wei & Parkins (21), who applied essentially the same acid etching technique as in experiment II, found a demineralization rate of about 0.24 μm sec^{-1} using 0.5 N $HClO_4$.

With regard to the Ca/P ratios found in the surface enamel, it has been reported to range from about 1.80 (15) to 2.08 by weight (4). Kock & Friberger (12) found that in the first demineralized layer of 8 μm the ratio was 2.18 as opposed to 2.06 in the subsurface layers. The present study showed that the Ca/P ratio was 2.14 ± 0.08 for both enamel layers having a depth of about 6.5 μm, each.

The high fluoride level in the saliva samples collected during and after impression taking indicate that a considerable amount of fluoride is diffused directly to the saliva and/or to the oral

tissues bathed with the saliva. The fluoride clearance was, however, rapid, nevertheless the salivary fluoride was still slightly elevated compared with the baseline values 4 hours after impression taking.

Aasenden, Brudevold & Richardson (1) found that the average fluoride concentration in saliva collected after 5 minutes of topical treatment with an APF-solution containing 1.2 % F was 93 ppm. The F^- concentration of the expectorate decreased due to salivary dilution and selective F^- absorption through the mucous membrane (2,8).

Plasma fluoride data indicate that the ingestion of the saliva during and after impression taking lead to fairly high plasma fluoride levels. Marked intersubject variation is expected and, beside other factors, is due to the considerable differences in the salivary secretion rate.

Henschler, Büttner & Patz (9) have demonstrated that fluoride plasma peaks appeared approximately 30 minutes after a single dose of 0.5 – 100 mg F^- as NaF. This was also the case following the application of single and double impressions.

In the light of our findings it appears that one alginate impression may give a plasma peak lower than the intake of 3 mg fluoride as NaF in aqueous solution. Higher peaks and prolonged fluoride profiles in the plasma were obtained following two and four impressions (Fig. 1).

The present study suggests that alginate materials could be applied as a vehicle for topical fluoride application. In order to reach an optimal cariostatic effect some modifications on the product are needed.

Alginate materials are economical, and it could be convenient to use them as a source of fluoride release. This matter needs to be explored more thoroughly. Furthermore, the readily distribution of fluoride from the alginate material to the saliva and blood justifies an efficient ejection of the saliva and careful inspection of the mouth in order to remove fragments of alginate that may lodge between the teeth or are fastened to the oral tissues. This practice is especially recommended in case of children to avoid the risk of fluoride overdosage.

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