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Examination of the Acid Etching Process used in Preventative Dentistry

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AN EXAMINATION OF THE ACID ETCHING PROCESS USED IN PREVENTATIVE DENTISTRY

by

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ABSTRACT

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Nuva-Seal is a bisphenol-A-glycidyl-methacrylate monomer which in its polymerized form seals a tooth to prevent carie formation.(1) Prior to application the tooth surface is pretreated with an etching solution to increase the bond strength. The etchant solution is 50% by weight H_3PO_4 and 7% by weight ZnO. Previous investigations performed at Union College have determined qualitatively that a substantial portion of enamel is removed by the acid pretreatment.(2) In addition, an extensive literature search into the development of the etching process was performed in order to validate or repute its usefulness.(3)

The <u>in vitro</u> study presently being performed at Union College incorporates a gravimetric analysis as well as ion selective electrode methods for Ca^{+2} and F^-. The specific parts of the tooth affected by the acid etching process can be approximated from this data.

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INTRODUCTION

In the past ten years there has been a rather broad expansion of practical methods of preventative dentistry which have become widely accepted. Perhaps the most acclaimed preventative treatment against carie formation, other than proper daily care and fluoride treatment, has been the application of a sealant to the enamel of teeth. Of the many different sealants advocated by various researchers the most widely accepted is is that marketed as Nuva-Seal. (L.D. Caulk Co., Div. of Dentsply International Inc.)(4) Nuva-Seal was first introduced by Michael Buonocore in 1970.(5)

Although the polymer itself is not the subject of this investigation, it would be appropriate to briefly explain its composition. Nuva-Seal is based on the reaction product of bisphenol A, glycidyl methacrylate and methyl methacrylate monomer. Benzoin methyl ether is added as an ultraviolet light sensitive catalyst. The monomer is rapidly converted to a hard solid by free radical polymerization when exposed to ultraviolet light (wavelength 366mn) for one minute.(6)

Before the sealant can be applied the teeth are pretreated with a phosphoric acid etching solution. This increases the roughness of the tooth surface so the polymer binds more tightly. The etching process was first introduced by Buonocore in 1955.(7) The initial studies were done with 85% by weight phosphoric acid solutions with a total exposure time of thirty seconds. Presently, a 50% by weight phosphoric acid solution is used which contains 7% by weight ZnO for a total exposure time of one minute. The etching process removes enamel, but no study has clearly shown chemically to what extent, except by micrograph analysis.(8) The purpose of this investigation is to determine the chemical loss from the tooth due to the acid etch pretreatment.

Previous investigations at Union relied upon gravimetric analysis alone to determine the effect of the acid etch.(2) In this study ion selective electrode methods to determine fluoride and calcium ion concentrations in the etching solution (after total exposure of two minutes) are used in addition to the gravimetric analysis of the teeth. If more $[Ca^{+2}]$ is indicated by ion selective methods than by gravimetric methods, it may be hypothesized that an attack on the underlying layers of the teeth has occurred. The fluoride electrode reads free ion which can be related to an equivalent molar concentration of Ca_2FPO_4. Knowing the total $[Ca^{+2}]$ from the calcium ion selective electrode permits the calculation of Ca_2OHPO_4 and $Ca_3(PO_4)_2$ concentrations from two equations

and two unknowns. The total weight loss(gravimetrically determined)minus the Ca_2FPO_4 equals the concentration of Ca_2OHPO_4 and $Ca_3(PO_4)_2$; as does the total Ca^{+2} concentration minus the fluorophosphate calculated. Using these two equations the relative amounts of each component can be determined. The Ca_2OHPO_4(calcium hydroxyphosphate)and $Ca_3(PO_4)_2$ (calcium phosphate)together form the enamel structure, with the hydroxyphosphate mainly in the surface layers. Therefore, the results of this study attempt to varify the hypothesis that underlying layers, as well as surface enamel, is removed by the acid etch pretreatment.

PREVIOUS RESEARCH AT UNION COLLEGE

This project was originally undertaken by Vicki Joan Herzl in partial fulfillment of her chemistry degree, under the direction of Robert W. Schaefer, Associate Professor of Chemistry at Union College. Her research included a preliminary study of the weight loss due to etching time and was completed in March 1976. More recently an extensive literature search has been conducted by Judith Ann Komoroski. It is upon this compilation that laboratory procedures were begun in the spring of 1978.

LITERATURE

The Nuva-Seal treatment presently being used resulted from a number of developmental stages. Prior to its wide acceptance, a number of other preparative treatments and polymers were used.(9) What set the Nuva-Seal process apart from the others was its relatively simplistic approach and successful durability. The purpose of the acid etch pre-treatment is to increase the surface area of the tooth so as to increase the adhesion of the monomer. Superficially the results of acid etching can be seen as the replacement of the tooth's natural luster with a "chalky-white" appearance. While the desired results may well be achieved, it still remains unclear as to what actually happens to the tooth's surface. Questions about what portions of the tooth are removed are still unanswered.

Buonocore in his initial article on the acid etching technique, hypothesized that it not only removed portions of the enamel, but first removed the organic pellicle covering the tooth.(10) Once this outer layer has been removed the unexposed(to the oral environment)underlying layers of the

tooth are effected by the etching process. Buonocore hypothesized that there are four different ways that the enamel surface can be etched. These four ways are as follows:

1) preferential dissolution of the prism cores of the enamel.
2) preferential dissolution of the prism peripheries.
3) formation of a pitted surface.
4) featureless dissolution.(11)

Of the four possibilities, the dissolution of the prism cores is believed to be the most common.

The effectiveness of the etching process is dependent upon a variety of parameters. The exposure time of the teeth to the etching process plays an important role(as discussed in detail later), as does the structure and composition of the enamel.(12) This last parameter appears to be one of the greatest hurdles in proposing any encompassing conclusions about the tooth's susceptability to the acid etch because of the effect of heredity on tooth structure. Tooth structure and composition are to a great extent characteristic of heredity, with the specific environment effecting the extent to which the heredity limits are reached. Therefore, it is difficult to prescribe an etchant process which will work the same on all teeth. This should be kept in mind when experimental data is examined.

The chemical process of the acid attack on the enamel surface has been investigated by Neweseley.(13) Neweseley hypothesizes that the hydrogen ions attack the phosphate and hydroxy portions of the hydroxy apatite($Ca_5(PO_4)_3OH$, enamel).

Once attacked the hydroxy apatite forms $Ca_5(PO_4)_3^+$, $Ca_5(HPO_4)(PO_4)_2^{+2}$, $CaHPO_4$, and $Ca(H_2PO_4)_2H_2O$.(13) Other researchers have also found this last compound to be present, monocalcium phosphate monohydrate.(14, 15, 16)

Perhaps the most extensively studied aspect of the etching process has been the time dependence of weight loss. The organic pellicle previously mentioned is believed to be removed within the first ten seconds of exposure. It is not until this surface has been removed that the mineral salts begin to be removed.(17) Leach has reported that 90% of the enamel lost from two days of exposure was lost in the first five minutes.(18) Other studies report the loss increased up to one minute of exposure.(19) Wickwire et al. reported the following depths of enamel removed due to the indicated exposure times.

TABLE #1 Depth of Etch Related to Exposure Time

Total Time Etch	Total Depth Etch
2 min.	5-10 microns
4 min.	5-15 microns
6 min.	20-30 microns(20)

(Note: These investigations were using phosphoric acid as in the present study. Other acids were used by other investigators(21), but they aren't considered in this study.)

Some researchers have reported that a maximal weight loss due to etching occurs. This final etch level is called the "characteristic etch level".(22) A variety of reasons why this would occur have been suggested. The matrix of the tooth may change deeper in the enamel preventing acid attack. The calcium and phosphorous ions released from previous etching may

protect the remaining enamel. The insoluble salt $Ca(H_2PO_4)_2H_2O$ (monocalcium phosphate monohydrate)may act as a protective coating as well.(23, 24)

The idea of a maximum enamel loss seems to contradict some other findings. Jennings and Ranly report that the outer 20% of the enamel is the hardest and therefore most resistant to acid attack.(25) Worn areas will be attacked first. If the enamel gets completely removed by the etching process a direct attack on the dentin layer will occur.(26) The dentin is more porous than enamel permitting the acid to penetrate even further into the tooth, perhaps even to the point of pupal irritation. Two studies which investigated this possibility found conflicting results. Lee et al. found that the acid did not penetrate to the pulp,(27) while Retief et al. found that irritation did occur. This present research project will attempt to prove that the underlying layers are being attacked by the etching process.

Another variable which effects the susceptability to the acid etch is the age of the teeth. Most researchers have found that older teeth are less susceptable than younger teeth.(28, 29) Older teeth have been exposed to an oral environment for a longer period of time and therefore have more of an organic pellicle on the surface to protect against the acid etch.

One final note should be made on the methods of examination. The duration of the study in many cases requires the teeth to be kept for a long time out of an oral environment. It has been found that the enamel solubility does not differ for teeth re-

cently extracted and those which have been stored for a period of time.(30)

EXPERIMENTAL: MATERIALS AND METHODS

One objective of this research project is to present some qualitative trends in the acid etch susceptability of teeth based on age characteristics and total etch time. The main objective, however, is to quantitatively determine what type and amount of chemical compounds are removed by the etching process and from what sections of the tooth.

A large number of teeth have been studied such that the data may be considered statistically valid. A geographical consideration was introduced due to the availability of teeth in the Schenectady and Oswego areas. A comparative analysis of 66 teeth from the Oswego area and 52 teeth from the Schenectady area was performed. Two age groups contained sufficient teeth to statistically analyze for the age dependence of acid etch susceptability: 20 years and under and 20 to 45 years. In the 20 and under age group there are 24 and 34 teeth from the Oswego and Schenectady areas respectively. In the 20 to 45 age group there are 38 and 21 teeth from the Oswego and Schenectady areas respectively.

The geographic consideration which must be made concerns

the amount of fluoride ion expected in the etching solutions. The amount of fluoride taken up in the enamel structure is partially dependent upon the amount of fluoride in the water supply of the area. In the Oswego area the fluoride ion concentration is maintained around 1.00 ppm(31, 32), while in the Schenectady area it is around 0.05 ppm. The reason why the Schenectady water contains so much less is due to the inhibiting effects of MnO_2, due to the oxidation of Mn^{+2} by iron bacteria present in the grid of the water system.(33) This inhibiting effect doesn't occur in the Oswego water system because of the lack of Mn^{+2} in the water. The characteristic difference in fluoride concentration in the water may effect the amounts of fluorophosphate expected to be found for each tooth. Therefore, intuitively the Oswego teeth might be expected to contain more fluorophosphate in the enamel.

Before any etching was done an examination of the previous technique used by Vicki Herzl involving test tubes and an inversion technique was performed.(34) This technique was found to be invalid when a purple dye solution absorbed onto the root as well as the crown enamel. Remembering that only the exposed enamel is sought to be etched, this previous method had to be abandoned.

A new technique was developed in which a hemostat was used to simply lower the tooth into the etching solution. This enabled better control of which surface actually got etched. Each tooth was etched in an individual etching solution(50 ml beakers containing approximately 40 ml of etching solution). The beakers were covered with paraffin film in between etching

periods to prevent evaporation. The etching process was conducted in 20 second intervals for a total etch time of two minutes.

Throughout the investigation a gravimetric analysis of the weight loss after each etch period was performed. After each 20 second exposure the teeth were thoroughly rinsed in distilled water. A Sartorius 2432 analytic balance was used for all weight determinations. The teeth were originally dried in a vacuum desiccator until they reached constant weight($CaCl_2$ was was the desiccant). Constant weight was reached when a tooth remained ± 0.0005 g for a period of two days. This plateau was usually reached three weeks after the etching exposure. Once constant weight was reached another 20 second exposure to the etchant solution was performed. The vacuum tended to pull the teeth apart so it was discontinued. Instead, dry nitrogen was blown across the teeth and into the desiccator to remove the water on the teeth from rinsing. This drying procedure was continued every couple of days to allow the formation of a new water vapor equilibrium in the desiccator. This increased the rate at which a new constant weight was achieved. The constant weights reached after each 20 second etch interval were recorded and the percent weight loss was determined. Plots of percent weight loss vs. time of etch are shown in Figure #1— Figure #4.

The amount of Ca^{+2} and F^- present in the etchant solutions after a total exposure of two minutes was determined using ion selective electrodes. A Beckman 39600 Fluoride Electrode and an Orion 42-20 Calcium Electrode were used. Standard curves

of known concentrations of Ca^{+2} and F^- were prepared using the etching solution. The etching solution was used as the solvent because the electrodes might be influenced by other ions present in the solutions, such as Zn^{+2} in the case of the calcium selective electrode. By using the same solution the teeth were etched in the errors systematically cancel out. Plots of mv vs. -log [ ] of the standard solutions appear in Figures #5 and #6. Extrapolation from these plots using the mv readings of the etchant solutions permit the concentrations of Ca^{+2} and F^- to be determined.

EXPERIMENTAL DATA: GRAVIMETRIC ANALYSIS

Each tooth was etched individually with the gravimetric analysis being performed independently of the other teeth. The change of weight by the etching process is dependent upon the surface area exposed to the etching solution. Therefore, the larger teeth will loose a greater absolute amount than the smaller teeth. In order to permit the comparison of all teeth, the percent weight loss, rather than the absolute weight loss was used for evaluation.

The etching process was begun on each group of teeth at different times due to the availability and preparation of the teeth. Treatment of teeth 2-22 was begun in March 1978, while groups B1—B66 and C1—C32 were started in September 1978. The majority of the teeth were molars, but some bicuspids were also used. The teeth obtained in the Schenectady area came from a dental clinic(St. Claire's Hospital)and from the dental office of Dr. Schlansker. Those teeth from Oswego were obtained from the operating suite in the Oswego Hospital. Before etching was started the teeth were cleaned with a hard tooth brush and surgical scapel. The scapel was used to remove tissue that was still present on the teeth.

The gravimetric analysis for the teeth can be seen in Tables #2—#22. Absolute weights after each etch period are shown in Tables #2—#8, while percent differences and absolute differences are shown in Tables #9-#22. The average percent weight differences for each etch period are shown in age categories in Table #23. These values are comparatively plotted in Figures #1—#4. The plots compare percent weight losses of two age groups: under 20 years and #20—#45 years. Those age groups compared in the graphs were collected at the same time and from the same geographic area. Groups A & B and C & D are from Oswego, while E & F and G & H are from the Schenectady area. The plots are shown as straight lines, but this is not meant to imply that the percent weight loss was at a steady rate. More realistically the loss follows a curved function, yet for simplicity the plots were made linear.

Table #2 Absolute weight(grams ±.0002)After Each Etch Interval

Tooth Number	Initial	After 20 sec.	After 40 sec.	After 60 sec.	After 80 sec.	After 100 sec.	After 120 sec.
2	1.4562	1.4576	1.4557	1.4532 * 1.4449	1.4434	1.4413	1.4353
4	1.9555	1.9586	1.9600	1.9590 1.9500	1.9485	1.9480	1.9432
5	1.3880	1.3855	1.3833	1.3818 1.3747	1.3723	1.3710	1.3672
6	1.4171	1.4167	1.4151	1.4146 1.4066	1.4044	1.4035	1.3991
7	1.3551	1.3541	1.3531	1.3517 1.3440	1.3421	1.3415	1.3376
8	1.4196	1.4181	1.4169	1.4165 1.4111	1.4097	1.4095	1.4066
9	1.8519	1.8384	1.8360	1.8303	1.8290	1.8270	1.8265
10	1.6530	1.6413	1.6396	1.6353	1.6346	1.6327	1.6325
11	1.5324	1.5311	1.5286	1.5226	1.5207	1.5182	1.5167
12	1.7804	1.7812	1.7788	1.7722	1.7703	1.7685	1.7681
13	1.8025	1.8046	1.8008	1.7929	1.7900	1.7876	1.7871
14	1.1034	1.1024	1.1009	1.0970	1.0954	1.0944	1.0943
15	1.6640	1.6638	1.6632	1.6565	1.6552	1.6545	1.6539
16	1.0423	1.0430	1.0414	1.0375	1.0370	1.0361	1.0360
17	1.4093	1.4109	1.4103	1.4060	1.4057	1.4052	1.4056
18	1.3722	1.3722	1.3713	1.3670	1.3653	1.3646	1.3648
19	0.9950	0.9950	0.9953	0.9940	0.9923	0.9930	0.9922
20	1.5342	1.5355	1.5316	1.5246	1.5233	1.5220	1.5211
21	1.5261	1.5267	1.5258	1.5220	1.5217	1.5212	1.5212
22	1.6220	1.6240	1.6223	1.6184	1.6178	1.6172	1.6165

* values obtained after the teeth dried over the summer

Table #3 Absolute weight(grams ±.0002)After Each Etch Interval

Tooth Number	Initial	After 20 sec.	After 40 sec.	After 60 sec.	After 80 sec.	After 100 sec.	After 120 sec.
B1	1.1449	1.1433	1.1460	1.1453*	------	------	------
B2	1.6059	1.6026	1.6008	1.5953	1.5958	1.6028	1.6040
B3	2.3067	2.3064	2.3048	2.2967*	------	------	------
B4	1.5162	1.5125	1.5094	1.5043*	------	------	------
B5	1.4670	1.4637	1.4604	1.4527	1.4520	1.4482	1.4503
B6	1.4444	1.4416	1.4390	1.4312	1.4312	1.4338	1.4310
B7	1.7207	1.7173	1.7116	1.7022*	------	------	------
B8	1.2833	1.2829	1.2811	1.2785	1.2787	1.2793	1.2883
B9	1.6272	1.6262	1.6258	1.6222	1.6203	1.6257	1.6215
B10	1.8960	1.8936	1.8900	1.8841	1.8837	1.8828	1.8875
B11	1.3862	1.3850	1.3834	1.3785	1.3763	1.3753	1.3784
B13	1.2786	1.2766	1.2715	1.2635	1.2623	1.2607	1.2605
B14	1.7645	1.7633	1.7628	1.7540	1.7594	1.7565	1.7565
B15	1.4408	1.4386	1.4369	1.4300	1.4313	1.4332	1.4372
B17	1.0277	1.0260	1.0210	1.0209	1.0188	1.0192	1.0209
B18	1.5719	1.5702	1.5720	1.5661	1.5627	1.5603	1.5594

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #4 Absolute weight(grams ±.0002)After Each Etch Interval

Tooth Number	Initial	After 20 sec.	After 40 sec.	After 60 sec.	After 80 sec.	After 100 sec.	After 120 sec
B21	1.5994	1.5958	1.5935	1.5864	1.5830	1.5812	1.5805
B22	1.4366	1.4330	1.4308	1.4240	1.4227	1.4205	1.4200
B23	1.7145	1.7103	1.7088	1.7020	1.7017	1.7034	1.7082
B24	1.9207	1.9160	1.9142	1.9046	1.9039	1.9038	1.9106
B25	1.3387	1.3362	1.3351	1.3284	1.3272	1.3244	1.3248
B26	1.6243	1.6211	1.6190	1.6135	1.6091	1.6068	1.6066
B27	2.1135	2.1096	2.1076	2.0981	2.0945	2.0942	2.0960
B28	0.8747	0.8738	0.8729	0.8712	0.8715	0.8720	0.8707
B29	1.7359	1.7316	1.7286	1.7210	1.7177	1.7145	1.7128
B30	2.2840	2.2771	2.2734	2.2641	2.2632	2.2670	1.2686
B32	2.1304	2.1236	2.1200	2.1178	2.1230	------	------
B33	1.3365	1.3328	1.3322	1.3354	1.3373	------	------
B34	1.5036	1.4995	1.4962	1.4949	1.4931	------	------
B35	1.2821	1.2777	1.2748	1.2712	1.2707	------	------@

@Note: Indicates that the data has not been obtained at this time.

Table #5 Absolute weight(grams ±.0002)After Each Etch Interval

Tooth Number	Initial	After 20 sec.	After 40 sec.	After 60 sec.	After 80 sec.
B36	1.6307	1.6254	1.6237	1.6220	1.6213
B37	1.3020	1.2990	1.3000	1.3000	1.2999
B39	1.2400	1.2360	1.2343	1.2333	1.2341
B40	1.6792	1.6743	1.6706	1.6680	1.6651
B41	1.3874	1.3835	1.3826	1.3824	1.3830
B42	1.0166	1.0128	1.0118*	------	------
B43	1.0335	1.0301	1.0282	1.0260	1.0250
B44	0.8671	0.8642	0.8611	0.8600	0.8589
B45	1.2046	1.2008	1.1986	1.1967	1.1988
B46	0.9432	0.9406	0.9389	0.9376	0.9362
B47	2.0620	2.0538	2.0486	2.0419	2.0408
B48	1.3629	1.3579	1.3557	1.3535	1.3525
B49	1.4114	1.4057	1.4016	1.4008	1.3997
B50	1.1944	1.1903	1.1875	1.1865	1.1863
B51	1.7834	1.7774	1.7765	1.7738	1.7760
B53	1.0006	1.0002	*	------	------
B54	0.8328	0.8308	0.8301	0.8331	0.8334

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #6 Absolute weight(grams ±.0002)After Each Etch Interval

Tooth Number	Initial	After 20 sec.	After 40 sec.	After 60 sec.	After 80 sec.
B55	1.9630	1.9567	1.9548	1.9577	1.9619
B56	1.6408	1.6360	1.6338	1.6324	1.6320
B57	1.9241	1.9204*	------	------	------
B58	1.5636	1.5577	1.5540	1.5504	1.5496
B59	1.7315	1.7299*	------	------	------
B60	2.2675	2.2588	2.2546	2.2504	2.2515
B62	1.6674	1.6647*	------	------	------
B63	1.1945	1.1905	1.1900	1.1894	1.1900
B64	1.1854	1.1807	1.1747	1.1769	1.1807
B65	0.8719	0.8691	0.8668	0.8651	0.8642
B66	0.8136	0.8107	0.8091	0.8073	0.8068
C1	1.8622	1.8516	1.8490	1.8457	1.8445
C2	1.4600	1.4520	1.4495	1.4461	1.4451
C3	1.8004	1.7910	1.7860	1.7817	1.7798
C4	1.7915	1.7803	1.7758	1.7722	1.7700
C5	2.2604	2.2476	2.2433	2.2396	2.2368

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #7 Absolute weight(grams ±.0002)After Each Etch Interval

Tooth Number	Initial	After 20 sec.	After 40 sec.	After 60 sec.	After 80 sec.
C6	1.6378	1.6293	1.6265	1.6218	1.6209
C7	1.9970	1.9865	1.9842	1.9800	1.9791
C8	1.5930	1.5822	1.5789	1.5752	1.5743
C9	2.1537	2.1407	2.1361	2.1306	2.1294
C10	1.5192	1.5108	1.5077	1.5042	1.5031
C11	1.6100	1.6000	1.5965	1.5945	1.5945
C12	1.4475	1.4394	1.4342	1.4308	1.4302
C13	2.0956	2.0831	2.0793	2.0753	2.0742
C14	2.0006	1.9903	1.9866	1.9830	1.9832
C15	1.4543	1.4466	1.4434	1.4411	1.4400
C16	1.6338	1.6239	1.6214	1.6200	1.6193
C17	1.5018	1.4950	1.4931	1.4902	1.4883
C18	1.7226	1.7148	1.7112	1.7082	1.7062
C19	1.5560	1.5484	1.5455	1.5430	1.5430
C20	1.6287	1.6211	1.6182	1.6145	1.6128

Table #8 Absolute weight(grams ±.0002)After Each Etch Interval

Tooth Number	Initial	After 20 sec.	After 40 sec.	After 60 sec.	After 80 sec.
C21	1.5496	1.5424	1.5395	1.5376	1.5364
C22	1.3308	1.3245	1.3220	1.3202	1.3200
C23	1.1877	1.1827	1.1800	1.1782	1.1764
C24	1.5573	1.5475	1.5433*	------	------
C25	1.8162	1.8056	1.8003	1.7962	1.7938
C26	1.1393	1.1327	1.1303	1.1270	1.1259
C27	1.4845	1.4773	1.4744	1.4713	1.4703
C28	1.0068	1.0010	0.9983	0.9954	0.9933
C29	1.5321	1.5250	1.5226	1.5203	1.5187
C30	1.7883	1.7777	1.7742	1.7708	1.7702
C31	1.1716	1.1653	1.1625	1.1596	1.1585
C32	1.2722	1.2669	1.2650	1.2628	1.2622

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #9 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	20 Sec. Etch		40 Sec. Etch		60 Sec. Etch.	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
2	+0.0014	+0.096 ±.027	-0.0005	-0.030 ±.030	-0.0030	-0.210 ±.030
4	+0.0031	+0.160 ±.020	+0.0045	+0.230 ±.020	+0.0035	+0.180 ±.020
5	-0.0025	-0.180 ±.030	-0.0047	-0.340 ±.030	-0.0062	-0.450 ±.030
6	-0.0004	-0.030 ±.030	-0.0020	-0.140 ±.030	-0.0025	-0.180 ±.030
7	-0.0010	-0.074 ±.030	-0.0020	-0.150 ±.030	-0.0034	-0.250 ±.030
8	-0.0015	-0.110 ±.030	-0.0027	-0.190 ±.030	-0.0031	-0.220 ±.030
9	----------	----------	-0.0024	-0.131 ±.022	-0.0055	-0.300 ±.022
10	----------	----------	-0.0017	-0.104 ±.024	-0.0043	-0.262 ±.024
11	-0.0013	-0.085 ±.026	-0.0025	-0.163 ±.026	-0.0060	-0.392 ±.026
12	+0.0008	+0.045 ±.022	-0.0024	-0.135 ±.023	-0.0066	-0.371 ±.022
13	+0.0021	+0.117 ±.022	-0.0038	-0.211 ±.022	-0.0079	-0.439 ±.022
14	-0.0010	-0.091 ±.036	-0.0015	-0.136 ±.036	-0.0039	-0.354 ±.036
15	-0.0002	-0.012 ±.024	-0.0006	-0.036 ±.024	-0.0067	-0.403 ±.024
16	+0.0007	+0.067 ±.038	-0.0016	-0.153 ±.038	-0.0039	-0.374 ±.038
17	+0.0016	+0.114 ±.029	-0.0016	-0.043 ±.029	-0.0043	-0.305 ±.028
18	no change	no change	-0.0009	-0.066 ±.029	-0.0043	-0.314 ±.029
19	no change	no change	+0.0003	+0.030 ±.040	-0.0013	-0.131 ±.040
20	+0.0013	+0.085 ±.026	-0.0039	-0.254 ±.026	-0.0070	-0.457 ±.026
21	+0.0006	+0.040 ±.027	-0.0009	-0.059 ±.026	-0.0038	-0.249 ±.026
22	+0.0020	+0.123 ±.025	-0.0017	-0.105 ±.025	-0.0039	-0.240 ±.025

Table #10 Absolute(in grams) and Percent Weight Changes After Etching

Tooth Number	80 Sec. Etch		100 Sec. Etch		120 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
2	-0.0015	-0.104 ±.028	-0.0021	-0.145 ±.028	-0.0060	-0.416 ±.028
4	-0.0015	-0.076 ±.021	-0.0005	-0.026 ±.021	-0.0048	-0.246 ±.021
5	-0.0024	-0.175 ±.029	-0.0013	-0.095 ±.024	-0.0038	-0.277 ±.029
6	-0.0022	-0.156 ±.028	-0.0009	-0.064 ±.028	-0.0044	-0.314 ±.029
7	-0.0019	-0.141 ±.030	-0.0006	-0.045 ±.030	-0.0039	-0.291 ±.030
8	-0.0014	-0.099 ±.028	-0.0002	-0.014 ±.028	-0.0029	-0.206 ±.030
9	-0.0013	-0.071 ±.022	-0.0020	-0.109 ±.022	-0.0005	-0.027 ±.022
10	-0.0007	-0.043 ±.025	-0.0019	-0.116 ±.024	-0.0002	-0.012 ±.024
11	-0.0019	-0.125 ±.026	-0.0025	-0.164 ±.026	-0.0015	-0.099 ±.026
12	-0.0019	-0.107 ±.023	-0.0018	-0.102 ±.023	-0.0004	-0.023 ±.023
13	-0.0029	-0.162 ±.022	-0.0024	-0.134 ±.022	-0.0005	-0.028 ±.022
14	-0.0016	-0.14 ±.037	-0.0010	-0.091 ±.036	-0.0001	-0.009 ±.027
15	-0.0013	-0.078 ±.024	-0.0007	-0.042 ±.024	-0.0006	-0.036 ±.024
16	-0.0005	-0.048 ±.038	-0.0009	-0.087 ±.039	-0.0001	-0.010 ±.040
17	-0.0003	-0.021 ±.028	-0.0005	-0.036 ±.029	+0.0004	+0.028 ±.028
18	-0.0017	-0.124 ±.029	-0.0007	-0.051 ±.029	+0.0002	+0.015 ±.030
19	-0.0017	-0.171 ±.040	+0.0007	+0.070 ±.029	-0.0008	-0.081 ±.41
20	-0.0013	-0.085 ±.026	-0.0013	-0.085 ±.026	-0.0009	-0.059 ±.026
21	-0.0003	-0.020 ±.027	-0.0005	-0.033 ±.026	0.0000	0.000
22	-0.0006	-0.037 ±.025	-0.0006	-0.037 ±.025	-0.0007	-0.043 ±.025

Table #11 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	20 Sec. Etch		40 Sec. Etch		60 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
B1	-0.0016	-0.140 ±.035	+0.0027	+0.236 ±.035	*----------	----------
B2	-0.0033	-0.205 ±.025	-0.0018	-0.112 ±.025	-0.0049	-0.306 ±.025
B3	-0.0003	-0.013 ±.017	-0.0016	-0.069 ±.017	-0.0076	-0.330 ±.017*
B4	-0.0037	-0.244 ±.026	-0.0031	-0.205 ±.026	*----------	----------
B5	-0.0033	-0.225 ±.027	-0.0033	-0.225 ±.027	-0.0077	-0.527 ±.027
B6	-0.0028	-0.194 ±.028	-0.0026	-0.180 ±.028	-0.0078	-0.542 ±.028
B7	-0.0034	-0.198 ±.023	-0.0057	-0.332 ±.031	-0.0094	-0.549 ±.023*
B8	-0.0004	-0.031 ±.031	-0.0018	-0.140 ±.031	-0.0021	-0.164 ±.031
B9	-0.0010	-0.061 ±.024	-0.0004	-0.025 ±.025	-0.0036	-0.221 ±.025
B10	-0.0024	-0.127 ±.021	-0.0036	-0.190 ±.021	-0.0059	-0.312 ±.021
B11	-0.0012	-0.087 ±.029	-0.0016	-0.116 ±.029	-0.0049	-0.354 ±.029
B13	-0.0020	-0.156 ±.030	-0.0051	-0.399 ±.031	-0.0080	-0.629 ±.031
B14	-0.0012	-0.068 ±.023	-0.0005	-0.028 ±.022	-0.0088	-0.499 ±.023
B15	-0.0022	-0.153 ±.029	-0.0017	-0.118 ±.028	-0.0069	-0.480 ±.028
B17	-0.0017	-0.165 ±.039	-0.0050	-0.487 ±.039	-0.0005	-0.049 ±.039
B18	-0.0017	-0.108 ±.025	+.0018	+0.115 ±.026	-0.0059	-0.375 ±.025

*Note: Indicates that the tooth was omitted due to severe cracking.

Table #12 Absolute(in Grams)and Percent Weight Changes After Etching

Tooth Number	80 Sec. Etch		100 Sec. Etch		120 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
B2	+0.0005	+0.031 ±.025	+0.0069	+0.432 ±.025	+0.0012	+0.075 ±.025
B5	-0.0007	-0.048 ±.027	-0.0038	-0.262 ±.028	+0.0020	+0.138 ±.028
B6	0.0000	0.000	+0.0026	+0.182 ±.028	-0.0028	-0.195 ±.028
B8	+0.0002	+0.016 ±.032	+0.0006	+0.047 ±.031	-0.0028	-0.195 ±.028
B9	-0.0019	-0.117 ±.025*	+0.0052	+0.321 ±.025	+0.0090	+0.704 ±.031
B10	-0.0004	-0.021 ±.021	-0.0009	-0.048 ±.021	-0.0042	-0.258 ±.025
B11	-0.0022	-0.160 ±.029	-0.0010	-0.073 ±.029	+0.0050	+0.265 ±.021
B13	-0.0012	-0.095 ±.032	-0.0016	-0.127 ±.032	+0.0031	+0.225 ±.029
B14	+0.0054	+0.308 ±.023	-0.0029	-0.165 ±.023	-0.0002	-0.016 ±.032
B15	+0.0013	+0.091 ±.028	+0.0016	+0.112 ±.028	0.0000	0.000
B17	-0.0021	-0.206 ±.039	+0.0004	+0.039 ±.039	+0.0040	+0.279 ±.028
B18	-0.0034	-0.217 ±.026	-0.0024	-0.154 ±.026	+0.0016	+0.157 ±.039

*Note: Indicates that the tooth was omitted due to severe cracking.

Table #13 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	20 Sec. Etch		40 Sec. Etch		60 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
B21	-0.0033	-0.206 ±.025	-0.0023	-0.114 ±.020	-0.0074	-0.464 ±.025
B22	-0.0036	-0.251 ±.028	-0.0022	-0.154 ±.028	-0.0066	-0.454 ±.028
B23	-0.0042	-0.245 ±.023	-0.0015	-0.088 ±.023	-0.0066	-0.386 ±.023
B24	-0.0047	-0.245 ±.021	-0.0018	-0.094 ±.021	-0.0094	-0.491 ±.021
B25	-0.0025	-0.187 ±.030	-0.0011	-0.082 ±.030	-0.0065	-0.487 ±.030
B26	-0.0032	-0.197 ±.025	-0.0021	-0.130 ±.025	-0.0060	-0.371 ±.025
B27	-0.0039	-0.185 ±.019	-0.0020	-0.095 ±.019	-0.0100	-0.474 ±.009
B28	-0.0009	-0.103 ±.046	-0.0009	-0.103 ±.046	-0.0019	-0.218 ±.046
B29	-0.0043	-0.248 ±.023	-0.0030	-0.173 ±.023	-0.0075	-0.434 ±.023
B30	-0.0106	-0.464 ±.018	-0.0091	-0.400 ±.018	-0.0011	-0.049 ±.018
B32	-0.0068	-0.319 ±.019	-0.0036	-0.170 ±.019	-0.0022	-0.104 ±.019
B33	-0.0037	-0.277 ±.030	-0.0008	-0.060 ±.030	+0.0032	+0.240 ±.030
B34	-0.0041	-0.273 ±.027	-0.0033	-0.220 ±.027	-0.0013	-0.087 ±.027
B35	-0.0044	-0.343 ±.031	-0.0029	-0.227 ±.031	-0.0036	-0.282 ±.031

Table #14 Absolute(in grams)and Percent Weight Changes After Etching

	80 Sec. Etch		100 Sec. Etch		120 Sec. Etch	
Tooth Number	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
B21	-0.0031	-0.195 ±.025	-0.0018	-0.114 ±.025	-0.0009	-0.058 ±.026
B22	-0.0016	-0.112 ±.028	-0.0022	-0.155 ±.028	-0.0008	-0.051 ±.026
B23	-0.0005	-0.029 ±.023	+0.0014	+0.082 ±.023	-0.0005	-0.035 ±.028
B24	-0.0009	-0.047 ±.018	-0.0004	-0.021 ±.021	+0.0048	+0.282 ±.024
B25	-0.0014	-0.105 ±.030	-0.0028	-0.211 ±.030	+0.0067	+0.352 ±.022
B26	-0.0039	-0.241 ±.025	-0.0023	-0.143 ±.025	+0.0063	+0.023 ±.031
B27	-0.0031	-0.148 ±.019	-0.0003	-0.014 ±.016	-0.0003	-0.019 ±.025
B28	+0.0015	+0.057 ±.015	+0.0005	+0.066 ±.052	+0.0018	+0.086 ±.019
B29	-0.0034	-0.198 ±.023	-0.0032	-0.186 ±.023	-0.0013	-0.149 ±.046
B30	+0.0033	+0.146 ±.018				
B32	+0.0050	+0.236 ±.019				
B33	+0.0019	+0.142 ±.030				
B34	-0.0018	-0.120 ±.027				
B35	-0.0005	-0.039 ±.031				

Table #15 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	20 Sec. Etch		40 Sec. Etch		60 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
B36	-0.0053	-0.325 ±.025	-0.0017	-0.105 ±.025	-0.0017	-0.105 ±.025
B37	-0.0030	-0.230 ±.031	+0.0010	+0.077 ±.031	0.0000	0.000
B39	-0.0040	-0.323 ±.032	-0.0017	-0.131 ±.031	-0.0010	-0.081 ±.024
B40	-0.0049	-0.292 ±.024	-0.0036	-0.277 ±.031	-0.0026	-0.156 ±.024
B41	-0.0039	-0.281 ±.029	-0.0009	-0.065 ±.029	-0.0002	-0.0145 ±.029
B42	-0.0038	-0.374 ±.039	*----------	----------	----------	----------
B43	-0.0034	-0.329 ±.039	-0.0021	-0.204 ±.039	-0.0022	-0.214 ±.039
B44	-0.0029	-0.334 ±.046	-0.0030	-0.347 ±.046	-0.0011	-0.128 ±.047
B45	-0.0035	-0.291 ±.033	-0.0022	-0.183 ±.033	-0.0019	-0.159 ±.033
B46	-0.0026	-0.276 ±.042	-0.0017	-0.181 ±.042	-0.0013	-0.138 ±.042
B47	-0.0083	-0.403 ±.019	-0.0052	-0.253 ±.019	-0.0067	-0.327 ±.020
B48	-0.0050	-0.367 ±.029	-0.0023	-0.169 ±.030	-0.0022	-0.162 ±.029
B49	-0.0058	-0.411 ±.028	-0.0041	-0.292 ±.028	-0.0008	-0.057 ±.029
B50	-0.0041	-0.343 ±.034	-0.0028	-0.235 ±.034	-0.0010	-0.084 ±.034
B51	-0.0061	-0.342 ±.022	-0.0014	-0.078 ±.022	-0.0027	-0.152 ±.023
B53	-0.0005	-0.050 ±.040	*----------	----------	----------	----------
B54	-0.0020	-0.240 ±.048	-0.0007	-0.084 ±.048	+0.0030	+0.361 ±.048

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #16 Absolute(in grams)and Percent Weight Changes After Etching

	80 Sec. Etch	
Tooth Number	Absolute ±.0004	Percent
B36	-0.0007	-0.043 ±.025
B37	-0.0001	-0.008 ±.024
B39	+0.0008	+0.065 ±.033
B40	-0.0029	-0.174 ±.024
B41	+0.0006	+0.043 ±.029
B43	-0.0010	-0.097 ±.039
B44	-0.0011	-0.128 ±.047
B45	+0.0018	+0.150 ±.033
B46	-0.0016	-0.171 ±.043
B47	-0.0014	-0.069 ±.020
B48	-0.0015	-0.111 ±.030
B49	-0.0013	-0.093 ±.029
B50	-0.0002	-0.017 ±.034
B51	+0.0019	+0.107 ±.023
B54	+0.0002	+0.024 ±.048

Table # 17 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	20 Sec. Etch		40 Sec. Etch		60 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
B55	-0.0063	-0.321 ±.020	-0.0021	-0.107 ±.020	+0.0029	+0.148 ±.020
B56	-0.0048	-0.293 ±.024	-0.0022	-0.134 ±.024	-0.0014	-0.086 ±.025
B57	-0.0037	-0.192 ±.021	*----------	----------	----------	----------
B58	-0.0059	-0.377 ±.026	-0.0037	-0.238 ±.026	-0.0036	-0.232 ±.026
B59	-0.0016	-0.092 ±.023	*----------	----------	----------	----------
B60	-0.0087	-0.384 ±.018	-0.0038	-0.168 ±.018	-0.0042	-0.186 ±.018
B62	-0.0027	-0.162 ±.024	*----------	----------	----------	----------
B63	-0.0040	-0.335 ±.034	-0.0005	-0.041 ±.033	-0.0006	-0.051 ±.034
B64	-0.0047	-0.396 ±.034	-0.0057	-0.483 ±.034	+0.0022	+0.187 ±.034
B65	-0.0028	-0.321 ±.046	-0.0021	-0.178 ±.034	-0.0017	-0.196 ±.046
B66	-0.0029	-0.356 ±.049	-0.0016	-0.198 ±.049	-0.0018	-0.222 ±.049
C1	-0.0106	-0.569 ±.021	-0.0026	-0.140 ±.022	-0.0033	-0.178 ±.022
C2	-0.0080	-0.548 ±.027	-0.0020	-0.188 ±.028	-0.0034	-0.235 ±.027
C3	-0.0094	-0.522 ±.022	-0.0050	-0.279 ±.028	-0.0034	-0.141 ±.022
C4	-0.0112	-0.625 ±.022	-0.0045	-0.253 ±.030	-0.0043	-0.203 ±.022
C5	-0.0128	-0.566 ±.018	-0.0040	-0.178 ±.018	-0.0037	-0.165 ±.018

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #18 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	80 Sec. Etch	
	Absolute ±.0004	Percent
B55	+0.0037	+0.189 ±.020
B56	-0.0004	-0.025 ±.025
B58	-0.0010	-0.064 ±.026
B60	+0.0011	+0.049 ±.018
B63	+0.0006	+0.050 ±.033
B64	+0.0038	-0.323 ±.034
B65	-0.0011	-0.127 ±.046
B66	-0.0005	-0.062 ±.050
C1	-0.0011	-0.060 ±.022
C2	-0.0009	-0.062 ±.028
C3	-0.0018	-0.101 ±.022
C4	-0.0020	-0.113 ±.023
C5	*----------	----------

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #19 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	20 Sec. Etch		40 Sec. Etch		60 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
C6	-0.0085	-0.519 ±.024	-0.0033	-0.203 ±.025	-0.0047	-0.289 ±.025
C7	-0.0105	-0.526 ±.020	-0.0027	-0.136 ±.020	-0.0042	-0.212 ±.020
C8	-0.0108	-0.678 ±.025	-0.0030	-0.190 ±.025	-0.0037	-0.234 ±.025
C9	-0.0130	-0.604 ±.019	-0.0041	-0.192 ±.019	-0.0055	-0.257 ±.019
C10	-0.0084	-0.553 ±.026	-0.0031	-0.205 ±.026	-0.0035	-0.232 ±.027
C11	-0.0100	-0.621 ±.025	-0.0030	-0.188 ±.025	-0.0020	-0.125 ±.025
C12	-0.0081	-0.560 ±.028	-0.0054	-0.375 ±.028	-0.0034	-0.237 ±.028
C13	-0.0125	-0.596 ±.019	-0.0041	-0.197 ±.019	-0.0040	-0.192 ±.019
C14	-0.0103	-0.515 ±.020	-0.0040	-0.201 ±.020	-0.0036	-0.181 ±.020
C15	-0.0077	-0.529 ±.028	-0.0034	-0.235 ±.028	-0.0023	-0.159 ±.028
C16	-0.0099	-0.606 ±.025	-0.0027	-0.166 ±.025	-0.0014	-0.086 ±.025
C17	-0.0068	-0.453 ±.027	-0.0025	-0.167 ±.027	-0.0029	-0.194 ±.027
C18	-0.0078	-0.453 ±.023	-0.0034	-0.198 ±.023	-0.0030	-0.175 ±.023
C19	-0.0076	-0.488 ±.026	-0.0029	-0.187 ±.026	-0.0025	-0.162 ±.026
C20	-0.0077	-0.473 ±.025	-0.0031	-0.191 ±.025	-0.0037	-0.229 ±.025

Table #20 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	80 Sec. Etch	
	Absolute -,0004	Percent
C6	-0.0009	-0.055 ±.024
C7	-0.0009	-0.045 ±.020
C8	-0.0009	-0.057 ±.025
C9	-0.0012	-0.056 ±.019
C10	-0.0011	-0.073 ±.027
C11	0.0000	0.000
C12	-0.0006	-0.042 ±.028
C13	-0.0011	-0.053 ±.019
C14	+0.0002	+0.010 ±.020
C15	-0.0011	-0.076 ±.028
C16	-0.0007	-0.043 ±.025
C17	-0.0021	-0.141 ±.027
C18	-0.0020	-0.117 ±.037
C19	0.0000	0.000
C20	-0.0017	-0.105 ±.025

Table #21 Absolute(in grams)and Percent Weight Changes After Etching

Tooth Number	20 Sec. Etch		40 Sec. Etch		60 Sec. Etch	
	Absolute ±.0004	Percent	Absolute ±.0004	Percent	Absolute ±.0004	Percent
C21	-0.0072	-0.465 ±.026	-0.0029	-0.188 ±.026	-0.0019	-0.123 ±.026
C22	-0.0063	-0.473 ±.030	-0.0025	-0.189 ±.030	-0.0018	-0.136 ±.030
C23	-0.0050	-0.421 ±.034	-0.0027	-0.228 ±.034	-0.0018	-0.153 ±.034
C24	-0.0098	-0.629 ±.026	-0.0042	-0.271 ±.026	*----------	----------
C25	-0.0108	-0.595 ±.022	-0.0056	-0.310 ±.022	-0.0041	-0.228 ±.022
C26	-0.0066	-0.579 ±.035	-0.0019	-0.168 ±.035	-0.0033	-0.292 ±.035
C27	-0.0072	-0.485 ±.027	-0.0027	-0.183 ±.027	-0.0031	-0.210 ±.027
C28	-0.0058	-0.576 ±.040	-0.0025	-0.250 ±.040	-0.0031	-0.311 ±.040
C29	-0.0071	-0.463 ±.026	-0.0025	-0.164 ±.026	-0.0023	-0.151 ±.026
C30	-0.0102	-0.571 ±.022	-0.0038	-0.219 ±.023	-0.0034	-0.192 ±.023
C31	-0.0061	-0.521 ±.034	-0.0030	-0.257 ±.034	-0.0029	-0.249 ±.034
C32	-0 0053	-0.417 ±.032	-0.0020	-0.158 ±.031	-0.0022	-0.174 ±.032

*Note: Indicates that the tooth was eliminated due to severe cracking.

Table #22 Absolute(in grams)and Percent Weight Changes After Etching

	80 Sec. Etch	
Tooth Number	Absolute ±.0004	Percent
C21	-0.0012	-0.078 ±.026
C22	-0.0002	-0.015 ±.030
C23	-0.0018	-0.153 ±.034
C25	-0.0024	-0.134 ±.022
C26	-0.0011	-0.980 ±.035
C27	-0.0010	-0.068 ±.027
C28	-0.0019	-0.191 ±.040
C29	-0.0014	-0.092 ±.026
C30	-0.0006	-0.034 ±.023
C31	-0.0011	-0.095 ±.035
C32	-0.0006	-0.048 ±.032

Table #23 Average % Weight Loss For Etch Times

Group & Age		20 Sec.	40 Sec.	60 Sec.	80 Sec.	100 Sec.	120 Sec.
Under 20 Years							
Oswego							
B1-B18	A	-0.136 ±.027	-0.188 ±.027	-0.381 ±.027	-0.096 ±.022	-0.138 ±.027	+0.067 ±.030
B51-B54	C	-0.211 ±.037	-0.081 ±.027	-0.152 ±.023	+0.066 ±.027	----------	----------
Schenectady							
9-10	E	----------	-0.118 ±.023	-0.281 ±.023	-0.057 ±.024	-0.113 ±.023	-0.020 ±.023
C1-C28	G	-0.544 ±.025	-0.203 ±.026	-0.201 ±.026	-0.077 ±.025	----------	----------
20-45 Years							
Oswego							
B21-B35	B	-0.253 ±.028	-0.151 ±.026	-0.331 ±.026	-0.123 ±.025	-0.121 ±.024	+0.048 ±.027
B36-B46 & B55-B66	D	-0.273 ±.034	-0.190 ±.030	-0.131 ±.031	-0.090 ±.030	----------	----------
Schenectady							
C29-C32	H	-0.493 ±.029	-0.200 ±.029	-0.192 ±.029	-0.067 ±.029	----------	----------
2-7 & 11-22	F	-0,059 ±.026	-0.126 ±.027	-0.320 ±.029	-0.105 ±.028	-0.077 ±.028	-0.111 ±.028

Figure #1

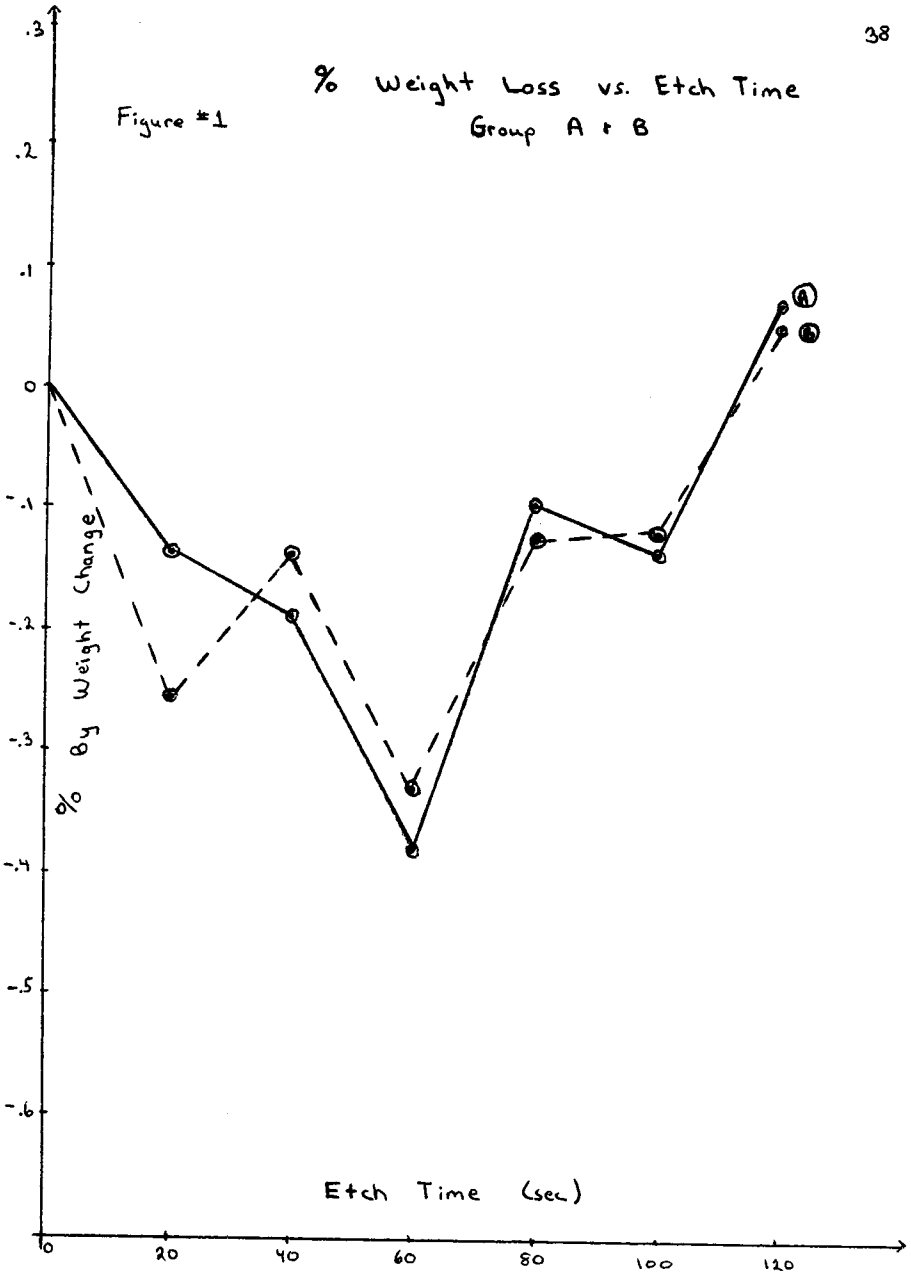

% Weight Loss vs. Etch Time
Group A & B
.3
.2
.1
0
-.1
-.2
-.3
-.4
-.5
-.6
% By Weight Change
A
B
Etch Time (sec)
0
20
40
60
80
100
120

Figure # 2

% Weight Loss vs. Etch Time
Group C & D

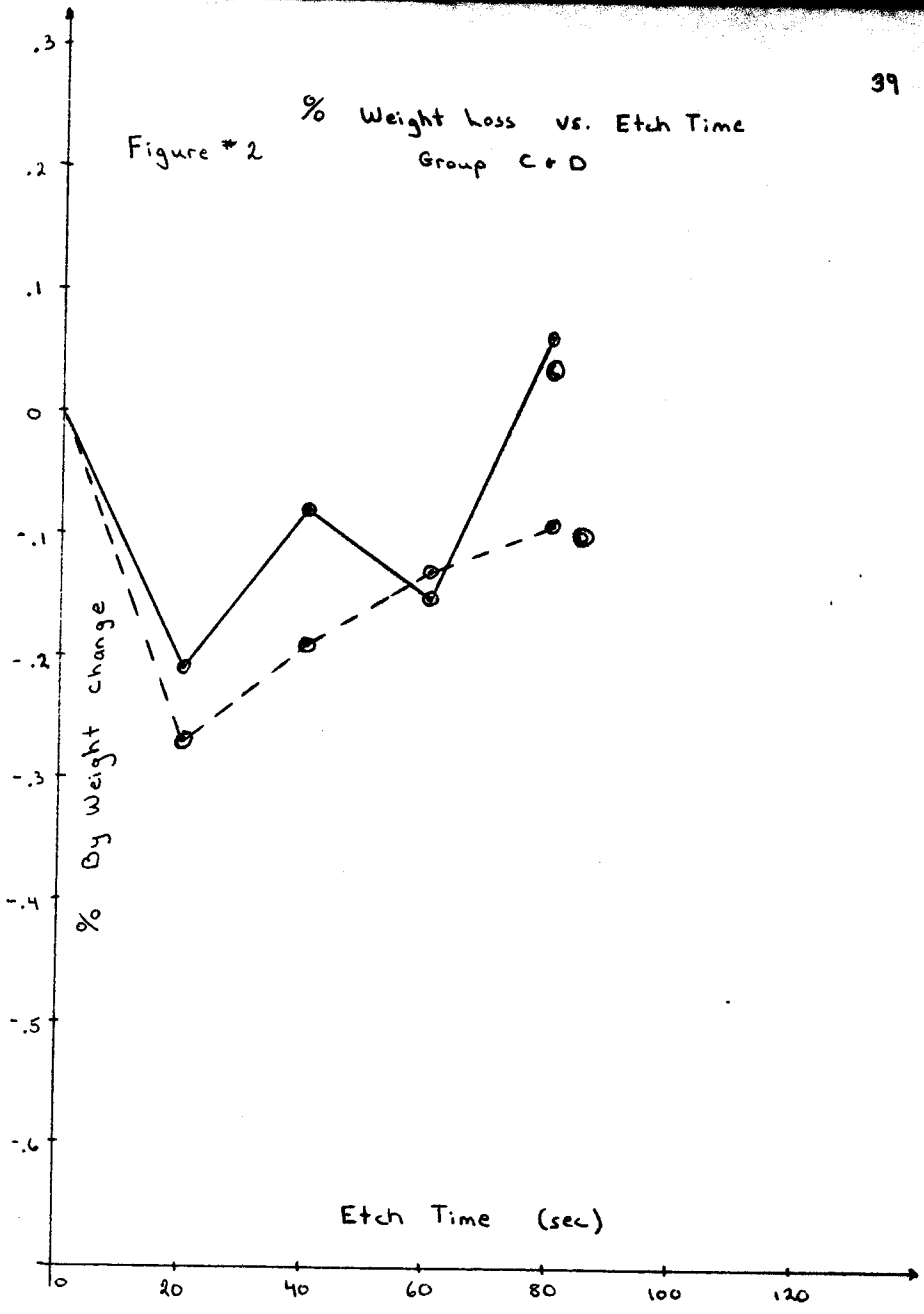


Figure #3

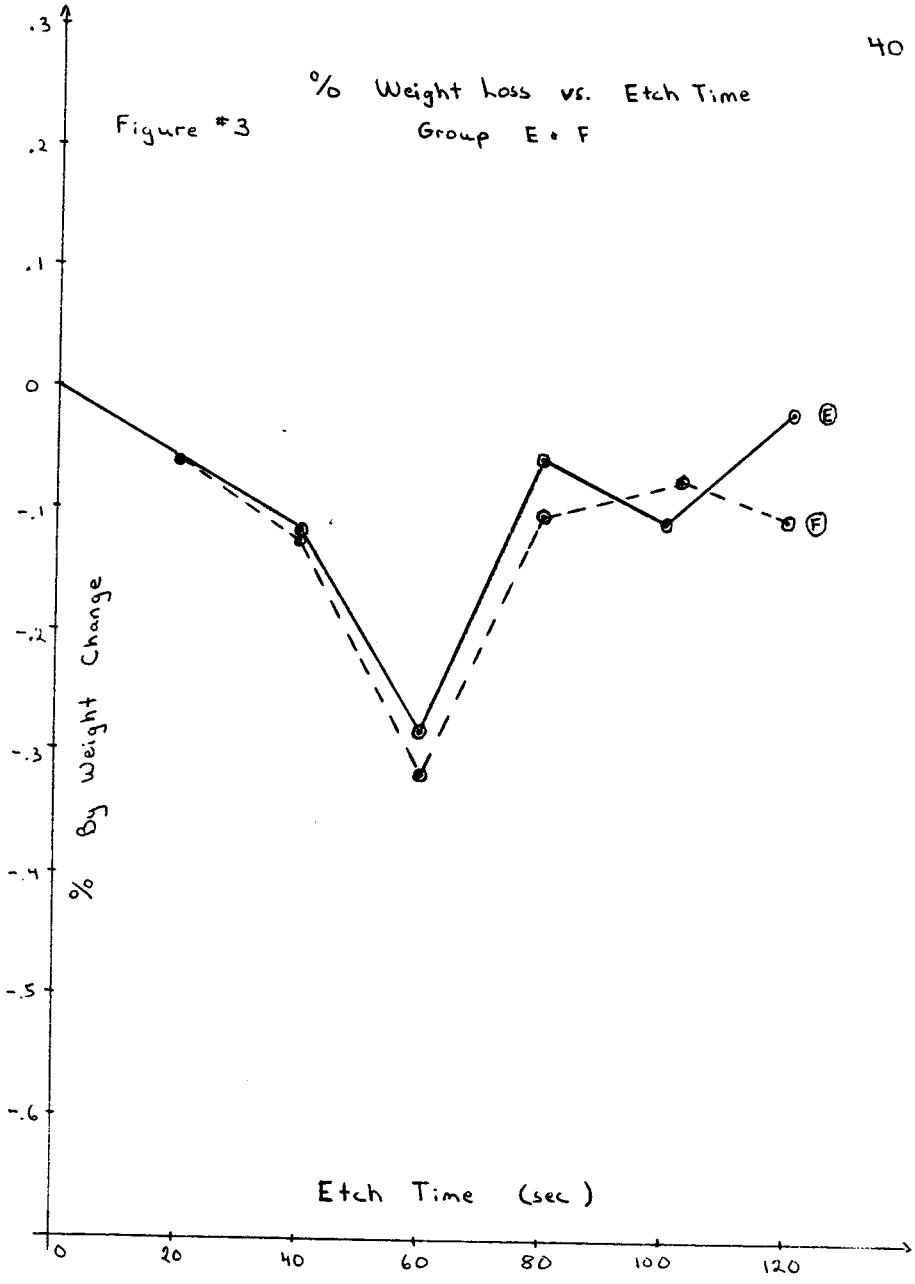
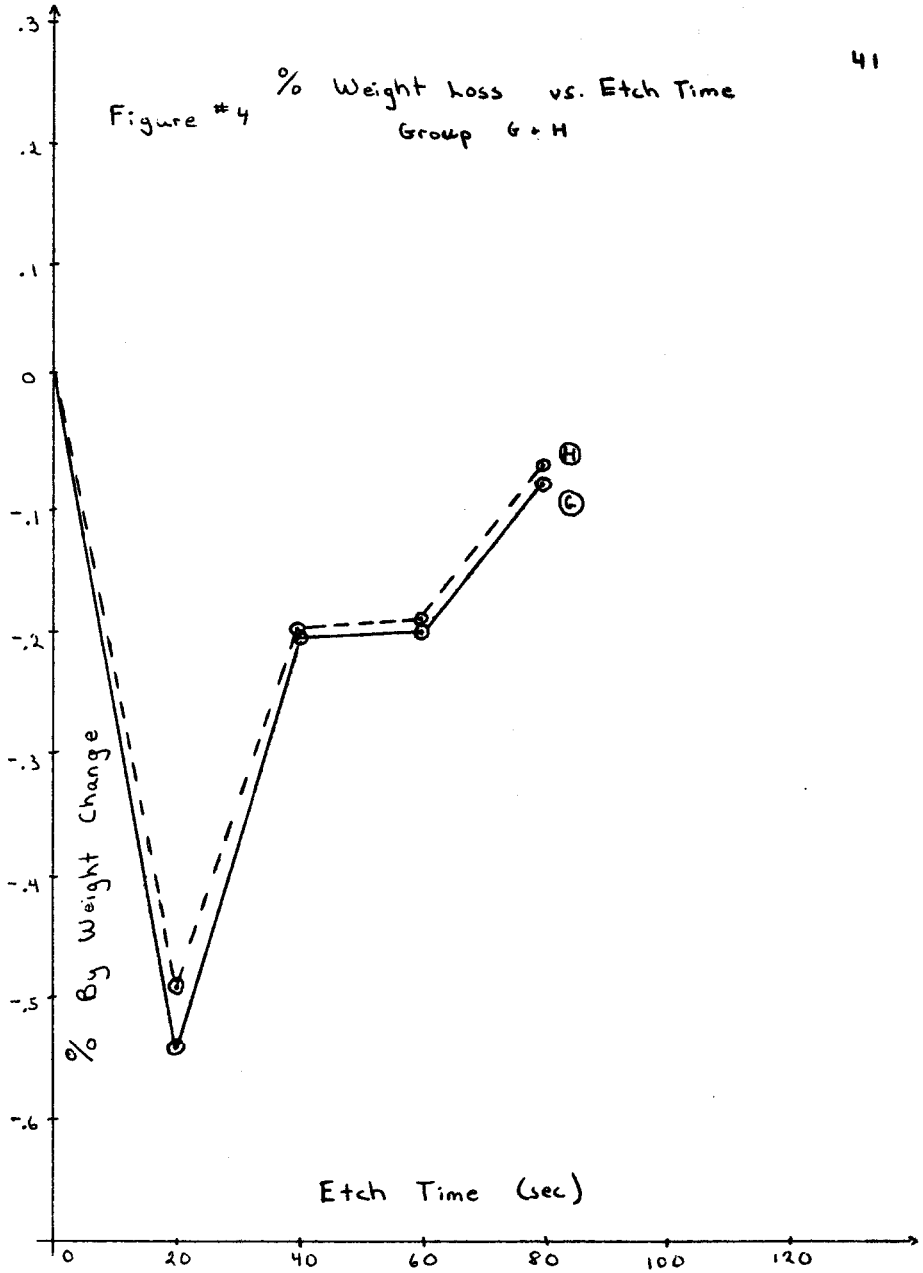

% Weight Loss vs. Etch Time
Group E • F
.3
.2
.1
0
-.1
-.2
-.3
-.4
-.5
-.6
% By Weight Change
E
F
Etch Time (sec)
0
20
40
60
80
100
120

Figure #4 % Weight Loss vs. Etch Time
Group G + H



DISCUSSION

A number of different trends can be seen from the gravimetric data. Except for groups G & H from Schenectady, all teeth generally reflect similar trends of percent weight loss. It is interesting that the increased fluoride concentration in the Oswego water system did not significantly decrease the teeth's susceptability to the etching solution. A maximum percent weight loss tended to occur at the 60 second etch period, which is the exposure time dentists use *in vivo*. Groups G & H seem to contradict these general observations. These teeth were obtained from Dr. Schlansker's office. No apparent physical characteristics can account for the different trends. Further study of these teeth may provide some explanation for this interesting phenomenon.(Two minute etch hasn't been reached on these teeth.)

The age of the teeth appears to play a significant role in their susceptability to the etching process. All groups, except G & H, show that the older teeth are less resistant to the etching process. This decrease in resistance is most pro-

nounced in the first minute of the etching process. This is contradictory to the majority of findings by other authors. (p. 8) Again, groups G & H are contradictory to the other groups studied. The additional loss observed for the majority of the older teeth studied may be attributed to the excess organic pellicle found on their surface. The longer a tooth is exposed to the oral environment the greater the build up of the pellicle. Evidently this pellicle is more easily removed than enamel and contributes greatly to the weight loss. Once the pellicle is removed the enamel appears to be removed at about the same rate as with younger teeth. This is perhaps best illustrated with groups A & B in Figure #1. The later etch periods show smaller differences in percent weight loss between the two age groups. It must be noted, however, that no clear trend is shown by all of the teeth studied. The behavior of groups G & H alone indicates that encompassing theories are difficult to propose for teeth. Again this can be related to the effect of heredity on tooth structure.

One characteristic exhibited by all teeth studied was the presence of random rises and falls in the percent weight loss. The characteristic etch level advocated by some authors (p. 7) never appeared in the present study. After the 60 second etch the teeth generally lost a smaller portion of enamel. In fact, some teeth actually gained weight from the previous etch period. This is most probably due to remineralization of the teeth resulting in an increase in weight. The calcium and phosphorous ions released from previous etchings may protect the remaining enamel. The insoluble salt monocalcium phosphate monohydrate

($Ca(H_2PO_4)_2\ H_2O$) may be deposited on the teeth acting as a protective coating as well. The effect of remineralization can be better understood once the data from the ion selective electrode methods has been examined.

EXPERIMENTAL DATA: ION SELECTIVE METHODS

The etchant solutions were analyzed for $[Ca^{+2}]$ and $[F^-]$ after the teeth were exposed for a total of two minutes. At this time the only solutions analyzed were for teeth 2-8 from Schenectady. More teeth had been exposed for two minutes, but problems with electrode stability prevented reproducable data from being obtained. (A Beckman 39600 Fluoride electrode and an Orion 42-20 Calcium electrode were used.)

The standard reference solutions, as well as the etchant solutions, had to be adjusted to alkaline pH 10 to ensure stable electrode readings. In order to do this the solutions were first diluted 1:10(5 ml diluted to 50 ml)and then made alkaline by the addition of eight milliters of concentrated NH_4OH. Some precipitation would occur if the pH of the solution wasn't maintained at a high enough level. The solutions for fluoride analysis had the further addition of an equal volume of a Fluor-Ade solution. The Fluor-Ade solution does some additional pH adjustment. (The Fluor-Ade solution comes with the electrode.)

Standard references of known concentrations were run for both the calcium and fluoride electrodes. Extrapolation of mv readings for the etchant solutions gives concentration values.

The standard reference for the calcium electrode and the etchant solution values appear in Table #24 and Table #25 respectively. A plot of mv vs. -log $[Ca^{+2}]$ is shown in Figure #5. Similarly the standard reference for the fluoride electrode and the etchant solution values appear in Table #26 and Table #27 respectively. A plot of mv vs. -log $[F^{-}]$ is shown in Figure #6. All mv readings were obtained using an Orion research grade digital ionaliyzer model 701A.

DISCUSSION

The chemical structure of enamel is not precisely known, but generally hydroxyapatite is given the structure $Ca_5OH(PO_4)_3$. In actuality the enamel is a mixture of $Ca_3(PO_4)_2$ and Ca_2OHPO_4. The fluoride present in the enamel is in the form $Ca_5F(PO_4)_3$ or Ca_2FPO_4. Ideally this knowledge would permit the calculation of relative amounts of each substituent being removed. The total weight loss of calcium minus the calcium fluorophosphate equals the summation of Ca_2OHPO_4 and $Ca_3(PO_4)_2$. Similarly, the total $[Ca^{+2}]$ determined using the calcium electrode, minus the calcium fluorophosphate should equal the summation of Ca_2OHPO_4 and $Ca_3(PO_4)_2$. Two equations with two unknowns results permitting the calculation of relative amounts of Ca_2OHPO_4 and $Ca_3(PO_4)_2$ lost during the etching process.

1. total weight loss of calcium—
   $Ca_2FPO_4 = Ca_2OHPO_4 - Ca_3(PO_4)_2$

2. total Ca^{-2} from electrode—
   $Ca_2FPO_4 = Ca_2OHPO_4 - Ca_3(PO_4)_2$

Unfortunately, the effects of remineralization prevent the calcium ion concentration of the etching solution from remaining at the theoretically expected level. If we assume that all

the fluoride in the enamel is in the form of Ca_2FPO_4, we would expect two moles of Ca^{+2} released for every mole of F^- in the etching solutions.

3. $Ca_2FPO_4 \rightarrow 2\ Ca^{+2} + F^- + PO_4^{-3}$

The experimental data, however, shows that 75 percent of the etchant solutions examined had higher molar concentrations of fluoride ion than calcium ion.(Table #28) The difference between the expected and observed must be due to remineralization. The remineralization evidently doesn't incorporate the fluoride ion, because if it did the same theoretical concentration ratios would hold true. Remineralization probably occurrs in the form of monocalcium phosphate monohydrate($Ca(H_2PO_4)_2\ H_2O$). Sufficient amounts of phosphate, calcium ion, and water are present to permit the remineralization. The percent remineralization for the examined solutions are shown in Table #29.

The effects of re ineralization are much greater than originally anticipated. The difference between expected and observed calcium ion concentration may be partially due to calcium ion loss in the rinsing process. This probably only accounts for a small percentage of the difference, such that the majority of the difference is due to remineralization. Once more ion selective electrode data is available on the other teeth a qualitative analysis of the relative amounts of $Ca_3(PO_4)_2$ and $Ca_2OH\ PO_4$ lost by etching can be made.

Table 24 Standard Calcium Reference

$[Ca^{+2}]$	$-\log[Ca^{+2}]$	mv ($\pm$.1)
2.50×10^{-6}	5.60	-33.0
5.00×10^{-6}	5.30	-38.6
7.50×10^{-6}	5.12	-42.0
1.00×10^{-5}	5.00	-42.7

Table #25 Calcium Readings For Teeth Samples

Tooth Etching Sol.	mv (±.1)	$-\log[Ca^{+2}]$	$[Ca^{+2}]$	$[Ca^{+2}]$ Corrected by Dilution Factor
2	-30.3	5.73	1.86×10^{-6}	1.86×10^{-5}
4	-30.0	5.77	1.70×10^{-6}	1.70×10^{-5}
5	-31.3	5.68	2.09×10^{-6}	2.09×10^{-6}
6	-31.7	5.67	2.14×10^{-6}	2.14×10^{-6}
7	-30.8	5.72	1.91×10^{-6}	1.91×10^{-6}
8	-30.2	5.76	1.73×10^{-6}	1.73×10^{-6}

mV vs. $-\log [Ca^{++}]$

Figure # 5

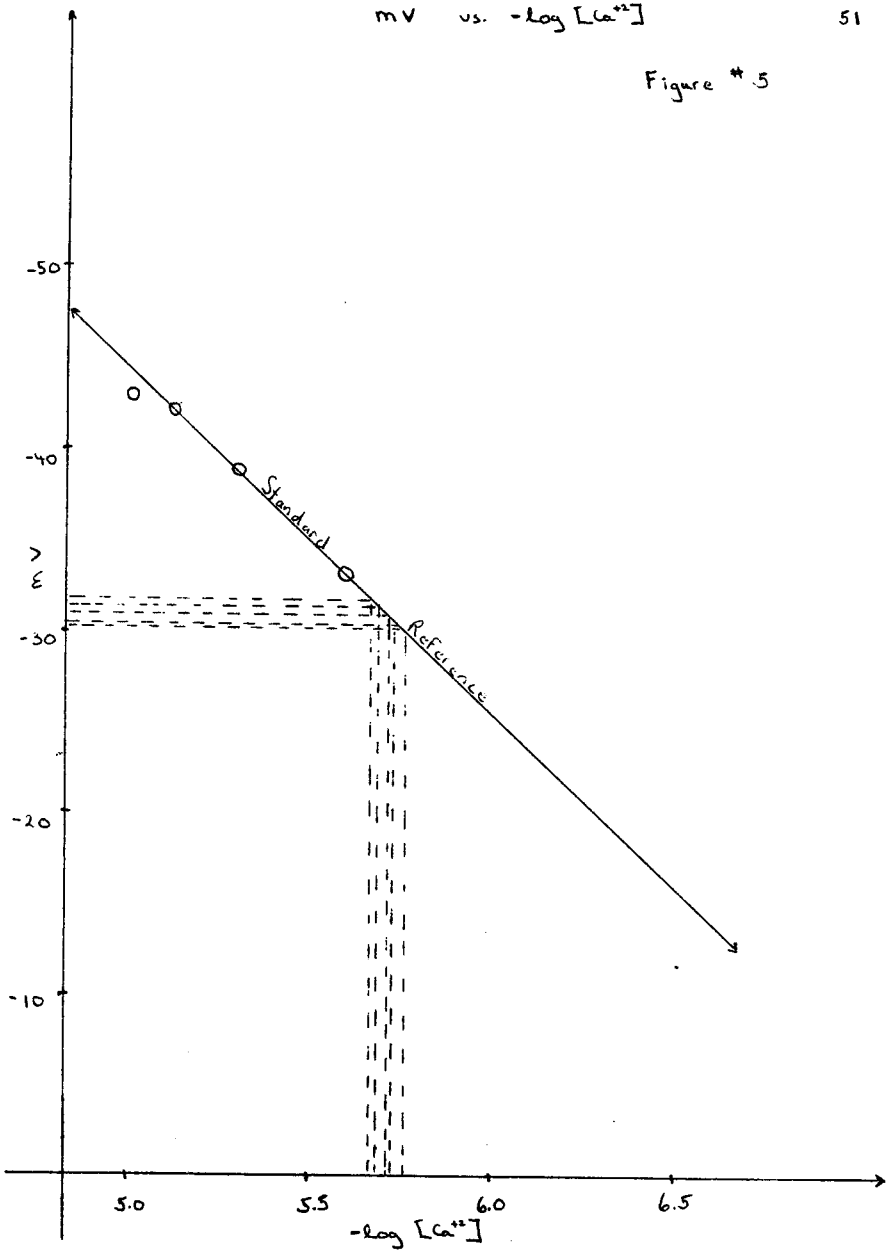


Table #26 Standard Fluoride Reference

$[F^-]$	$-\log[F^-]$	mv (±.1)
9.78×10^{-7}	6.01	80.9
1.96×10^{-6}	5.71	81.0
2.93×10^{-6}	5.53	81.2
3.91×10^{-6}	5.41	81.5
4.89×10^{-6}	5.31	82.0
9.78×10^{-6}	5.01	82.3
1.47×10^{-5}	4.83	82.5

Table #27 Fluoride Readings For Teeth Samples

Tooth Etching Sol.	mv (±.1)	$-\log[F^-]$	$[F^-]$	$[F^-]$ Corrected by Dilution Factor
2	84.2	----	----------	----------
4	84.0	4.00	----------	----------*
5	81.3	5.57	2.69×10^{-6}	2.69×10^{-5}
6	81.2	5.62	2.40×10^{-6}	2.40×10^{-5}
7	81.2	5.62	2.40×10^{-6}	2.40×10^{-5}
8	80.9	5.79	1.62×10^{-6}	1.62×10^{-5}

*Note: These values couldn't be extrapolated from the standard reference curve.

mv vs. -log [F⁻]

Figure # 6

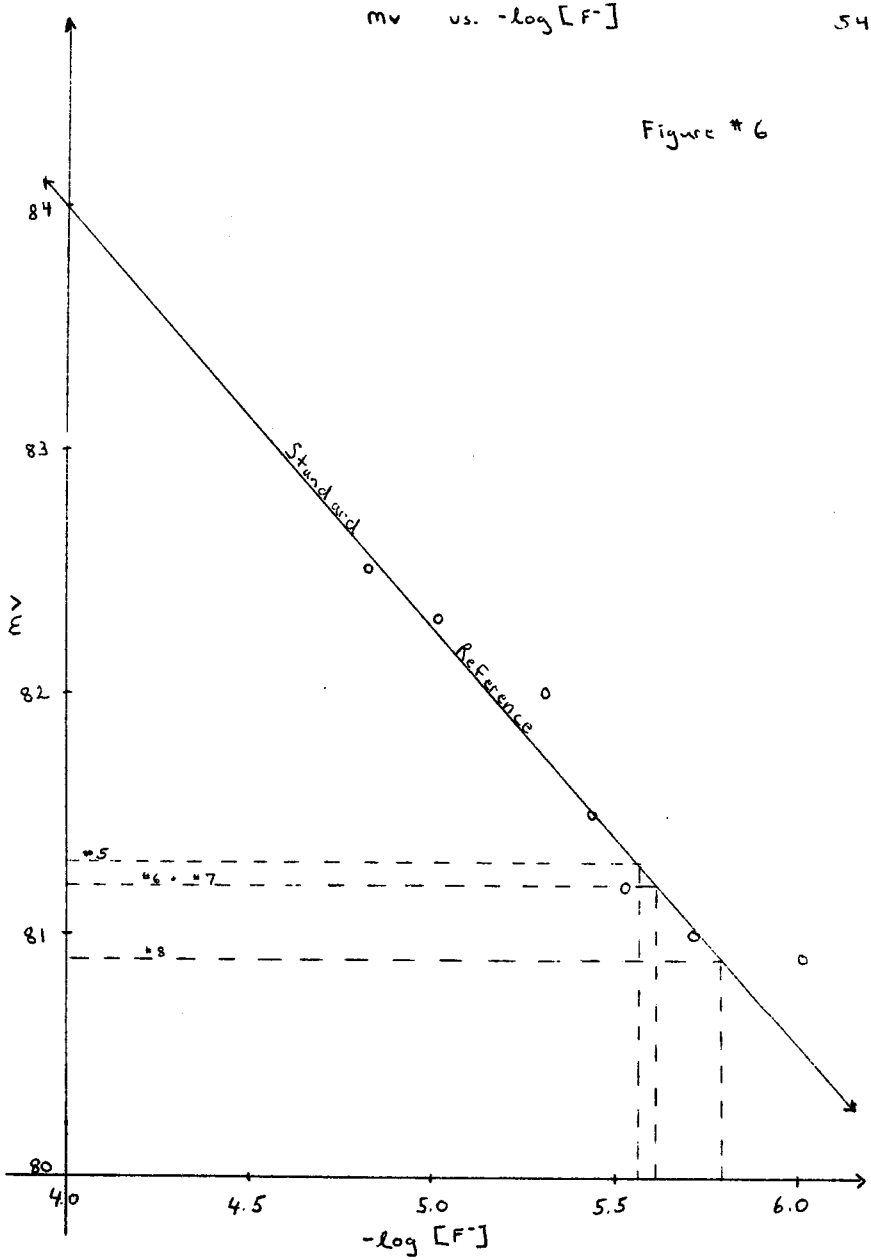


Table #28 Summation of Gravimetric and Ion Selective Methods

Tooth No.	Wt. Loss $[Ca^{+2}]$	Electrode $[Ca^{+2}]$	Electrode $[F^{-}]$
2	8.91×10^{-5}	1.86×10^{-5}	----------
4	6.31×10^{-5}	1.70×10^{-5}	----------
5	6.96×10^{-5}	2.09×10^{-5}	2.69×10^{-5}
6	6.96×10^{-5}	2.14×10^{-5}	2.40×10^{-5}
7	5.94×10^{-5}	1.91×10^{-5}	2.40×10^{-5}
8	4.17×10^{-5}	1.73×10^{-5}	1.62×10^{-5}

Table #29 Percent Remineralization of monocalcium phosphate monohydrate

Tooth No.	Electrode $[F^-]$	Expected $[Ca^{+2}]$	Electrode $[Ca^{+2}]$	Difference	% Remineralization
5	2.69×10^{-5}	5.38×10^{-5}	2.09×10^{-5}	3.29×10^{-5}	61
6	2.40×10^{-5}	4.80×10^{-5}	2.14×10^{-5}	2.66×10^{-5}	55
7	2.40×10^{-5}	4.80×10^{-5}	1.91×10^{-5}	2.89×10^{-5}	60
8	1.62×10^{-5}	3.24×10^{-5}	1.70×10^{-5}	1.54×10^{-5}	48

SUGGESTIONS FOR FURTHER RESEARCH

Further research should concentrate on the effects of remineralization. Additional teeth have reached the two minute etch and their solutions should be analyzed for $[Ca^{+2}]$ and $[F^-]$ content. Ion selective methods for these solutions presently have not shown good reproducibility. The concentration of phosphoric acid is great enough to cause some side precipitate reactions. If the solutions could be adjusted to proper pH values without the precipitate formation, better results could be obtained. The present use of concentrated NH_4OH to adjust pH is yielding better results, but the optimum amount to add hasn't been determined. The problem doesn't arise in the theoretical basis of the research project, but instead in the mechanical process of carrying out the analysis.

The present research will continue until data has been obtained on all the teeth collected. Once this data is obtained, quantitative analysis of the remineralization process and the chemical process of etching may be performed.

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