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ALUMINIUM COMPOUNDS IN FLUORINATED TOOTHPASTES AND DENTAL PROPHYLAXIS PASTES

by

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One of the principal problems in the composition of fluorine-containing dentifrices is the limited compatibility of fluorine compounds, on the one hand, and abrasives and other common dentifrice constituents, on the other. In a previous publication by the present author (*Ericsson* 1961 b) data obtained with the use of radioactive fluorine were presented, which threw some light on these problems. The present article reports investigations carried out with the same technique on the compatibility of fluorides with some compounds of aluminium. Several aluminium compounds appear suitable as abrasives in dentifrices owing to their moderate degree of hardness and their consistency when incorporated in pastes. *Manly & Bibby* (1949) reported that aluminium ions had a solubility-reducing effect on dental enamel, which in their tests was only slightly inferior to that of fluoride ions. *Torell* (1954) found that enamel surfaces treated with fluoride and aluminium ions in acid buffers acquired great resistance against acid dissolution. Finally, *Burnett* (1957) reported that mixtures of aluminium hydroxide and aluminium oxide do not react appreciably with fluoride ions.

MATERIAL AND METHODS

The fluorides employed in the tests to be presented are sodium fluoride, NaF, stannous fluoride, SnF_2, zirconium fluoride, ZrF_4, and sodium monofluorophosphate, Na_2PO_3F. The reasons for the selection of sodium fluoride, stannous fluoride, and sodium monofluorophosphate are given in a previous publication (*Ericsson* 1961 b). Zirconium fluoride was chosen for the following reasons. The zirconium ion may be thought to depress the solubility of dental enamel to a similar extent as tin (*Manly & Bibby* 1949) without having the disadvantage of occasionally forming brown or black sulfides in the enamel surface. Preliminary tests, *in vitro* as well as clinical, have also indicated the usefulness of zirconium fluoride for topical application to tooth surfaces (*Rosenkranz & Torell* 1959, *Torell & al.* 1960). A later investigation by *Torell* (1960; published at the time of the present investigation) has, however, given negative result for ZrF_4 as well as FeF_3.

The aluminium compounds selected for the experiments were aluminium hydroxide $Al(OH)_3$, and aluminium oxide Al_2O_3, both substances analytically pure; further precipitated aluminium silicate (*purum* quality of British Drug House; formula approximately $Al_2SiO_5 \cdot 2H_2O$) and kaolin (Devolite brand; about 83.9 % clay, 14.8 % felspar, 0.85 % Fe_2O_3, 0.21 % MgO, 0.19 % CaO; particle size: 99.95 % below 44 μ, 48 % below 10 μ).

The production of F^{18} and the labelling of the different fluorine compounds have been described in previous publications (production and purification of F^{18}: *Ericsson* 1958; labelling of Na_2PO_3F: *Ericsson* 1961 a; labelling of NaF and SnF_2, counting and calculation: *Ericsson* 1961 b). F^{18}-labelling of zirconium fluoride solutions was performed in the same way as with sodium fluoride and stannous fluoride, *i.e.* simply by mixing a zirconium fluoride solution with a solution containing carrier-free F^{18} as fluoride ions, together with a minimum of other ions.

Counting and recalculation were done as in our previous work on F^{18}-labelled dentifrices (*Ericsson* 1961 b). The counting error was below 1 per cent except in one test with NaF—Al-silicate and enamel powder, in which it reached 3—4 per cent.

SOLUBILITY OF THE ALUMINIUM COMPOUNDS

Since some of the combinations of fluorides and aluminium compounds were to be tested at pH values about 5, the solubilities of the aluminium compounds and the resulting pH values were tested under the conditions intended for the main experiments. 2-gram portions of the abrasives were shaken for 30 min. with 6 ml 0.1-M acetate buffer pH 5.0. The resulting pH values were determined, the solids were centrifuged down and aliquots of the supernatants evaporated. The evaporation residue of a like aliquot of the pure buffer was determined and subtracted, and the percentage of the abrasive dissolved was calculated. The results appear in Table 1.

Table 1

Aluminium compound	Final pH	% dissolved
Aluminium hydroxide	5.20	0.165
Aluminium oxide	7.40	0.57
Aluminium oxide*)	7.25	0.525
Aluminium trisilicate	4.90	0.00
Kaolin	5.15	0.09

*) heated at 900° for 1 hour.

Aluminium oxide was thus the only compound that showed any appreciable solubility and change of the pH level.

COMPATIBILITY OF FLUORINE COMPOUND SOLUTIONS AND ALUMINIUM COMPOUND ABRASIVES

Experiments were performed according to the following methods: 2-gram portions of the abrasives were shaken for 30 min. in plastic tubes with 3 ml of the F^{18}-labelled fluoride solutions and 3 ml of a 0.2-M acetate buffer of a pH value chosen to give the desired final reaction. The fluoride solutions were 40-mM NaF, 40-mM Na_2PO_3F, 20-mM SnF_2 or 10-mM ZrF_4, thus containing equivalent concentrations of fluorine. In some of the tests 0.2-M sodium chloride, with or without small pH-adjusting quantities of hydrochloric acid or ammonia, replaced the acetate buffers.

After shaking, the solids were centrifuged down and the supernatants removed by suction. The radioactivities and the pH values were determined. Two 1-ml portions of each supernatant were then shaken for 30 min. with 100-mg portions of powdered enamel. The enamel powder had been prepared according to *Manly & Hodge* (1939), and the fraction passing sieve No. 24 but not No. 40 was selected for the tests (mesh widths of these sieves were 0.25 and 0.15 mm, respectively).

Shaking with the enamel powder was performed in small plastic tubes fitting into the well of the scintillation crystal used for determination of the radioactivities. The tubes were kept standing during the shaking period in order to avoid losses of enamel particles adhering to the stoppers. After it had been found that the enamel particles sedimented completely without centrifugation, this step was omitted following the shaking, and the supernatant and three successive washings with 4 ml each of distilled water were removed directly by suction.

The activity of the enamel powder was then determined.

Results

The results of the experimental series appear in Table 2.

It appears from Table 2 that the fluoride solutions as a rule lost most of their activity on shaking with aluminium oxide or aluminium silicate. The subsequent uptake by the enamel powder was very low. Tests with another precipitated aluminium silicate (Merck) gave about the same results as those listed in the table. These abrasives are thus clearly unsuitable for fluoride-containing toothpastes.

The fixation of fluoride or monofluorophosphate ions to aluminium hydroxide and kaolin shows considerable variation and is clearly pH-dependent in the case of sodium fluoride, the fluoride-binding decreasing with increasing pH. Stannous fluoride, zirconium fluoride, and sodium monofluorophosphate gave somewhat inconsistent results in this respect. pH values at or above neutrality are apparently necessary to prevent binding of a substantial fraction of the fluoride ions of NaF, while the tin and zirconium ions seem to prevent most of the loss of fluoride even in the pH range about 5. The loss of F^{18} from labelled Na_2PO_3F appears little dependent on the pH values.

The F^{18} uptake from sodium fluoride by the powdered enamel was clearly pH-dependent, which also seems to be the case for

Table 2

F^{18} uptake by abrasives and by enamel powder from supernatants.

In the table the uptake by the enamel powder is expressed as average of the duplicate tests and percentage of the activity of 0.1 ml of the original fluoride-buffer mixture.

Fluorine compound	$Al(OH)_3$			Al_2O_3			Al-silicate			Kaolin		
	pH	Abrasive uptake, per cent	Enamel uptake	pH	Abrasive uptake, per cent	Enamel uptake	pH	Abrasive uptake, per cent	Enamel uptake	pH	Abrasive uptake, per cent	Enamel uptake
NaF	5.15 5.4 8.3 8.9 8.95	63.4 62.8 2.5 0.0 0.0	72 56 41 29 18	7.1 8.2	97.7 65.4	4 13	4.9 6.3 6.5	95.2 96.3 96.4	11 13 10	5.2 6.8	57.9 18.4	66 48
SnF_2	5.05 5.1 5.1	23.3 44.7 0.0	26 72 87	5.8	99.6	1.5	4.7	91.8	18	4.97 5.35	11.7 17.0	78 70
ZrF_4	5.2 6.0	18.0 37.0	96 72	6.1	99.6	1.5	4.8	99.43	12	4.75 7.70	23.3 11.1	96 42
Na_2PO_3F	5.3 7.85	9.0 9.1	35 19	7.5 9.1	81.4 9.2	2.3 8.5	4.8 6.3	93.6 95.7	1.9 1.0	5.20 6.88	23.3 12.7	29 30

zirconium fluoride. Stannous fluoride, which was only tested at pH values about 5, showed great variation after shaking with aluminium hydroxide.

TESTS WITH SIMPLIFIED TOOTHPASTES CONTAINING DIFFERENT FLUORIDES AND ALUMINIUM HYDROXIDE OR KAOLIN

Since aluminium hydroxide and kaolin were found to be satisfactorily compatible with fluoride and monofluorophosphate ions these abrasives were also tested together with the four fluorine compounds in simplified toothpastes containing in addition sodium lauryl sulfate, carboxymethyl cellulose (CMC) and sorbitol, and buffered at different pH levels in the same way as the solutions described in the previous section. The composition of these pastes appears from the following example:

5.5 g kaolin
0.2 g sodium lauryl sulfate
1 g sorbitol
0.15 g CMC
5 ml 0.2-M acetate buffer pH 5.0
5 ml 0.125-M solution of sodium fluoride, labelled with F^{18}.

Since these pastes contained more water than ordinary toothpastes, the liquid phase could be separated by centrifugation and further tested by shaking with enamel powder. The adopted procedure was as follows:

After mixing, the toothpastes were shaken for 30 min. and then centrifuged. The supernatants were removed by suction and their activities and pH values analyzed. Duplicate 1-ml volumes of each supernatant were shaken for 30 min. with 100-mg portions of powdered enamel, the procedure being the same as that described in the preceding section. The F^{18} uptake of the enamel powder was then determined.

Results

The results appear in Table 3.

In this series there was also a greater fixation at lower pH values of F^{18} from NaF both to the abrasives and to the enamel

Table 3

F^{18} uptake by solid phase of toothpastes, and by enamel from liquid phase. In the table the uptake by the enamel powder is expressed as average of the duplicate tests and percentage of the activity of 0.1 ml of the original liquid phase.

Fluorine compound	$Al(OH)_3$-paste			Kaolin-paste		
	pH	Solid phase uptake, per cent	Enamel uptake	pH	Solid phase uptake, per cent	Enamel uptake
NaF	5.95 7.98	18.9 8.1	72 26	6.06 7.87	65.3 22.0	17 22
SnF_2	4.85 4.90	24.6 27.3	39 29	4.90 5.05	0.0 11.6	40 42
ZrF_4	4.85 5.45	23.0 19.8	51 38	4.85 8.55	6.7 29.5	40 25
Na_2PO_3F	5.45 6.75	0.0 2.3	29 18	5.70 7.35	13.9 10.3	9.0 9.5

powder. The results with zirconium fluoride were again somewhat inconsistent.

The F^{18} uptake from Na_2PO_3F by abrasives and enamel powder showed a rather small variation with pH in both previous test series, in contrast to the corresponding uptake from NaF.

DISCUSSION

The first result of these investigations is the elimination of aluminium oxide and synthetic aluminium silicate as fluoride-incompatible abrasives. The report by *Burnett* (1957) on the fluoride compatibility of $Al(OH)_3$—Al_2O_3 mixtures may be due either to a low Al_2O_3 content of his material or to some mistake.

The compatibility of aluminium hydroxide and kaolin with the tested fluorides is fairly good, with the exception of NaF at the lower pH values. The much better results obtained with stannous fluoride in combination with kaolin than with stannous fluoride — calcium pyrophosphate, as reported in a previous article (*Ericsson* 1961 b), appears especially interesting because the latter combination has repeatedly been stated to have a notable cariostatic effect.

The F^{18} uptake by enamel powder was greater throughout in these experiments with aluminium hydroxide and kaolin than in the investigation mentioned above, where other abrasives were tested. Even if the greater part of the fluoride content of sodium fluoride was often lost to the aluminium hydroxide or kaolin at the lower pH values, the subsequent uptake by the enamel powder was notably high. Greater still was the fluoride uptake by the enamel from zirconium fluoride in the lower pH range.

The competitive action of phosphate ions and of several organic anions on the fluoride binding by aluminium compounds, which has been reported by, *inter al., Swenson, Cole & Sieling* (1949), should be tested for its influence on the compatibility of the fluoride-abrasive combinations. Preliminary tests with the combinations $NaF + Al(OH)_3$ or kaolin + phosphate or citrate, and $SnF_2 + Al(OH)_3$ or kaolin + citrate resulted in a somewhat reduced fluoride binding to the abrasives and increased uptake by the enamel powder.

With the exception of the inconsistencies of the results obtained with stannous fluoride (well-known from previous literature) the relative fluorine uptake by enamel powder from SnF_2, NaF, and Na_2PO_3F agreed on the whole with the results obtained in the author's previous investigations (*Ericsson* 1961 b). Stannous fluoride thus gave a greater uptake at pH about 5 than sodium fluoride at about neutrality, and both fluorides gave a greater uptake in the enamel than sodium monofluorophosphate at any tested pH value.

The variations of the results obtained with stannous fluoride might be explained by the lability of this substance: minor changes in the experimental conditions will cause notable variations in the degree of oxidation and tin hydroxide precipitation. It should also be kept in mind that the pH values given in the tables are the final values, which were reached from different sides during the tests.

The relative insensitiveness of the sodium monofluorophosphate to pH changes and the probable difference in the mode of reaction of this salt with the enamel, as compared with the simple fluoride ions, may possibly be utilized to obtain a combined effect of the two ions.

According to the results obtained in this investigation the following fluoride-abrasive combinations appear to be worthy of clinical testing in the first rank:

(1) NaF-$Al(OH)_3$ and NaF-kaolin in the pH range 5—7.

(2) SnF_2-$Al(OH)_3$ and SnF_2-kaolin at pH about 5.

(3) ZrF_4-$Al(OH)_3$ and ZrF_4-kaolin at pH 5—6.

(4) Na_2PO_3F-$Al(OH)_3$ and Na_2PO_3F-kaolin at pH about and above 7.

Clinical testing should, however, preferably also be preceded by investigations on the solubility-decreasing effect of these fluoride-abrasive combinations on standardized or randomized tooth surfaces.

SUMMARY

The compatibility of the fluorine compounds NaF, SnF_2, ZrF_4, and Na_2PO_3F with some aluminium compounds, which might be employed as abrasives in toothpastes and dental polishing pastes, was tested using F^{18} as a label. Aluminium oxide and synthetic aluminium silicate were found to be incompatible with all the tested fluoride compounds while aluminium hydroxide and kaolin could be used in different pH ranges with the different compounds. The F^{18} uptake by powdered dental enamel from the labelled fluorides was greater than previously found by the author when testing the same fluorides in combination with other abrasives.

The results are discussed and the indications for clinical testing summarized.

RÉSUMÉ

COMPOSÉS D'ALUMINIUM DANS DES PÂTES DENTIFRICES ET PÂTES À POLIR FLUORISÉES

On a examiné, en utilisant l'isotope de fluor radioactif F^{18}, la compatibilité des composés NaF, SnF_2, ZrF_4 et Na_2PO_3F avec quelques poudres de composés d'aluminium, qui pourraiant être utilisés comme abrasifs dans des pâtes dentifrices et des pâtes à polir dentaires. On a trouvé que l'oxyde d'aluminium et le silicate d'aluminium synthétique sont incompatibles aves tous les composés de fluor examinés, tandis que l'hydroxyde d'aluminium et le kaolin s'accordent à des pH de niveaux différents avec les différents composés. L'absorption par l'émail dentaire pulvérisé de F^{18} provenant des solutions de fluorures marquées était plus grande que celle préalablement trouvée par l'auteur dans des études sur les mêmes fluorures avec d'autres abrasifs.

Les résultats sont discutés, et les indications en ce qui concerne les essais cliniques sont résumées.

ZUSAMMENFASSUNG

ALUMINIUMVERBINDUNGEN IN FLUORIDHALTIGEN ZAHNPASTEN UND ZAHNÄRZTLICHEN POLIERPASTEN

Die Kompatibilität der Fluorverbindungen NaF, SnF_2, ZrF_4 und Na_2PO_3F mit einigen Aluminiumverbindungen, die als Schleifmittel in Zahnpasten und zahnärztlichen Polierpasten verwendbar erscheinen, wurde mit Hilfe von F^{18}-Markierung untersucht. Es stellte sich heraus, dass Aluminiumoxyd und synthetisches Aluminiumsilikat mit allen geprüften Fluorverbindungen unvereinbar waren, während Aluminiumhydroxyd und Kaolin zusammen mit diesen Fluoriden in verschiedenen pH-Gebieten verwendbar waren. Die F^{18}-Aufnahme von pulverisiertem Zahnschmelz aus Lösungen von gemerkten Fluoriden war grösser als früher vom Verfasser gefunden wurde, wenn dieselben Fluoride zusammen mit anderen Schleifmitteln untersucht wurden.

Die Ergebnisse und die Indikationen für die klinische Prüfung werden diskutiert.

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