underwent a complex reaction with the fluorosulfonate at 200–350° in a pressure vessel. At 200°, 40 g. of arsenic fluorosulfonate and 30 g. gave a gas which infrared analysis showed to contain COFCl, CF_2Cl_2, SO_2, COF_2, $COCl_2$ and SO_2F_2 in the approximate molar ratios of 8:8:1:1:1:trace, respectively. At 300° the amounts of SO_2, SO_2F_2 and COF_2 increased, and significant quantities of CF_3Cl were formed.

Arsenic fluorosulfonate was vaporized in a stream of nitrogen through a nickel tube heated to 500°. The condensate in the liquid nitrogen trap contained trace amounts of SO_2F_2 and SO_2; the remainder of the condensate consisted solely of arsenic fluorosulfonate. This experiment and the mass spectrographic data point to a reversible decomposition of the fluorosulfonate.

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[CONTRIBUTION FROM THE IDAHO STATE COLLEGE]

Adsorption of Fluoride from Dilute Aqueous Solution. Adsorption by Synthetic Zirconyl Silicate and Other Materials

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Some studies on the fluoride adsorbancy of synthetic calcium monohydrogen phosphate and synthetic sintered and unsintered zirconium silicate and beryllium silicate were made. Ten p.p.m. of fluoride was passed at about 0.3 ml./min. through chromatographic tubes packed with the material under study together with diatomaceous earth, and the concentration of the fluoride in the effluent solution determined. The materials which were sintered with glass adsorbed very slight amounts of fluoride. Calcium phosphate and unsintered beryllium silicate adsorbed about half of the fluoride from 50 ml. of 10 p.p.m. fluoride solution. Unsintered zirconium silicate adsorbed all detectable fluoride from such a solution. One gram of zirconium silicate adsorbed as much as 5 mg. of fluoride from solution. Passing 0.1 *N* sodium carbonate through the zirconium silicate columns caused adsorbed fluoride to be released; however, the extent of fluoride recovery by this method varied unpredictably between 30 and 100%.

This paper is a report on a study of fluoride adsorption by certain selected materials. The enamel and dentine of teeth, bone and hydroxylapatite are known to adsorb fluoride[1] as is glass.[2] R. C. Specht[2] showed that borosilicate glass and soft glass could adsorb fluoride and release it quantitatively upon treatment with ferric sulfate solution and sodium hydroxide solution. He packed finely ground glass into glass tubing through which he passed the fluoride and subsequently the ferric sulfate and sodium hydroxide solutions. A similar approach was used for this study.

The materials investigated included a calcium phosphate prepared by adding phosphoric acid to a suspension of calcium carbonate and sintered and unsintered beryllium and zirconyl silicates precipitated from water glass. X-Ray diffraction indicates that the calcium phosphate is principally calcium monohydrogen phosphate. Calcium phosphate was selected since it is a major constituent of the enamel of teeth. Both beryllium and zirconium in solution are strongly attracted to fluoride ions,[3] hence their silicates might adsorb fluoride. The silicates were chosen because of their insolubility and since glass, a silicate, is a fluoride adsorber. The zirconium and beryllium silicates were sintered with glass in an effort to modify their surfaces and their fluoride adsorbing ability. Preliminary studies (see Table I) showed that only the unsintered zirconium silicate completely removed the fluoride from a 10 p.p.m. fluoride solution passed through it.

Apparatus and Procedure.—The apparatus consisted of chromatographic tubes packed with the material under investigation with glass–Teflon needle valves (Emil Greiner Co., N. Y. C.) attached to the top of the tubes and connected by rubber tubing to Marriotte bottles which contained the solutions to be passed through the columns. The needle valves were connected at the top of the tubes to lessen the chance of their becoming clogged. The most convenient tube was a 400 × 20 mm. one piece unit fitted with a coarse fritted disc. The glass–Teflon needle valve was the most controllable of the valves tried at the 0.3 ml./min. rate of flow used.

The chromatographic tubes were packed as follows. One gram of diatomaceous earth was made into a slurry which was poured into the bottom of the tube to protect the fritted disc from the active materials; then another slurry containing about two grams of the active material mixed with about two grams of diatomaceous earth was poured into the tube and followed by a third slurry of 2 g. of diatomaceous earth to protect the active layer when solutions above the packing material were changed. After this pad had formed, the excess water above which contained the fine slow settling particles was poured off, and the column was refilled with water and washed for about 5 hours at 1.5 ml./min. Then the water flow was stopped, the water poured off and 10 p.p.m. of fluoride solution added to the column and allowed to flow at about 0.3 ml./min. Next, in the case of the zirconium silicate columns, the fluoride solution was poured off and 0.1 *N* sodium carbonate passed through the column at about 0.4 ml./min. Sodium carbonate was used for removal of fluoride since sodium hydroxide appeared to react with the zirconium silicate and the fritted disc. A basic solution was used since it is known to attack silicates.

In the case of zirconium silicate, two general procedures for running the columns were employed. In one about 100 ml. of solution containing 10 p.p.m. of fluoride was passed through the column and collected as a single sample; then about 150 ml. of 0.1 *N* sodium carbonate was passed through, collected in two fractions and the fluoride concentrations in these fractions determined. This procedure yielded the more quantitative recovery of fluoride but no information about the total adsorptive ability of the material. In the second procedure about five 100-ml. fractions of effluent from the 10 p.p.m. of fluoride were collected, and then from two to six fractions of about 1000 ml. each were collected. Determinations of fluoride in these fractions were performed while the columns were running to determine the time when the column packing material would not adsorb more fluoride. Actually, for the total volume of fluoride solution run

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[1] J. F. Volker, H. C. Hodge, H. J. Wilson and S. N. Voorhis, *J. Biol. Chem.*, **134**, 534 (1940).

[2] R. C. Specht, *Anal. Chem.*, **28**, 1015 (1956).

[3] F. Feigl, "Specific, Selective and Sensitive Reactions," Academic Press, New York, N. Y., 1949.

TABLE I

CHARACTERISTICS OF MATERIALS INVESTIGATED IN INITIAL SURVEY

Nature of reacting material	Substances used in production of reacting material	Amt. in column, g.	Ml. of 10 p.p.m. F- affluent	μg. F- taken up	Ml. of 1 *N* Na_2CO_3 affluent	μg. F- released	Fraction recovered
Calcium phosphate	$Ca(OH)_2 + H_3PO_4$	..	60	00	..	...	..
$CaHPO_4$	$CaCO_3 + H_3PO_4$	5	150	890	..	...	..
Beryllium silicate (sintered with soft glass)	$Be(NO_3)_2$ + water glass + soft glass tubing	1	90	00	..	...	..
Zirconium silicate (sintered with soft glass)	$ZrOCl_2$ + water glass + soft glass tubing	1	75	130	..	...	..
		2	90	00	..	...	..
Beryllium silicate	$Be(NO_3)_2$ + water glass	2	90	500	..	...	..
Zirconium silicate	$ZrOCl_2$ + water glass	2	90	900	..	...	..
		12.6	8000	35000	1320	35000	1.00
		12.6	8000	34000	1650	40000	1.18
Zirconium silicate	$ZrOCl_2$ + water glass (new from above)	6	1280	4200	175	4200[a]	1.00[a]
		6	980	4500	185	4700[a]	1.04[a]
		6	870	3500	160	1200	0.29
		6	890	3400	160	1500	.44
		6	1400	5300	135	2700	.51
		6	940	4600	135	2400	.52
		6	960	5500	105	2900	.53
		6	940	6400	175	4600	.72
			Three months time lapse				
		6	900	00	..	...	..
		6	900	100	..	...	..
		6	970	00	32[b]	00	0.00
		6	960	00	22[b]	00	.00
Zirconium silicate	$ZrOCl_2$ + water glass (new from above)	6	970	1100	36[b]	400	.36
		6	910	760	41[b]	400	.53

[a] Data questionable. [b] Recycled.

through these columns, this point did not usually occur; the fluoride concentration in the effluent would approach asymtotically, but not equal, the concentration in the solution flowing into the column. About 250 ml. of 0.1 *N* sodium carbonate solution was passed through these columns and collected in five 50-ml. fractions. The highest fluoride concentration ever reached in these fractions was 150 p.p.m.; this high value usually occurred in the second fraction.

Fluoride Determination.—The analytical method for fluoride used for this study was a colorimetric method developed by Megregian[4] using the zirconium–eriochrome cyanine R lake. A Beckman Model DU spectrophotometer was used. Previous studies had shown that this method is rapid, accurate and less subject to interferences than other colorimetric methods. The A.O.A.C. standard fluoride method using alizarin sulfonate and thorium[5] was very time consuming and, when the fluoride distillation step was omitted, subject to excessive interference. As used the method had a range of 0.01 to 1.40 p.p.m. of fluoride with a standard deviation of about 0.05 p.p.m. This meant that all fluoride fractions were diluted tenfold with water to put them within the range of the method. The dilution for the sodium carbonate samples was determined by a rough preliminary determination in the case of each sample.

Experimental Results

Table I summarizes the initial survey of materials. Micrograms of fluoride adsorbed was the change in fluoride concentration after passage through a column multiplied by the volume of effluent. Fluoride released is the fluoride concentration in the sodium carbonate effluent multiplied by the volume of effluent. Fraction of fluoride recovered is the ratio of these two quantities. Unsintered zirconium silicate was the only material capable of adsorbing completely the fluoride from a 10 p.p.m. solution. Additional work showed that this quality of the zirconium silicate was maintained only as long as there was an excess of zirconyl chloride to water glass in the precipitation of the material, *i.e.*, more than one gram of zirconyl chloride octahydrate per ml. of water glass. Additional work with beryllium silicate and calcium phosphate might show that changes in the ratios of amounts of precipitating substances would produce more fluoride adsorbant forms.

Table II summarizes the fluoride adsorption and recovery of two batches of the best grade of zirconium silicate produced. In the case of those columns in which a large volume of fluoride was passed through after the effluent fluoride concentration was close in value to the affluent fluoride concentration the standard deviation of the fluoride determination method becomes significant and accounts for part of the large deviations in the values of fluoride adsorbed. These deviations also take into account the maximum and minimum values of fluoride adsorbed in each of the sets of four columns whose average performances are given in the table. There was an indication on the basis of four columns that passing 100 ml. of 0.1 *N* HAc through the column before passing fluoride through would tend to stabilize recovery of fluoride at much closer to 100% than was the case with most columns. Similar pretreatment with 0.1 *N* sodium carbonate made fluoride recovery zero and reduced fluoride adsorption by half.

Zirconium Silicate Preparation.—The best grade zirconium silicate was produced by slowly adding with stirring 100 g. of C.P. zirconyl chloride octahydrate dissolved in 100 ml. of water to a near boiling solution of 100 ml. of water glass added to 200 ml. of water. The solution and the white precipitate which formed instantly were allowed to stand together for 24 hours to increase the yield and, some batches indicated, the fluoride adsorbancy), then filtered, washed and dried at 110–120°. After drying the precipitate was light yellow at the surface and white underneath. Yield was 86 grams. Density when ground to a fine powder was 0.81 g./cc.

Determination of zirconium in this product by the method outlined in Kolthoff and Sandell[6] for silicate rocks gave 25 and 16% for the zirconium silicate used in the initial survey and listed in Table I. Analysis of the water glass (purchased from a local drug store) showed that 100 ml. contained

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(4) S. Megregian, *Anal. Chem.*, **26**, 1161 (1954).

(5) Assoc. Offic. Agr. Chemists, "Official Methods of Analysis," 1955.

(6) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," revised ed., The Macmillan Co., New York, N. Y., 1943.

TABLE II

CHARACTERISTICS OF THE BEST GRADE ZIRCONIUM SILICATE

Each entry is an average of four columns run as a group. Zirconium silicate used came from two batches labeled A and B in this table.

Material no.	Ml. of 10 p.p.m. F-affluent	μg. of F- adsorbed	μg. of F- released	Fraction of F-recovered
Procedure: 100 ml. of 10 p.p.m. fluoride was passed through each column followed by about 150 ml. of 0.1 N Na_2CO_3.				
A	100	880 ± 300	650 ± 200	0.8 ± 0.3
A	100	860 ± 200	740 ± 200	0.8 ± .3
A	100	950 ± 250	970 ± 200	1.0 ± .3
A	100	820 ± 200	700 ± 200	0.8 ± .3
A	100	980 ± 300	680 ± 300	0.7 ± .3
B	100	1000 ± 250	940 ± 200	1.0 ± .3
Procedure: 10 p.p.m. of fluoride was passed through each column for some time after the column had stopped completely adsorbing the fluoride from the solution.				
A	3100	6500 ± 3000	6000 ± 3000	0.9 ± 0.5
A	3100	4000 ± 2000	6000 ± 1000	1.5 ± .5
A	3000	4800 ± 2500	2600 ± 1000	0.5 ± .5
B	6600	9800 ± 3500	14000 ± 2000	1.4 ± .5
B	5000	7600 ± 3500	7200 ± 2000	1.0 ± .5

51.4 g. of $Na_2O \cdot 3.35SiO_2$. Determination of silica was by the method in Kolthoff and Sandell.[6] Sodium oxide was determined by titrating a sample of the water glass against a standard HCl solution with modified methyl red as the indicator.

Fluoride Recovery.—The amount of fluoride recovered from zirconium silicate was in general not quantitative. Attempts to correlate the variation in the value for fraction of fluoride recovered with time lapse between adsorption and recovery or total running time of the column were unsuccessful. A possibly significant relationship appeared to exist between the age of the prepared material and the fraction of fluoride recovered.

No thorough study of the possibility of further increasing fluoride concentration in the sodium carbonate effluent by recycling was made. However, since the *p*H of the first one or two hundred ml. of sodium carbonate passed through a gram of zirconium silicate is reduced from 11 to about 8, it would be necessary to restore the original *p*H by the addition of more sodium carbonate. The reason for this loss of alkalinity is unknown; however, sodium carbonate effluents usually effervesced a little on shaking. Wash water showed no change in *p*H on passage through zirconium silicate, nor did 10 p.p.m. of fluoride solution.

Discussion

In no case was so much fluoride solution passed through a column that there was a certainty that the column could not adsorb more fluoride, so total adsorptive ability of the zirconium silicate used is unknown. A rough calculation indicated that, if simple surface adsorption were hypothesized as the mechanism of fluoride adsorption of the zirconium silicate, it would have a layer of fluoride ions 100 atoms deep on its surface at the point at which it stopped completely adsorbing fluoride. This calculation did not assume the presence of any other materials mixed with this layer of fluoride ions. The radius of the fluoride ion was taken to be 1.36 Å.[2] Density of the zirconium silicate as measured by weighing powder packed in a graduated cylinder was 0.81 g./cc. The surface areas of the zirconium silicate particles and their volumes were calculated from measurements taken with a micrometer microscope of a sample containing over 100 particles. The particles were roughly parallelepipeds; the average size was about 50 × 50 × 10 μ. The deviation in size was about fivefold on each side of this value. R. C. Specht performed a similar calculation based on his measurements of the total adsorbancy of glass and obtained values which indicated that a layer of fluoride ions 1.6 atoms deep on borosilicate glass and five layers deep on soft glass would be present if simple surface adsorption were assumed. As he points out, the negative charge on the fluoride ion would prohibit such layers from forming. This could be explained by assuming the particles had large internal surfaces, or that some kind of chemical reaction occurred. Since the material which adsorbed fluoride best was precipitated in an excess of zirconyl chloride, it is probable that the bond is with zirconium. As the fluoride solutions were made from sodium fluoride, measurement of the sodium ion concentration in the fluoride effluent might provide information about the bond. With a very few columns there was evidence that the fluoride adsorbancy of a column which was quite saturated with fluoride would be rejuvenated somewhat by time.

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