Dietary intake of fluoride ashed (total fluoride) *v*. unashed (inorganic fluoride) analysis of individual foods

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1. Fluoride content in ninety-three individual food items from a hospital in a fluoridated area was determined by ashing (total fluoride) *v*. unashing (inorganic fluoride) analysis.

2. No discrepancy between the two methods was found by food group but two dry cereals and black pepper did show significantly more fluoride after ashing. The reason for the unavailability before ashing was not determined.

3. Daily fluoride intake was estimated at 1·783 mg which is midway between the 1·211 and 2·201 mg reported from studies in which composite diets were analysed.

4. Daily intake from food at 0·4 mg was one-quarter of the daily total intake of 1·8 mg; a ratio consistent with those previously reported in serum, urine and bone between residents from a non-fluoridated *v*. fluoridated community.

In spite of a controversy about the intake of fluoride (Kintner, 1971; Taves, 1979), there is no reliable information on the fluoride content of individual foods. Singer *et al.* (1980) and SanFilippo & Battistone (1971) have reported values for the fluoride content of composite diets rather than individual foods and while their values are more reasonable than those published by Spencer's group (Kramer *et al.* 1974), there are some discrepancies which need explanation. First, Singer *et al.* (1980) give no explanation for a daily intake which is only 55% of that reported by SanFilippo & Battistone (1971). Second, the agreement that Singer *et al.* (1980) claim between ashed and unashed food analyses includes marked differences in two out of twelve food groups. In the case of green leafy vegetables, the value they report after ashing is 180% of the unashed value while in root vegetables the ashed value is 33% of the unashed value. It would be of interest to know if these discrepancies represent analytical difficulties that are inherent to the food type. A higher value with destructive analysis might reflect the presence of an organic form of fluoride which is liberated on ashing. Foods showing more fluoride on ashing would be of interest as possible sources of organic fluoride in human serum (Guy *et al.* 1976). The lower value on ashing might represent the loss of a volatile complex of fluoride. Information on the fluoride content of individual foods is of interest for three reasons. First, Singer *et al.* (1980) reported on composite food groups so the discrepancy might be considerably greater in some individual foods in a group. Second, both Singer *et al.* (1980) and SanFilippo & Battistone (1971) list meat as the food group with the second highest fluoride content with values ranging from 0·22 to 1·04 μg/g (11–55 nmol/g), levels considerably higher than would be expected from indirect evidence. Serum fluoride concentration in the animal is generally less than 4 μM (0·04 μg/g) (Taves, 1971) and, according to ^{18}F distribution studies, fluoride concentrations in muscle would be expected to be lower than in blood (Wallace-Durbin, 1954; Hein *et al.* 1956; Carlson *et al.* 1960). Third, some fluoride balance studies in patients require the ability to prescribe a low-fluoride diet.

METHODS

The individual foods and beverages analysed were regular hospital diets served for 6 d in 1977. Three food items were bought from a grocery store in 1982 for repeat analysis. The hospital is in a fluoridated area; consequently, any foods prepared with water reflect this factor. For analytical purposes, solid foods were homogenized with double-distilled and deionized water. Analysis for inorganic fluoride (unashed) was by 1 d diffusion at 25° with hexamethyldisiloxane (HMDS) into 0·1 ml 1·65 M-sodium hydroxide which was dried down and added to 0·5 ml 0·66 M-acetic acid before measurement with the fluoride electrode (Waterhouse *et al.* 1980). Analysis for total fluoride (inorganic plus organic) was done on the same food homogenate. A 1–3 g portion was 'fixed' with 2·5 ml 2 M-magnesium chloride in a 20 ml platinum crucible, covered and dried overnight in a 105° oven, transferred to a muffle furnace and ashed at 300° for 3 h and at 600° for a further 3 h. Special precaution was taken to avoid contamination with trace amounts of freon which is frequently present in laboratory areas. A stream of fresh air was supplied continuously to the chamber of the muffle furnace and the door was not opened after starting the furnace until the temperature was below 200°. After ashing, the sample was prepared for acid-labile diffusion in the same crucible by first adding 6 ml double-distilled and deionized water, rinsing material from the lid and side walls with 2 ml 6 M-fluoride-free hydrochloric acid, depositing a Parafilm-wrapped steel ball (10 mm diameter) on top of the ash, floating an inverted 12 × 75 mm Falcon tube cap (Falcon, California) containing 0·1 ml 1·65 M-NaOH in the centre well and covering with a 35 × 10 mm Falcon tissue-culture dish bottom. The inner rim of this 'cover' had been lined with petroleum jelly and a hole had been made in the cover's surface with a soldering iron. At this point, the crucible was suspended in a cool water bath shaker, 2 ml 6 M-HCl (HMDS-saturated) was added quickly through the hole in the cover, and this was immediately sealed with petroleum jelly and a Parafilm square. The shaker action causes the Parafilm ball to roll, thereby expediting the ash-dissolving process. After 1 d diffusion, the NaOH trapping-solution was treated in the identical manner to that described for the inorganic fluoride method.

Percentage recovery was determined for total fluoride with each run by ashing standards (see Table 1). No correction for incomplete recovery was applied to the sample values, i.e. the standard curve was made from standards which were neither ashed nor diffused. Analysis on the food was duplicated in alternate runs. Initially, duplication within 10% was attempted but it became apparent that homogeneity of the homogenate often was not adequate to make this requirement practical. Consequently, values for both methods reflect duplicate analysis regardless of deviation, except for the few initial samples. Condiments were from small packets, therefore duplication was by packet rather than portion.

Table 1. *Percentage recovery for ashing analysis determined by adding known amounts of fluoride*

Number of samples	Amount of fluoride added (nmol)	Recovery (%) Mean	Recovery (%) SD
2*	2·5	71·5	13·44
14	5	85·3	13·19
13	10	93·0	6·23
8	25	97·0	3·33
3	50–100	97·0	3·33

* This food item was on the 2-days' menus (see p. 300).

RESULTS

Table 2 lists ninety-three separate food items by commodity food group as described by SanFilippo & Battistone (1971). The inorganic (unashed) or total (ashed) fluoride value for each food includes the number of analyses, mean values and standard deviations. Comparability between unashed and ashed values is given in percentage agreement calculated with 'unrounded' numbers rather than the rounded numbers given in Table 2. No systematic errors were noted by food group. In general, close agreement was found between unashed and ashed values. Of the ninety-three comparisons in Table 2, seven show a discrepancy greater than 25% between the mean values of the 'unrounded' numbers. In two cases, the amount of fluoride involved was less than the mean (±SD) ashing 'blank' of 2·6 nmol ± 0·74, so these two discrepancies are not reliable. The difference in three comparisons (Rice Krispies®, Shredded Wheat Miniatures® and ground black pepper) was more than 3 nmol/g and was statistically significant, with each showing a higher fluoride level after ashing.

Follow-up analyses were done on the three items. As the hospital food was packaged in individual serving boxes, larger boxes of each item were purchased at a store. The same pattern emerged with 552 and 827% more fluoride in Rice Krispies and 205% more in Shredded Wheat Miniatures after ashing. A regular-sized shredded wheat of another brand showed a comparability agreement of 110%. Eight brands of black pepper, ranging from regular grind to whole peppercorns, were analysed and showed from 111 to 291% more fluoride after ashing with a mean (±SD) of 210 ± 57·5.

Table 3 shows that the average total intake of 1·78 mg fluoride per day falls between Singer *et al.*'s (1980) value of 1·21 mg and SanFilippo & Battistone's (1971) value of 2·20 mg. In comparison with Singer *et al.* (1980), the difference is due to the intake estimated for beverages (1·38 *v.* 0·79) but in comparison with SanFilippo & Battistone (1971), the major difference reflects disagreement between the values for dairy and meat products.

DISCUSSION

This study shows only three clear discrepancies in fluoride content of individual foods before and after ashing and these are not in the food groups with discrepancies in Singer *et al.*'s (1980) values. Their food group discrepancies were two to three times the 25% agreement criteria for the individual food analysis in the present study, so they were not likely to have been missed in the present study had they been real. This finding suggests that the cause of the food group discrepancy was analytical in origin and not specific to food type. However, it is clearly shown that destructive analysis liberated additional fluoride in two types of cereal and in black pepper because of the magnitude and repeatability of the difference in several samples over a 4-year period. The non-availability of the fluoride is due either to physical sequestration or organic bonding. Personal communication with the manufacturer has not disclosed a source of organic fluoride in the cereal but the most likely organic fluoride contaminant is a perfluorinated long-chain carbon compound which is not very toxic (Guy *et al.* 1976). Therefore, in neither case is there reason to think it is hazardous.

The fluoride values and standard deviations for meat and dairy products were considerably less than those reported by previous investigators. One explanation for the extent of variability with meat may be contamination with bone dust in the butchering process. An alternative explanation for the high values of SanFilippo & Battistone (1971) is the possibility that their colorimetric method gave a false positive value even though the food was dried before diffusion. A direct comparison of fluoride concentration between the colorimetric and fluoride electrode methods would be needed to settle this point.

The major source of fluoride found in the present study was the grain and cereal group

Table 2. *A list by food group of inorganic and total fluoride contents of individual foods as determined by unashed v. ashed analysis respectively of all items forming the 6-d diets from a hospital in a fluoridated area*

Commodity group	Inorganic F (nm/g)			Total F (nm/g)			Comparability (%) ashed:unashed
	n	Mean	SD	n	Mean	SD	
1. Dairy products							
Butter	8	2	< 1	7	2	< 1	119
Cottage cheese	2	43	1	2	50	2	115
Ice cream, vanilla	2	7	< 1	2	7	2	97
Milk	10	1	< 1	10	1	< 1	108
2. Meat, fish, poultry							
Bacon	2	8	1	2	9	3	112
Beef, ground	4	8	1	4	7	1	81
Beef, roast	2	2	< 1	2	1	1	58
Beef, steak	2	2	< 1	2	2	< 1	91
Eggs, scrambled	6	3	1	6	4	1	113
Fish, broiled	2	8	< 1	2	6	1	73
Fish, fried	2	11	1	2	10	< 1	88
Ham, baked	2	16	2	2	17	1	102
Pork, roast	2	22	1	2	21	< 1	93
Sausage	2	27	1	2	25	6	93
Turkey, roast	2	11	1	2	10	< 1	95
Veal cutlet	2	19	< 1	2	23	4	117
3. Grain and cereal products							
Bread, whole wheat	2	15	6	2	17	3	111
Bun, hard	2	21	1	2	23	1	106
Cake, chocolate	2	10	< 1	2	13	< 1	128
*Cheerios®	2	39	< 1	2	33	3	85
Cookie, lemon	2	14	< 1	2	12	2	87
Cookie, oatmeal	2	15	1	2	17	2	109
Cookie, sugar	2	11	< 1	2	9	< 1	86
*Corn Flakes	2	4	< 1	2	4	< 1	108
*Corn Pops®	2	24	2	2	24	2	98
Crackers, Ritz®	6	14	3	6	14	2	99
Eclair, chocolate	2	7	1	2	8	1	108
*Frosted Flakes	2	4	< 1	2	5	< 1	115
Hominy grits, cooked	2	46	< 1	2	47	1	103
Noodles	3	44	3	2	46	< 1	105
Oatmeal, cooked	2	106	4	2	106	2	100
*Puffed Rice®	2	9	< 3	2	8	3	98
*Puffed Wheat®	2	8	< 1	2	10	1	122
*Raisin Bran®	2	18	< 1	2	18	3	97
Rice, cooked	2	33	4	2	35	4	103
Rice Krispies®	2	9	< 1	2	59	6	633
Roll, dinner	10	19	2	9	19	1	103
Shredded Wheat Miniatures®	2	4	< 1	2	8	< 1	184
Spaghetti and sauce	2	31	< 1	2	33	5	107
Special K®	2	19	2	2	21	1	112
Toast	10	25	5	10	27	6	108
*Wheaties®	2	19	< 1	2	20	< 1	105
4. Potatoes							
Boiled	2	26	2	2	25	1	96
Hashed brown	2	23	3	2	23	4	102
Mashed	4	44	4	4	43	5	100
Sweet	2	11	< 1	2	11	2	99
5. Leafy vegetables							
Broccoli, cooked	2	4	< 1	2	6	< 1	125
Cabbage, raw	2	8	< 1	2	7	< 1	91
Greens, raw	6	14	3	6	15	5	109

Table 2. (*cont.*)

Commodity group	Inorganic F (nm/g)			Total F (nm/g)			Comparability (%) ashed:unashed
	n	Mean	SD	*n*	Mean	SD	
Lettuce, raw	3	7	1	3	6	1	82
Spinach, cooked	2	37	1	2	37	1	99
6. Legume vegetables							
Green beans, cooked	2	26	< 1	2	27	< 1	103
Peas, cooked	2	30	4	2	30	5	101
7. Root vegetables							
Asparagus, cooked	4	21	3	4	21	4	100
Beets, pickled	2	14	< 1	2	14	< 1	105
Carrots, cooked	2	25	2	2	24	1	96
8. Garden fruits							
Squash, cooked	2	1	< 1	1	2		
9. Fruits							
Apple sauce	4	3	1	4	3	2	100
Cranberry sauce	2	1	< 1	2	1	< 1	100
Fruit cup, canned	2	4	< 1	2	1	< 1	95
Peach, canned	2	4	< 1	2	4	1	95
10. Oils and fats							
Dressing, French	2	23	1	2	21	2	92
Dressing, Lo-cal	2	13	< 1	1	16	5	119
Dressing, oil and vinegar	2	12	1	2	15	5	121
Margarine	2	1	0	2	1	< 1	108
Tartare sauce	2	16	1	2	15	3	96
11. Sugar and adjunct							
Ketchup	2	6	< 1	2	7	< 1	116
Jam, strawberry	2	10	1	2	8	1	80
Mustard	2	41	1	2	49	4	119
Pepper	8	18	5	8	28	5	158
Salt	8	13	1	8	13	2	105
Sugar	6	1	< 1	6	1	< 1	80
12. Beverages							
Apple juice	2	5	< 1	2	14	< 1	91
Coffee	12	51	8	12	50	7	98
Cranberry juice	4	49	4	4	45	8	91
Grapefruit juice	2	1	< 1	2	< 1	< 1	44
Grape juice	4	35	3	4	37	2	104
Ginger ale	2	40	2	2	38	2	95
Orange juice	4	33	2	4	36	3	109
Tea	6	144	28	6	141	28	98
Tomato juice	2	2	< 1	2	2	< 1	113
Non-classifiable							
Beef, tomato, pasta casserole	2	35	1	2	38	11	88
Clam chowder	2	19	< 1	2	20	1	105
Jellied strawberry mould	2	26	1	2	32	< 1	120
Jello®, strawberry	2	46	2	2	45	13	98
Macaroni and cheese	4	22	14	4	23	4	105
Minestone soup	2	45	< 1	2	41	1	91
Pea soup	4	40	4	4	37	5	92
Pudding, bread	2	39	1	2	37	1	94
Pudding, lemon	2	34	3	2	32	1	92
Pudding, vanilla	2	25	< 1	2	27	3	109
Turkey, broccoli, cheese bake	2	15	1	2	15	< 1	104
Turkey dressing bake	2	27	6	2	34	2	124

* Additional cereals selected for analysis because of large discrepancy between inorganic and total fluoride contents found in two cereals.

Table 3. *A comparison of daily fluoride intake (mg) as determined by individual food* v. *composite diet analyses*

(Mean values and standard deviations for 6-d diets from a hospital in a fluoridated area (SD given only for food group included in all 6 d; present study) and for 2-week composite diets from four US regions from values of Singer *et al.* (1980) and SanFilippo & Battistone (1971))

			Composite diet			
	Individual foods (present study)		Singer *et al.* (1980)		SanFilippo & Battistone (1971)	
Commodity group	Mean	SD	Mean	SD	Mean	SD
1. Dairy products	0·013	0·000	0·042	0·007	0·150	0·042
2. Meat, fish, poultry	0·044	0·035	0·110	0·087	0·218	0·102
3. Grain and cereal products	0·241	0·153	0·150	0·021	0·208	0·070
4. Potatoes	0·018	—	0·020	0·004	0·048	0·030
5. Leafy vegetables	0·027	0·019	0·007	0·002	0·040	0·022
6. Legume vegetables	0·037	—	0·021	0·009	0·015	0·006
7. Root vegetables	0·010	—	0·003	0·001	0·013	0·005
8. Garden fruits	0·000	—	0·012	0·001	0·033	0·033
9. Fruits	0·006	—	0·018	0·009	0·040	0·005
10. Oils and fats	0·003	0·001	0·013	0·003	0·038	0·036
11. Sugar and adjunct	0·001	0·000	0·023	0·005	0·055	0·013
12. Beverages	1·383	0·041	0·792	0·270	1·343	0·080
Total intake	1·783		1·211		2·201	
Total intake (minus beverages)	0·400		0·419		0·858	

which contributed 0·24 mg/d. At least two baked goods were included in each day's diet and, as these were made locally with fluoridated water, this finding is not surprising. The large standard deviation stems from the contributions from oatmeal and pasta, both high-fluoride foods and both present in the 2-days' diets. The daily intake of fluoride estimated by SanFilippo & Battistone (1971), Singer *et al.* (1980) and in the present study makes much better biological sense than that published by Spencer's group (Kramer *et al.* 1974). The fluoride intake from food is approximately one-quarter the total intake, a value which is close to the ratio found in bone (Zipkin *et al.* 1958), urine (McClure & Kinser, 1944) and serum (Taves & Guy, 1979) fluoride concentrations between non-fluoridated community residents and those in a fluoridated community.

The fluoride contribution of 1·38 mg/d from beverages is relatively high in the present study because orange juice, coffee and two teas were included routinely in each day's diet. Drinking water was not taken into account, however, so the excellent agreement with SanFilippo & Battistone's (1971) value may be fortuitous. While there appear to be a few foods which might contain organic fluoride, these are not staple foods which could provide an adequate explanation for the organic fluoride found in human serum after ashing.

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