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STRONTIUM, BARIUM AND CALCIUM

IN SOME COMPONENTS OF HUMAN DIET

by

W. E. Grummitt and G. Lahaie

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This report outlines procedures for the estima-
tion of natural calcium, strontium and barium and presents
results of the determination of these elements in the
more important components of the Canadian diet. Calcium
was measured gravimetrically, strontium and barium were
determined by neutron activation analysis.

Chalk River, Ontario

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INTRODUCTION

Natural strontium and barium are invariably present in plant and animal tissue and in surface waters, but the concentrations of these elements are several orders of magnitude lower than those of calcium and magnesium. Nevertheless, the amounts are sufficiently high to affect the chemical yield in the estimation of strontium-90 by carrier methods. This error can be minimized by increasing the weight of carrier substantially, by using strontium-85 for the estimation of yield, or by determining the natural strontium present in the sample and correcting the carrier weight accordingly. Frequently, it is sufficient to establish that the natural strontium/calcium ratio in a particular type of material is relatively low and hence introduces, at most, a small error.

In addition to the requirement for analytical purposes, the results can be used in an alternate manner. They allow the estimation of 'discrimination factors' for strontium in the food chain, or alternatively, if radiochemical data are available, the specific activity of strontium (strontium-90/natural strontium) may be calculated for particular food chains. This may sometimes be preferable as it avoids the concept of 'discrimination factor' or 'observed ratio'.

This report outlines procedures for the estimation of natural strontium, barium and calcium and presents results of the determination of these elements in the above mentioned materials.

Strontium and barium were determined by activation analysis. Both elements form short-lived radioactive isotopes,

strontium-87 (390 keV, $t_{\frac{1}{2}}$ = 2.8 h) and barium-139 (165 keV,

$t_{\frac{1}{2}}$ = 1.4 h) when irradiated in a flux of slow neutrons.

Following such an irradiation, and appropriate chemical purifica-

tion, the induced activity in each sample was compared with

standards on a γ scintillation spectrometer.

Calcium has been determined in order to establish

strontium-90/calcium ratios in components of the Canadian diet.

The method used was the classical oxalate precipitation (1) with

minor modifications.

SAMPLING PROCEDURES

Samples of flour, wheat and milk were available through

national networks originally proposed for the monitoring of

'fallout' in the Canadian diet. Other produce was sampled less

representatively through purchases from the retail market in

the major cities of Alberta, British Columbia, Manitoba, Ontario

and Quebec.

Wheat

Arrangements were made with the Grain Research Laboratory,

Winnipeg, to supply and composite samples of the 1959 and 1960

wheat crop from their 306 sampling districts. Nine composite

samples were prepared representing roughly similar geographical

areas within each of the three Prairie Provinces. A single

composite sample was made up for the years 1959 and 1960 by

combining aliquots from the three provinces in proportion to their

annual production.

Flour and bran samples were obtained by milling a portion of the wheat exported during the first quarter of 1959.

Skim Milk and Buttermilk Powder

The Canadian "Fallout" Monitoring Network has been described previously (2). Composite samples from each of the 17 stations were prepared by combining equal aliquots of 12 consecutive monthly collections, in order to minimize seasonal variations and allow geographical differences to be estimated.

Other Food Products

Purchases were generally obained in the larger population centres throughout the country, usually from "Chain" stores which retail over a province-wide area. Eight to ten separate purchases of a particular item were made at various times throughout the year. These were combined to provide a single composite sample for analysis. As the items comprising the composite sample were from various sections of the country, the produce is representative of the country as a whole, rather than a particular area.

EXPERIMENTAL

In most instances one-half to one kilogram of produce was ashed for the determination of natural strontium, barium and calcium. Water samples were evaporated to dryness and the residue was ashed at 600° C for 24 hours prior to analysis.

For activation analysis, samples of ash were irradiated in a flux of 2×10^{12} neutrons/cm^2/sec together with a strontium and a barium standard. Following a one hour period of decay, strontium carrier was added to the sample and separated chemically from interfering substances.

It has been shown that barium precipitates quantitatively
with strontium from 72% nitric acid (3), though losses of barium
are greater than those of strontium in both a ferric hydroxide
scavenge and a carbonate precipitation (4). Barium losses were
therefore measured in a separate experiment designed to establish
a correction factor.

The combined weight of the natural strontium and barium
present in a sample never exceeded 0.4% of the weight of the
carrier. This introduced a negligible error in the strontium yield.

Strontium-87 (390 keV, $t_{\frac{1}{2}}$ = 2.8 h) and barium-139
(165 keV, $t_{\frac{1}{2}}$ = 1.4 h) were counted simultaneously on a Υ
scintillation spectrometer. After correcting for radiochemical
yield, counting losses, and background radiation, the strontium-87
activity in the sample was compared with that in the strontium
standard at a specific time. In a similar manner the barium-139
activity was determined after correcting for the superposition of
the barium-139 photopeak on the strontium-87 Compton recoil continuum.

The counting equipment consisted of a 3" x 3" sodium
iodide thallium-activated crystal in conjunction with a 100-channel
pulse height analyzer.

Calcium was determined gravimetrically by the precipita-
tion of calcium oxalate after the removal of silica (1). A
second oxalate precipitation was necessary because of the presence
of magnesium, which co-precipitated to some extent with the
calcium (5). The method was checked for losses and purity of the
calcium oxalate precipitate by adding calcium-47 to the sample
and measuring the specific activity of calcium after rigorous

Details of the procedures are given in the appendices.

EVALUATION OF THE PROCEDURES

1. Standardization of the Calcium Oxalate Method

Although consistent and reproducible results for calcium were obtained by the oxalate method, it was not certain that the absolute content of calcium was known with sufficient accuracy. Early attempts to verify the analyses by an independent method, such as flame photometry, were unsuccessful. It was decided, therefore, to check chemical yields and stoichiometry of the oxalate precipitate by means of a radiochemical technique, using 4.7 d calcium-47 (510, 810, 1300 keV γ) as a tracer. A known quantity of the tracer was added to a solution of the sample prior to the removal of silica, and following the separation procedure described in Appendix 3, the calcium oxalate precipitate was weighed and counted. Calcium-47 losses averaged less than 0.1%.

The oxalate was dissolved in dilute nitric acid and calcium was re-precipitated twice with 85% fuming nitric acid. The precipitate of calcium nitrate was then dried and extracted twice with 10 ml of a one to one ethanol-ether mixture. Calcium nitrate is readily soluble in this solvent but barium and strontium nitrates are not. Rare-earths and other elements were removed by scavenging with ferric hydroxide. The calcium was then re-precipitated as oxalate for weighing and counting.

Throughout the procedure, the calcium-47 activity per gram of oxalate, i.e. the specific activity, remained unchanged, showing that two precipitations were sufficient to obtain pure

Table II presents the results of a series of determinations of calcium in wheat, obtained by modifications of the classical oxalate procedure. High values were invariably obtained, even titrimetrically, if the oxalate was precipitated without prior removal of silica. Double precipitation (Table I and column 3, Table II) eliminated the occasional, erroneously high value which may have resulted from occlusion of magnesium oxalate in the first precipitate.

2. Determination of Barium Yields

A comparison of strontium and barium losses was made by adding strontium carrier and barium-139 tracer to four different samples and then carrying out the chemical separation as outlined in Appendix 1. The strontium yield was determined gravimetrically. The yield of barium-139 was determined by comparing the barium activity recovered in the final strontium carbonate precipitate with that added to the sample. The results appear in Table III.

The recovery of barium, measured with barium-139 tracer, was consistently lower than the gravimetric yield of strontium and averaged 94% of the strontium yield in the four samples studied. This factor has been used as a correction in the estimation of the barium content.

3. Accuracy of the Results

The strontium and barium analyses and a portion of the calcium analyses were done in duplicate in order to estimate

determinations. This was subsequently reduced to ± 3.1% by the

elimination of systematic errors in the method. Accuracy in

the determination of barium is dependent on relative concentra-

tions of the two elements as the results are obtained by

difference (i.e. total count - strontium = barium). In these

analyses the coefficient of variation amounted to ± 13% and

± 8% for milk and produce respectively.

The coefficient of variation of the calcium results

was ± 2.0%.

DISCUSSION OF RESULTS

Tables IV and V give the results of analyses for calcium,

strontium and barium in biological samples. The results are

expressed per kilogram of produce, per gram of ash and as ratios

of the elements, one to the other. In general, metabolic

processes in the animal discriminate against strontium and barium,

so that meat and milk contain much smaller concentrations of

these elements than cereals and vegetables. As a consequence,

strontium/calcium and barium/calcium ratios are also lower in

animals and animal produce.

Except in the case of cereals, the concentration of

barium is generally below that of strontium, the average value

for the ratio of barium/strontium being 0.36. It is noticeable

that the results for barium are also more variable than those for

strontium. Erratic behaviour of barium is not surprising inasmuch

as it is chemically dissimilar to calcium and will not be regulated

to the same extent by the mechanisms controlling calcium uptake.

The results in Table IV establish the strontium/calcium relationship in flesh, bone and milk from the cow. The differences observed are small, with no discrimination against strontium in going from tissue to bone and a relatively small factor in the process of lactation (average ~1.3). The determinations of strontium in flesh and bone are directly comparable as the same carcasses were used for both samples (Table IV). Milk samples were taken from the national network and so cannot be directly related to flesh and bone. However, natural strontium levels in milk (Table V) do not show much variation with locality, even though rather large variations exist in the content of soils and plants (4). Hence the meat/milk ratio would also be expected to be similarly independent of locale and the ratio should permit the calculation of strontium-90 in meat for dietary surveys.

In contrast to strontium, barium levels in flesh appear to be unrelated to those in bone and the fluctuations are considerably greater than expected in composite samples (Table IV).

The results for milled wheat products show a pattern similar to that observed by Lee (7), in his study of the uptake of strontium-90 by plants. The distrubition of all three alkaline earth elements is surprisingly similar, with the highest concentration in the bran and the lowest in the flour fraction. In addition, strontium/calcium, barium/calcium and barium/strontium ratios are highest in bran and lowest in flour. Apparently, factors which contribute to the concentration of calcium in the outer layers of the kernel also operate for strontium and barium.

Some results for water have been included but insufficient samples have been done to date to establish a pattern.

ACKNOWLEDGEMENTS

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APPENDIX 1

Determination of Total Strontium and Barium

1. Dry sample at 100°C, then ash at 600°C for 24 hours in a muffle furnace.

2. (a) Weigh 100-200 mg of ash into a polythene capsule.
    (b) Insert sealed silica tubes containing strontium and barium standards into the sample (preparation of standards described in Appendix 2).

3. Irradiate sample and standards for two hours in a slow neutron flux of about 2×10^{12} neutrons/cm^2/sec.

4. Dissolve the irradiated ash in a Pyrex beaker containing 30 mg strontium chloride, 10 ml of 7 M hydrochloric acid and one drop of nitric acid. Heat to boiling for ten minutes to promote exchange.

5. Pass solution through a Dowex-1 anion exchange column containing 2 ml of resin (as received). Wash with 5 ml of 7 M hydrochloric acid.

6. Evaporate column effluent to dryness.

7. Dissolve solids in 2 ml of water.

8. Add 8 ml of yellow fuming nitric acid, specific gravity 1.49 - 1.50.

9. Cool in cold water bath for three minutes. Strontium and barium nitrates precipitate.

10. Centrifuge and discard supernatant liquid containing calcium.

11. Repeat steps 7, 8, 9 and 10 twice.

12. Dissolve precipitate in 6 ml of water.

13. Add 4 drops of iron carrier solution (2 mg Fe^{3+}/ml).

14. Heat in boiling water bath, then precipitate ferric hydroxide by bubbling in ammonia gas. Centrifuge.

15. Add 2 more drops of iron carrier, and centrifuge precipitate on top of first.

16. Decant supernatant liquid into a clean centrifuge tube.

17. Heat in boiling water bath for five minutes. Add three
    drops of saturated sodium carbonate solution, and continue
    heating for five minutes. (Heating causes sufficient
    mixing to ensure complete precipitation).

18. Centrifuge and discard supernatant liquid.

19. Wash precipitate twice with 1 ml of water, and twice with
    1 ml of ethanol.

20. Suspend precipitate in three drops of ethanol and pipette
    onto a tared counting tray. Dry under infra-red lamp and
    weigh as strontium carbonate to determine chemical yield of
    strontium.

21. Count

APPENDIX 2

Preparation of Standards

1. Make up standard solutions by dissolving Specpure*
   strontium or barium carbonate in a solution containing a
   minimum quantity of nitric acid (1.011 gm strontium
   carbonate or 0.862 gm barium carbonate per 100 ml gives
   6 mg/ml of strontium or barium). Determine the specific
   gravity.

2. Using a micro-balance weigh 10 μl of standardized solution
   (60 μg of strontium or barium) into a tared three mm I.D.
   thin-walled silica tube. Ref (6). Introduce the solution
   into the capillary in the following manner. Heat the
   capillary slightly to expel part of the air and place the
   tip in the liquid. On cooling, the liquid draws partially
   into the tube. Transfer the liquid to the closed end of
   the tube by centrifuging and flame-seal the open end.

3. Place in oven at 110°C for one hour. Discard if the solution
   has evaporated.

4. Irradiate as outlined in Annex 1, section 2(b) and 3.
   Allow a one hour period of decay after removal from the
   reactor.

5. Immerse the silica tube in boiling aqua regia for one to
   two minutes to remove contamination from the outside. Wash
   with water.

6. Crush the tube in a 10 ml Erlenmeyer flask containing 2 ml
   of carrier solution (20 mg strontium per ml). Mix and
   transfer the solution to a 5 ml volumetric flask.

7. Wash the Erlenmeyer flask three times with 0.5 ml of water,
   transferring the washings to the volumetric flask. Make
   up to volume.

8. Transfer 500 μl of the solution (6 μg of activated strontium
   or barium) to a counting tray.

9. Dry under infra-red lamp.

10. Count.

* Trademark of Johnson Matthey & Company

APPENDIX 3

Determination of Calcium (1)

1. Weigh about 1 g of the ash accurately into a 100 ml platinum dish and ignite in a furnace for one hour at 800°C.

2. Allow to cool and add 20 ml of distilled water. Cautiously add 20 ml of 60% perchloric acid and 20 ml of 40% hydrofluoric acid. Heat on a hot plate inside a fumehood and continue evaporation until dense white fumes of perchloric acid are evolved.

3. Allow to cool and add 10 ml of water and 20 ml of 40% hydrofluoric acid. Repeat the fuming, evaporating almost to dryness. Allow to cool and dissolve the residue in 20 ml of 1 M hydrochloric acid, with slight warming to facilitate solution.

4. Transfer the solution to a 250 ml beaker; wash the dish with a little water, adding the washings to the beaker. Heat to boiling on a hot plate to complete solution of difficulty soluble material.

5. Allow to cool and filter through a Whatman No. 41 paper into a 400 ml beaker. Wash the precipitate and paper with several portions of water, collecting the washings with the filtrate. Discard the precipitate and dilute the filtrate to about 60 ml with water.

6. Add 40 ml of 8% oxalic acid and 10 ml of 50% ammonium acetate solution. Heat to about 80°C and neutralize with 4 M ammonium hydroxide to pH 4.0, using bromocresol green indicator (colour change of green to blue). Stand the beaker in a warm place for three to four hours.

7. Remove the supernatant liquid through a medium porosity filter stick.

8. Dissolve the precipitate in 20 ml of 1 N hydrochloric acid, dilute to 60 ml with water and repeat step No. 6.

9. Filter the solution through a tared, medium porosity, sintered glass filter. Wash the precipitate three times with water and twice with methanol. Dry the filter in an oven at 110°C - 115°C to constant weight.

10. Weigh as $CaC_2O_4.H_2O$

$$g \; Ca/g \; ash = \frac{0.274 \times weight \; of \; CaC_2O_4.H_2O}{weight \; of \; ash}$$

Table I

Calcium Analyses of Wheat by Tracer Technique

Product	mg Ca/kg Product Second Precipitation	% recovery of Calcium-47	mg Ca/kg Product after Purification (corrected for losses)
Bran	690	99.6	700
Flour	164	99.6	174
Wheat	277	100.7	277
Wheat	246	99.9	241

Table II

Calcium Analyses of Wheat by Different Methods

Without Removal of Silica	With Removal of Silica	
	First Precipitation	Second Precipitation
350 mg/kg	339 mg/kg	321 mg/kg
650	611	556
470	496	448
490	517	490
410*	402	400
350*	309	312
380*	258	-

* Permanganate titration of oxalate.

Table III

Comparison of Strontium and Barium Yields

	Sr Yield	Ba Yield	Ba/Sr
Wheat	86.1%	83.8%	0.97
Milk	88.5%	82.8%	0.94
Bone	88.5%	85.0%	0.96
Peanuts	86.1%	76.4%	0.89

Average Ba/Sr = 0.94

Table IV

Concentration of Calcium, Strontium and Barium in Biological Samples

Sample	Sr mg/kg	Ba mg/kg	Ca mg/kg	Sr µg/g ash	Ba µg/g ash	Ca mg/g ash	Sr mg/g Ca	Ba mg/g Ca	Ba/Sr
1958-9 Wheat	1.47	2.91	313	88	174	18.7	4.71	9.30	1.98
exports Flour	0.34	0.55	134	77	126	30.5	2.54	4.12	1.62
Bran	4.05	9.32	815	81	186	16.3	4.97	11.42	2.30
1959 Wheat Composite	1.36	2.03	312	82	122	19.1	4.32	6.44	1.49
1960 Wheat Composite	1.34	2.16	274	78	126	15.9	4.87	7.88	1.62
Rice (polished)	0.34	0.15	241	66	29	47.3	1.40	0.61	0.44
Oatmeal	1.90	2.15	532	109	123	30.4	3.58	4.04	1.13
Potatoes	0.27	0.08	50	32	9	5.8	5.46	1.60	0.29
Carrots	2.35	0.65	345	174	48	25.5	6.80	1.89	0.28
Beans	2.03	0.37	351	124	23	21.5	5.78	1.06	0.18
Leafy Vegetables	2.78	0.27	450	199	19	32.1	6.18	0.59	0.10
Tomatoes	0.16	0.03	46	24	4	6.6	3.48	0.65	0.19
Fruit, mixed soft	0.93	0.28	116	110	34	13.8	8.00	2.43	0.31
Oranges	0.45	0.07	139	143	22	44.8	3.20	0.48	0.15
Apples	0.11	0.10	32	54	48	12.8	3.44	3.13	0.91
Peanuts	5.67	2.72	690	183	88	22.3	8.21	3.94	0.48
Minced Beef	0.14	0.10	191	14	9	19.1	0.74	0.50	0.67
Lean Beef	0.13	0.04	246	13	4	24.1	0.52	0.16	0.31
Beef Bone	–	–	–	192	297	368	0.52	0.81	1.55
Lean Pork	0.11	0.02	281	10	2	25.1	0.40	0.08	0.20
Pork Bone	–	–	–	186	7	368	0.51	0.02	0.04
Eggs	1.02	0.37	457	109	39	48.6	2.23	0.81	0.36
Sardines	5.76	0.06	3300	146	1	83.8	1.75	0.02	–
Salmon Flesh	0.80	0.01	236	63	1	16.8	3.75	–	–
Salmon Bones	–	–	–	1232	N.D.	328	3.76	–	–
Oysters	4.12	0.02	857	217	1	45.1	4.81	0.02	–
Powdered Skim Milk	6.32	1.36	13006	76	16	159	0.49	0.10	0.22
Powdered Buttermilk	–	–	–	41	–	123	0.34	–	–
Fluid Whole Milk	–	–	–	80	15	160	0.50	0.10	0.19

(1) All values are the average of at least two analyses.

N. D. - Not Detected

Table V

Detailed Results - Wheat and Milk

Sample		Sr mg/kg	Ba mg/kg	Ca mg/kg	Sr μg/g ash	Ba μg/g ash	Ca mg/g ash	Sr mg/g Ca	Ba mg/g Ca	Ba/Sr
1959 Wheat Composite										
Manitoba	1	1.26	1.53	294	72	87	16.8	4.29	5.20	1.21
	2	0.99	1.66	317	61	102	19.6	3.13	5.23	1.67
	3	1.27	1.52	324	75	90	19.2	3.92	4.70	1.20
Saskatchewan	4	1.14	1.75	308	73	112	19.7	3.70	5.69	1.54
	5	1.32	2.64	316	74	148	17.7	4.17	8.38	2.01
	6	1.75	2.04	350	111	129	22.2	4.99	5.82	1.17
Alberta	7	1.35	3.26	317	79	191	18.6	4.25	10.26	2.41
	8	1.71	2.70	310	106	167	19.3	5.52	8.69	1.58
	9	1.33	1.11	272	91	76	18.6	4.88	4.07	0.84
Powdered Skim Milk				x 10³						
Fraser Valley*		7.70	-	13.6	94	-	166	0.50	-	-
Calgary		5.73	2.62	13.3	70	32	162	0.43	0.20	0.46
Edmonton*		5.24	-	12.4	64	-	152	0.42	-	-
London		5.08	0.57	13.2	62	7	161	0.39	0.04	0.11
Walkerton		6.47	0.49	12.8	79	6	156	0.51	0.04	0.08
Ottawa		5.98	1.39	12.3	74	17	155	0.48	0.11	0.23
Granby*		7.70	-	12.8	94	-	156	0.60	-	-
Megantic		5.90	1.39	13.0	72	17	161	0.45	0.09	0.24
Ladurantaye		7.04	1.88	12.9	86	23	158	0.54	0.15	0.27
Chicoutimi		6.80	1.39	13.3	83	17	162	0.51	0.10	0.21
Florenceville		-	-	-	64	10	-	-	-	-
Sussex		5.57	1.15	12.8	68	14	159	0.43	0.09	0.21
Powdered Buttermilk										
Saskatoon		-	-	-	42	14	120	0.35	0.12	0.33
Winnipeg		-	-	-	38	8	135	0.28	0.06	0.21
Moncton*		-	-	-	43	-	113	0.38	-	-

Table V (cont'd)

Fluid Milk

Pembroke 1	-	-	-	70	13	160	0.44	0.08	0.19
Pembroke 2	-	-	-	91	17	160	0.57	0.11	0.19

Water	Sr µg/l	Ba µg/l	Ca mg/l
Lake, Lower Bass	36	1	-
Lake, Perch	30	9	4.4
Swamp, South	28	7	-
Ground, A Disposal Area	42	22	-
River, Ottawa	35	12	5.0
Well, Des Joachims	704	83	28.2

* Analysed by E. W. Carruthers (unpublished).