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DETERMINATION OF SELENIUM IN INDIVIDUAL FOOD ITEMS USING THE SHORT-LIVED NUCLIDE ^{77m}Se

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The selenium content of a variety of food items representing a normal hospital diet has been determined by cyclic instrumental neutron activation analysis (CINAA) through the 162-keV gamma-ray of the ^{77m}Se nuclide. The CINAA method is very simple and rapid. It involves irradiation of a sample for 20 s, decay for 20 s, and counting for 20 s. The precision of the method has been significantly improved by recycling the samples up to 4 times. The accuracy has been evaluated by analyzing a number of certified reference materials of varied selenium levels.

Introduction

Selenium is considered to be an essential element. Its role in animal nutrition is well established. At least forty animal species have been shown to demonstrate selenium-responsive diseases (1). These include liver, kidney and heart necrosis, muscular dystrophy, growth depression and exudative diathesis.

In human nutrition, certain selenoenzymes and selenoproteins are considered to be of vital importance. The best known biochemical function of selenium is demonstrated as part of the enzyme glutathione peroxidase, which protects vital components of the cell against oxidative damage. Other selenium-dependent enzymes have been identified in bacterial systems, including glycine reductase, formate dehydrogenase, nicotinic acid hydrogenase and thiolase (2). In the past decade, Chinese investigators have shown that selenium deficiency is one of the principal factors responsible for Keshan disease, a dilated cardiomyopathy that affects persons living in rural areas of certain selenium-deficient zones in China (3).
Dietary intake of selenium has been singled out as the major source of the element for humans. A simple and rapid cyclic instrumental neutron activation analysis (CINAA) method has been developed in the present study for the determination of low levels of selenium in individual food items and duplicate diets as part of a continuing research project on daily dietary intakes of trace elements of human nutritional importance.

Neutron activation analysis (NAA), spectrofluorometry and hydride generation atomic absorption spectrometry (AAS) are the most

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frequently used analytical techniques for the determination of selenium in biological materials. The fluorometric method is considered time-consuming and cumbersome, and the AAS method can suffer from matrix interferences, if appropriate precautions are not taken, when applied to such complex matrices as foods. The CINAA method avoids lengthy irradiation, decay and counting periods of conventional NAA thus allowing a significant reduction in total experimental time. The method is capable of simultaneous measurement of short and medium-lived nuclides, in addition to that of selenium.

Experimental

Sample Collection. Food samples, representative of normal, daily hospital meals, were collected over a 4 day period (excluding weekend) from the Victoria General Hospital, Halifax, Nova Scotia. Individual items were indicative of a normal serving size. The composition of each meal was recorded to allow for later conversion of Se concentrations of individual food items to Se levels of composite meals.

Sample Preparation. Individual food items were collected from the hospital trays into polyethylene bags, weighed and refrigerated. A weighed portion of the samples was subsequently freeze-dried for 48 h and the freeze-dried percent dry matter for each food item was calculated. Homogenization was carried out in a small blender with stainless steel blades and container. No selenium contamination from the blender blades was evident. The homogenized samples were stored in polyethylene vials and refrigerated.

Approximately 250-500 mg of each homogenized food item were weighed into small polyethylene vials (pre-washed with 4M HNO_3 and rinsed with deionized distilled water). The small vials (1.2 mL) were heat-sealed, and placed in medium-sized (7 mL) vials for CINAA.

Standards. Selenium comparator standards were prepared by depositing microlitre portions, containing microgram quantities, of an ultrapure Se atomic absorption standard solution (BDH Chemicals) on a sucrose support and evaporating them to dryness at low heat under an infared lamp. The standards were heat-sealed in small polyethylene vials.

Reference Materials. A number of standard reference materials obtained from the U.S. National Bureau of Standards (NBS SRM) and of certified reference materials and intercomparison samples from the International Atomic Energy Agency (IAEA) and U.S. Department of Agriculture (USDA) were analyzed for selenium content by the CINAA method. These materials were dried according to the procedures recommended by the issuing agencies. Between 250 and 300 mg of the samples were placed in the small vials for irradiations.

Irradiations and Counting System. Samples and standards were irradiated in the Dalhousie University SLOWPOKE-2 Reactor (DUSR) at a thermal neutron flux of 5×10^{11} n $cm^{-2}s^{-1}$. The composition, homogeneity, and reproducibility of the SLOWPOKE flux have been described elsewhere (5). Gamma-ray spectra of the irradiated materials were recorded using a 40-cm^3 PGT Ge(Li) detector with a full width at half maximum of 2.0 keV and an efficiency of 7.1% (measured at the 1332-keV photopeak of ^{60}Co) coupled with a ND-6700 model 4096 channel pulse height analyzer. The CINAA method involves the following timing parameters: irradiation time (t_i)= 20 s, decay time (t_d)= 10 s and counting time (t_c)= 20 s. The number of cycles (n) was typically 4. For certain food samples containing large amounts of Na, Cl and Al the number of cycles were reduced to 1 or 2.

Results and discussion

Cyclic INAA (CINAA) is particularly suitable for the high-precision determinations of elements through short-lived nuclides (half-life < 25 s). In CINAA, a sample is irradiated for a short period of time, rapidly transferred to a detector for counting, and the entire process repeated for an optimum number of cycles. The theory of CINAA has been previously reported in detail (4). The Se content of the individual food items have been measured in the present study using the DUSR rapid cyclic system which is capable of transferring a sample from the reactor core to the vertical counting position within 600 ms.

The timing parameters used in this work have been optimized for obtaining the best possible sensitivity, precision and accuracy within a short experimental time. It has been noted earlier that it is not always necessary to repeat the cycles 4 times to achieve the best analytical results for all samples; in fact, food samples such as beef, pork, turkey, etc. which contain high levels of Na and Cl are better analyzed for Se through 1 or 2 cycles due to less Compton interference.

The 162-keV gamma-ray of ^{77m}Se (17.4 s), used in this work, could be interfered with by the 164-keV gamma-ray of $^{116m2}In$ (2.16 s). No such interference was observed when half-life measurements were done starting at a t_d of 2 s. Considering the very low levels of In in biological materials and normal t_d of 10 s for routine analysis, it is highly improbable that any interference could be encountered. Moreover, the good agreement between the Se content measured in this work using CINAA and the certified values obtained using a number of different techniques for various reference materials indicates the absence of any detectable interference from the 164-keV photopeak of $^{116m2}In$.

To evaluate the accuracy of the CINAA method, a number of standard reference materials and two interlaboratory intercomparison diet samples have been analyzed. The averages of three determinations are shown in Table 1. The agreement with certified values is good for Oyster Tissue, Fish Homogenate, Bovine Liver

Table 1
Selenium content of standard reference materials by CINAA

Material	This work*	Reported Value*
Oyster Tissue (NBS SRM 1566)	1.91±0.089	2.1±0.5
Fish Homogenate (IAEA MA-A-2)	1.38±0.043	1.7±0.3
Bovine Liver (NBS SRM 1577)	1.13±0.026	1.1±0.1
Wheat Flour (NBS SRM 1567)	0.996±0.059	1.1±0.2
Bovine Liver (NBS SRM 1577a)	0.72±0.019	0.71±0.07
Rice Flour (NBS SRM 1568)	0.32±0.017	0.4±0.1
Animal Muscle (IAEA H4)	0.33±0.022	0.28±0.03
Animal Blood (IAEA A-13)	0.257±0.003	(0.24)
Total Diet (USDA TDD-1D)	0.262±0.005	(0.236)
Human Diet (IAEA H9)	0.097±0.015	(0.100)
Orchard Leaves (NBS SRM 1571)	0.080±0.019	0.08±0.01
Milk Powder (IAEA A-11)	<47.7	33.9±7.2

* all values reported in ppm except for Milk Powder which is in ppb.

(1577 and 1577a), Wheat Flour, Rice Flour, Orchard Leaves and Human Diet. The selenium content of Animal Muscle is slightly higher than the certified value. The experimental values for Animal Blood and the Total Diet standard are within ±10 % of the assigned and tentatively assigned values. Detection limit is reported for the Milk Powder standard.

In general, CINAA improves the precision of a measurement. The improvement in precision, expressed in terms of relative standard deviation, with increasing number of cycles for a few typical food items is presented in Table 2. The data indicate that the precision has become better from first through third or fourth cycle, in one case by as much as 40 times. Precision of ±1-3% can be easily achieved for Se by CINAA.

The limit of detection for Se in food largely depends on the amount of Al, Na and Cl in the sample under a given set of experimental conditions. For example, a limit of 3-5 ppb can be

Table 2
Effect of number of cycles on precision of measurement

Material	Cycle No.	ppm Se (dry wt.)	Rel. Std. Dev., %
Grilled Pork Chop	1	0.859±0.113	13.2
	2	0.860±0.022	2.6
	3	0.835±0.011	1.3
Beef & Vegetable Pie	1	0.162±0.072	44.4
	2	0.163±0.032	19.6
	3	0.176±0.034	19.6
	4	0.172±0.014	8.1
Fresh Roll	1	0.378±0.151	39.9
	2	0.404±0.066	16.3
	3	0.460±0.011	2.4
Brown Bread	1	0.430±0.112	26.0
	2	0.425±0.069	16.2
	3	0.393±0.052	13.2
	4	0.386±0.040	10.4
Ginger Snap Cookie	1	0.282±0.088	31.2
	2	0.278±0.023	8.3
	3	0.251±0.013	5.2
	4	0.243±0.002	0.8

obtained for desserts and vegetables, whereas a limit of 30-40 ppb is more realistic for such food items as meat and fish which contain large amounts of salt. The detection limits can be further improved by irradiating the samples at a higher neutron flux.

The Se levels, expressed as the mean and standard deviation of three replicate samples, of a number of food items have been determined by the CINAA method developed in this study and are shown in Table 3. Wherever possible, values from published literature are cited for comparison purposes. Eggs, fish and meat appear to be good sources of Se. The observations that the Se content of the boiled egg (0.48 ppm) is greater than that of the fried egg (0.29), and the value for grilled pork chop (0.37 ppm) is higher than corned pork (<0.1 ppm) suggest that cooking and processing at high temperatures could affect the selenium content of similar foods.

Table 3
Selenium content of individual food items by CINAA

Food Item	This study	Literature Value
Meat, Fish and Eggs		
Boiled Egg	0.482±0.033[a]	yolk 0.20 (14)
Fried Egg	0.289±0.020	white 0.06 (14)
Roast Beef	0.178±0.015	
Grilled Pork Chop	0.371±0.005	
Broiled Haddock Fillet	0.475±0.022	
Beef & Vegetable Pie	0.097±0.008	
Turkey Stew	<0.023[b]	
Corned Pork	<0.098	
Breads and Cereals		
White Bread	0.183±0.032	0.28 (10)
Brown Bread	0.243±0.026	0.66 (10)
Fresh Roll	0.384±0.022	
White Roll	0.388±0.028	
Whole Wheat Roll	0.312±0.022	
Shredded Wheat	0.062±0.010	0.05 (6)
All Bran	<0.107	0.04 (6)
Rolled Oats	<0.016	N.D. (6)
Vegetables		
Mashed Potato	<0.019	<0.01 (14)
Mashed Potato[c]	<0.017	
Boiled Potato	<0.010	
Boiled Potato[c]	<0.008	
Home Fried Potato	<0.018	
Green Peas	<0.019	
Carrot Coins	<0.004	<0.01 (14)
Green Salad	<0.003	
Spinach	<0.013	
Desserts		
Cherry Cookie	0.263±0.020	
Pumpkin Pie/Whip Cream	0.017±0.001	
Pineapple Cream Torte	0.085±0.007	
Ginger Snap Cookie	0.243±0.002	
Apple Dessert	0.079±0.009	
Pears in Syrup	0.010±0.002	
Soups		
Split Pea Soup	0.039±0.003	
Chicken/Rice Soup	<0.011	

Table 3 continued

Food Item	This study	Literature Value
Milk and Milk Products		
2% Milk	0.015±0.004	0.012 (10)
Cheddar Cheese	0.110±0.001	0.12 (14)
Miscellaneous		
Brown Sugar	<0.036	<0.01 (14)
Peanut Butter	<0.042	
Strawberry Jelly	<0.038	
Ketchup	<0.091	
Mustard	<0.099	
Orange Juice Concentrate	<0.033	
Instant Coffee Powder	<0.115	

a average and std. deviation of three determinations.
b based on limit of detection defined by $3\sqrt{\mu_B}$ where μ_B is the number of background counts under the photopeak.
c food sample collected on a different day.

Breads have been found to contain significant amounts of Se; white and whole wheat rolls being greater dietary sources of Se than white and brown breads. The difference between white and whole wheat bread is not as considerable as that reported by Morris and Levander (6). The Se values of some common cereals are similar to those reported by Schroeder (7). The high detection limit of 107 ppb for All Bran cereal results from large amounts of Na, Cl, Al, Mn and Mg present in the sample.

Vegetables, in general, have been found to contain very little Se, viz, less than 12 ppb Se (mean of samples). In an attempt to improve the detection limit for Se in vegetables, the thermal neutron flux was increased to $1x10^{12}$ n cm^{-2} s^{-1}; however, reliable values could not be obtained by the instrumental method and hence only the detection limits under normal flux are quoted in Table 3. Morris and Levander (6) also reported that most vegetables (uncooked) contained less than 10 ppb Se.

Selenium has been detected in all dessert items analyzed. The values range from 0.01 to 0.26 ppm Se.

The selenium content of milk (0.015 ppm) and of cheddar cheese (0.110 ppm) found in this work compare very well with the values cited in the literature (6,8).

Certain beverages and condiments could not be freeze-dried. Items such as jelly, mustard, ketchup, peanut butter and orange juice concentrate were directly pipetted into the small irradiation vials and sealed. Only detection limits can be reported for these items.

Table 4
Selenium content of a normal hospital diet

Day 1	Serving Size (grams)	ppm Se (wet wt.)	µg Se
Breakfast			
Shredded Wheat	40.0	0.062	2.5
Fried Egg	47.9	0.289	13.8
Whole Wheat Bread	34.1	0.243	8.3
2 % Milk	137.4	0.015	2.1
Lunch			
Split Pea Soup	107.3	0.039	4.2
Roast Beef	71.3	0.178	12.7
Mashed Potato	82.0	N.D.	--
Green Peas	62.0	N.D.	--
Apple Dessert	108.2	0.079	8.6
Fresh Roll	43.7	0.348	15.2
2 % Milk	137.4	0.015	2.1
Supper			
Beef & Vegetable Pie	185.7	0.097	18.0
Green Salad	71.0	N.D.	--
Pears in Syrup	93.2	0.010	0.9
Whole Wheat Bread	34.1	0.243	8.3
2 % Milk	135.4	0.015	2.1
TOTAL	1426.6	1.63	98.8
Day 2			
Breakfast			
Rolled Oats	126.1	N.D.	--
Brown Sugar	9.9	N.D.	--
Peanut Butter	19.0	N.D.	--
White Bread	30.7	0.183	5.6
2 % Milk	135.4	0.015	2.1
Lunch			
Chicken/Rice Soup	116.4	N.D.	--
Grilled Pork Chop	111.5	0.371	41.4
Boiled Potato	90.4	N.D.	--
Carrot Coins	90.6	N.D.	--
Pumpkin Pie/Whip Cream	138.2	0.017	2.4
Whole Wheat Roll	68.0	0.312	21.2
2 % Milk	135.4	0.015	2.1
Supper			
Turkey Stew	182.4	N.D.	--
Green Salad	71.0	N.D.	--
Cherry Cookie	20.2	0.263	5.3
Whole Wheat Bread	34.1	0.243	8.3
2 % Milk	137.4	0.015	2.1
TOTAL	1520	1.43	90.5

Table 5
Daily dietary selenium intake for adults
in selected countries

Population	Mean intake*	Reference
Canada		
Four composite diets from 3 cities	168	(10)
Total diet - Elderly women	78	(12)
Hospital diet 2-days	95	this study
United States		
Total diet study FY 81/82	102	(13)
Hospital diet 2-days	62	(7)
Japan		
Typical diet	100	(14)
High fish diet	500	(14)
United Kingdom		
Total diet	60	(8)
West Germany		
Total diet - females	55	(15)
Total diet - males	59	(16)
New Zealand		
Food consumed/capita	56	(17)
Finland		
Total diet	30	(18)

* average daily Se intake in µg/day.

Although the exact requirements for Se have not yet been established, the United States Food and Nutrition Board (9) has concluded that for healthy adults daily intakes of 50 to 200 µg Se represents a safe and adequate intake range. Several studies have shown that Se intakes of the above range can be obtained easily with a varied and balanced diet (7,10). Processing and geographical origin can affect the Se content of similar foods. In North American diets, cereal products are the dominant food of plant origin which supplies Se, with much of the cereal consumption in the form of rolls and breads. Meat and fish are good dietary sources of Se while fruits and vegetables are recognized as poor sources (11), an observation also supported by the results presented here.

The average daily intake of Se has been estimated in this study by means of the food samples (i.e. normal, duplicate diet from a local hospital) collected over a 2-day period, and is shown in Table 4. The Se intake of 95±4 µg/d is within the range of 50 to 200 µg Se/d suggested by the U.S. Food and Nutrition Board (9). Food items such as tea, butter, jam and salad dressing were not analyzed and are excluded from the menus and also from calculations of daily intakes of Se. Meat and eggs account for approximately 46% of the daily Se intake and 37%% of the intake is derived from breads and cereals.

Per capita Se intakes may vary significantly among different regions of a country as well as among different countries. Table 5 illustrates the various estimates of mean daily Se intakes for adults in various geographical locations. Differences largely arise due to the variation in the Se content of soils and soil-plant factors. The soils of New Zealand, Finland and Great Britain have been noted for poor Se content (17, 18, 8) thereby affecting the Se levels in agricultural products.

Conclusions

The CINAA method developed in this study for the determination of Se levels through its short-lived nuclide ^{77m}Se in individual food items and duplicate diets is simple and rapid. The precision of measurement is typically ±1-5%, and the accuracy is well within ±7% in most cases. A detection limit of 3-5 ppb can be easily achieved for a number of food items. A higher detection limit, viz. 30-40 ppb, can be obtained for samples containing large amounts of salt by the CINAA method. A method for preconcentrating Se from vegetables needs to be developed if CINAA is to be used for measuring concentrations at 1-3 ppb levels. Alternatively, a radiochemical NAA method using the long-lived ^{75}Se nuclide can be employed. The average dietary intake for a normal hospital diet has been estimated to be 95±4 µg Se per day.

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