

A feasibility study to measure low levels of boron in selected Canadian and Japanese foods by prompt gamma activation analysis using the JAEA JRR-3 facility

M. Fukushima · H. Matsue · A. Chatt

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Abstract A feasibility study was carried out to evaluate the potential of the thermal neutron capture prompt-gamma activation analysis (PGAA) for the measurement of low levels of boron in selected Canadian and Japanese foods using the PGA facility at the JRR-3 reactor of the Japan Atomic Energy Agency (JAEA) in Tokai. A method was optimized for this purpose. It is rapid and can be used without any chemical separation. The precision and accuracy of the method are good. The detection limit is around 0.5 mg kg^{-1} .

Keywords Prompt gamma activation · Boron · Foods

Introduction

Boron is known to be an essential element for plants. Its deficiency may lead to reduced growth and lower yield of the plant. Excess boron may cause the death of the whole plant [1]. It has been postulated that boron perhaps is an essential element for both animals and humans but no characteristic biochemical function has yet been put forward [2]. Boron has been reported to be nutritionally

important and to act as a co-factor for calcium metabolism. It is also toxicologically important as boron can accumulate in certain food items whose consumption may very well constitute a potential health hazard [3]. It is therefore necessary to have reliable methods available for the measurement of varying levels of boron in foods and diets.

The determination of light elements such as boron is rather difficult by almost all analytical techniques. In 1997 Sah and Brown [4] have extensively reviewed several sample preparation and analytical methods for measuring boron levels in a variety of matrices. Recently, colorimetry [5, 6], fluorimetry [7], solid-sampling graphite furnace atomic absorption spectrometry (AAS) [8], inductively-coupled plasma (ICP) atomic emission spectrometry (AES) [9], ICP-mass spectrometry (ICP-MS) [10], negative thermal ionization mass spectrometry (TIMS) [11, 12], and Laser-induced breakdown spectroscopy (LIBS) [13] have been used for analyzing boron.

Conventional instrumental neutron activation analysis (INAA) is not particularly suitable for boron determination. Boron consists of two stable isotopes, namely ^{10}B (19.82 %) and ^{11}B (80.18 %). ^{10}B has a low thermal neutron capture cross section (300 mb) and produces the stable isotope ^{11}B which has even a lower thermal neutron capture cross section of 6 mb producing ^{12}B [14]. The thermal neutron absorption cross section of natural boron is around 760 b [15, 16]. ^{12}B is a very short-lived nuclide with a half-life of 20.2 ms and emits Cerenkov radiation. A very fast pneumatic transfer system is required for its detection, as was available at Atominstytut Wien in Austria reported by Grass and coworkers [17] and the Risoe National Laboratory, Roskilde in Denmark reported by Heydorn and coworkers [18]. The transfer time of the Dalhousie University SLOWPOKE-2 Reactor (DUSR) pneumatic cyclic system was about 100 ms and therefore not suitable for the

M. Fukushima (✉)
Department of Basic Sciences, Ishinomaki Senshu University,
Ishinomaki, Miyagi, Japan
e-mail: fukushima@isenshu-u.ac.jp

H. Matsue
Department of Research Reactor and Tandem Accelerator, Japan
Atomic Energy Agency, Tokai, Ibaraki, Japan

A. Chatt
Trace Analysis Research Centre, Department of Chemistry,
Dalhousie University, 6274 Coburg Road, Room 212,
Box 15000, Halifax, NS B3H 4R2, Canada

analysis of boron by conventional INAA. So other non-destructive techniques were investigated using the facilities available in our laboratory at that time. In one such method it was assumed that the magnitude of the neutron flux reduction in the reactor would be proportional to the amount of boron present in a sample. So experiments were carried out with varying amounts of boron standards and the depressions in the neutron flux were recorded. The results were quantitative but the reproducibility was no more 80 %. Then an indirect INAA method [19, 20], based on measuring the activity of an easily activated indicator element (such as vanadium) in a sample containing different levels of boron, was modified by Moir and Chatt [21–23] and applied to study sodium borosilicate glasses designed to be the hosts for immobilized high-level radioactive waste. The indirect INAA method was suitable for this purpose but the absolute detection limit of 100 μg was too high for the analysis of boron in food samples. Other elements including selenium, indium and titanium were investigated as possible indicators. It was hoped that selenium and indium would be good indicator elements due to their short-lived ($^{77\text{m}}\text{Se}$, 17.4 s; $^{116\text{m}}\text{In}$, 14.1 s) and very sensitive nuclides but again the detection limits for boron were not low enough for food analysis.

Three other nuclear analytical techniques are highly suitable for the direct determination of low levels of boron in solid samples, namely neutron activation-mass spectrometry (NA-MS) [24, 25], particle-induced gamma-ray emission (PIGE) [26–30], and neutron capture prompt-gamma activation analysis (PGAA) [29]. In PGAA, the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction with a very high neutron absorption cross section of 3837 b is used for the determination of boron down to ppb levels in a variety of matrices. PGAA has been extensively used for the determination of boron in foods, diets, diet supplements, and biological reference materials [31–45]. Both thermal and cold neutron PGAA methods have been used for this purpose [40]. Thermal neutron PGAA has been used in the present work to measure boron levels in a variety of Canadian and Japanese foods.

Experimental

Samples, comparator standards, and reference materials

Four groups of samples were analyzed for boron by PGAA. One group contained Canadian vegetables, namely beans, beets, broccoli, cabbage, carrots, cauliflower, celery, corn cucumbers, lettuce, mushroom (canned), onion, peas, and peppers. The second group was Canadian food samples, namely beef, fish, flour, french fries, milk, pancakes, poultry, puddings, and frozen dinner. These market basket

foods were collected at the retail level in the Toronto area, Ontario, Canada. They were prepared and made to composites at the Kemptville Community College in Ontario, and sent to us by Health Canada samples in frozen condition. These samples were freeze dried, homogenized, and stored in Teflon containers in a freezer at $-20\text{ }^\circ\text{C}$. The moisture content of the samples was calculated.

The third group contained several Japanese vegetables which were chosen for comparison purposes. These were; broccoli, brown mushroom, ginger, okra, pumpkin, red pepper, shiitake mushroom, and snow peas. These vegetables were bought from farmers' market in Yamagata Prefecture, washed with tap water, freeze dried, homogenized, and moisture content calculated.

The fourth group contained different kinds of spice which were purchased in grocery stores in Sendai (S, Japan), Halifax (H, Canada) and Budapest (B, Hungary). These were: black pepper (S), cardamom (H), cinnamon (S), whole seed cloves (S), roasted garlic powder (H), ginger powder (H), paprika powder (B), and powdered tea (H). These samples were used on as is basis (dry weight) and moisture content was not available.

Boron levels were calculated from a calibration curve. A 1,000 ppm 99.999 % pure standard boron solution for atomic absorption spectrometry was purchased from the Wako Co. Ltd. and used as the stock solution. Comparator standards of boron were prepared by adding known amounts of the stock solution onto Whatman 42 filter papers and followed by drying under an IR lamp.

Two standard reference materials (SRM) purchased from the U.S. National Institute of Standards and Technology (NIST), namely SRM 1572 citrus leaves and SRM 1573 tomato leaves, were used in this work for the validation of the PGAA method.

Irradiation and counting

The PGA facility at the JRR-3 reactor of the Japan Atomic Energy Agency (JAEA) in Tokai was used in this work. The details of the PGAA system have already been published by Yonezawa and Wood [40]. Between 0.3 and 0.5 g of each sample was heat sealed in double FEP films of 15×15 mm. Then the sample bag was hung in PTFE frame by PTFE strings. Sample and sample holder were placed in PTFE sample box at an angle 45° to the neutron beam. The thermal neutron flux was 6.9×10^7 (5.7×10^8 , when focused) $\text{cm}^{-2} \text{s}^{-1}$ [46]. Air was purged from the sample box, and helium gas was allowed to flow through continuously during irradiation. Irradiation time varied between 1,000 and 3,000 s depending on the boron content of the sample.

The gamma-ray spectra were recorded using a Compton suppression system at JRR-3. This system has previously

Fig. 1 Gamma-ray spectra showing interference from sodium and correction applied to the boron peak

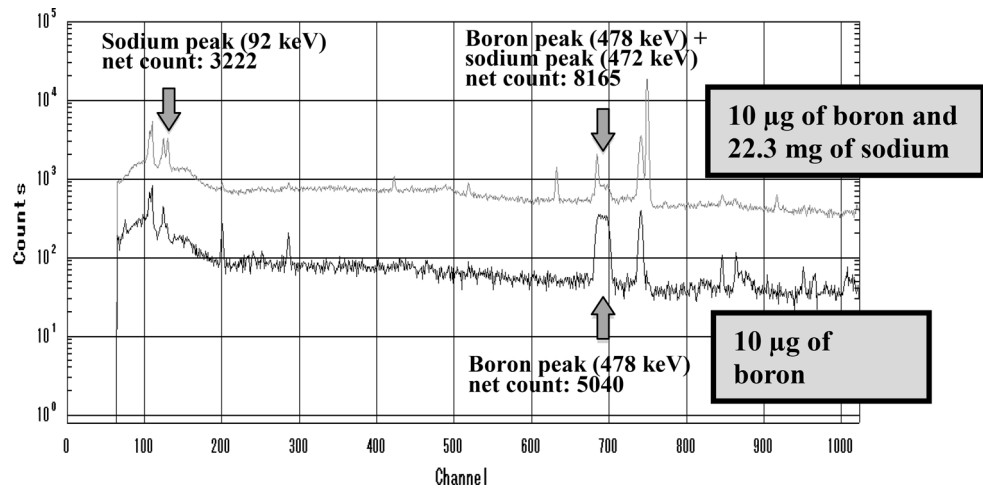


Table 1 Mass fractions of boron in select NIST SRMs by PGAA (mg kg^{-1})

	NIST SRM 1572 citrus leaves	NIST SRM 1573 tomato leaves	NIES No. 23 green tea
This work	66.4 ± 5.0	34.7 ± 2.7	13.6 ± 0.20
Detection limit (μg)	0.67	0.65	0.40
Cert/(info value)	–	(30)	–
Reference [32]	63.5 ± 0.2	38.3 ± 0.7	–
Reference [40]	65.8 ± 4.7	–	–

Table 2 Reproducibility of boron measurements in foods by PGAA (mg kg^{-1})

Code	Food	This work (wet weight)	Irradiation time (s)
A01	Milk, whole	0.62 ± 0.26	1,000
A01	Milk, whole	0.58 ± 0.20	49,806
G01	Baked beans	1.11 ± 0.20	2,000
G01	Baked beans	1.23 ± 0.16	3,000

been described by Yonezawa [47]. The photopeaks were analyzed using the SEIKO EG and G gamma-ray spectrum analysis program.

Results and discussion

Boron levels were calculated from the calibration curve using the 478 keV photopeak from the $^{10}\text{B}(n,\alpha)^7\text{Li}$ reaction. This peak is known to be broad due to the characteristic Doppler effect [16]. It is also well established that this peak could be interfered with by 472 keV peak of sodium which is known to be present in nutritional materials. The correction method proposed by Anderson et al. [32] was used in this work.

Table 3 Mass fractions of boron and sodium in select Canadian vegetables by PGAA (mg kg^{-1})

Code	Vegetable	B, this work (wet weight)	B, reference [36] (wet weight)	Na, this work (wet weight)
G01	Beans, baked	3.29 ± 0.58	–	$3,960 \pm 420$
G02	Beans	2.17 ± 0.20	–	$1,010 \pm 111$
G03	Beets	4.20 ± 0.61	1.15 ± 0.17 (canned)	$2,010 \pm 298$
G04	Broccoli	3.34 ± 0.41	2.47 ± 0.03 (boiled)	182 ± 266
G05	Cabbage	1.81 ± 0.28	1.07 ± 0.06 (boiled)	<395
G06	Carrots	3.19 ± 0.48	0.59 ± 0.09 (raw)	118 ± 187
G07	Cauliflower	1.39 ± 0.39	1.27 ± 0.06 (boiled)	<345
G08	Celery	2.04 ± 0.29	2.19 ± 0.01 (raw)	74 ± 130
G09	Corn	0.48 ± 0.48	0.49 ± 0.05 (boiled)	<612
G10	Cucumber	5.31 ± 1.83	0.94 ± 0.01 (raw, pared)	$26,900 \pm 1300$
G11	Lettuce	1.59 ± 0.37	0.83 ± 0.17 (raw)	<360
G12	Mushroom, canned	0.86 ± 0.70	0.56 ± 0.02 (canned)	$9,110 \pm 605$
G13	Onion	1.79 ± 0.30	1.39 ± 0.04 (raw)	<276
G14	Peas	4.26 ± 0.66	1.21 ± 0.09	$2,730 \pm 513$
G15	Peppers	0.85 ± 0.12	–	<135

As noted by Anderson et al. [32], interferences from sodium, chlorine and nitrogen are significant around the 475 keV photopeak area. The interference from the 472 keV photopeak of sodium in fresh vegetables is not as severe as that in vertebrates, marine and cooked food samples. For

Table 4 Mass fractions of boron and sodium in select Japanese raw vegetables by PGAA (mg kg^{-1})

Vegetable (wet weight)	B, this work (wet weight)	B, reference [36] (wet weight)	Na, this work (wet weight)
Broccoli	3.10 ± 0.37	2.47 ± 0.03 (boiled)	<437
Brown	1.50 ± 0.41	–	<401
Mushroom	–	–	–
Ginger	1.11 ± 0.66	–	<454
Okra	4.69 ± 0.42	–	<710
Pumpkin	3.51 ± 0.50	–	<610
Red pepper	10.2 ± 1.51	–	<1730
Shiitake	1.72 ± 0.40	–	<429
Snow pea	1.36 ± 0.25	–	<300

Table 5 Mass fractions of boron and sodium in select Canadian and Japanese spices by PGAA (mg kg^{-1})

Spice	B, this work (dry weight)	Na, this work (dry weight)
Black pepper	12.4 ± 1.6	<2,580
Cardamom whole seed	9.7 ± 1.3	<2,370
Cinnamon	9.6 ± 1.9	<2,210
Clove whole seed	27.8 ± 2.0	<4,200
Ginger powder	5.4 ± 1.5	<1,770
Paprika powder	11.6 ± 1.2	<1,600
Powdered tea	24.2 ± 2.3	–
Roasted garlic powder	10.8 ± 1.0	<1,990

correcting sodium interference, known amounts of sodium chloride were irradiated, counted, and the correction factors calculated from two different sodium peaks, namely 92 and 472 keV. Irradiation of 0.02445, 0.05648 and 0.11300 g of sodium chloride for 1,000 s gave a value of 1.057 ± 0.014 (mean + SD) on the average as the ratio of net counts in the 472/92 keV peak areas. Then known amounts of boron and sodium chloride were analyzed together. For example, as is

shown in Fig. 1, net count for 10 μg of boron at the 478 keV peak was 5,040. The net counts of 10 μg of boron + 0.05600 g of sodium chloride were 3,222 and 8,165 for the 92 and 472 keV, respectively. The net count for boron was then calculated as: $8,165 - (3,222 \times 1.057) = 4,759$. It is evident that the net count after the correction (4,759) differs from the actual net count (5,040) by 5.6 %. The correction factor for boron could very well depend on the ratio of boron-to-sodium in a given sample. In future work, the correction factor will be checked for different boron-to-sodium ratio. The 92 keV peak of sodium was detected only in some Canadian vegetables.

The PGAA method was validated in this work using two control samples and the results are shown in Table 1. Our average value of $66.4 \pm 5.0 \text{ mg kg}^{-1}$ of three analyses for the NIST SRM 1572 citrus leaves agrees well with the literature values of $63.5 \pm 0.2 \text{ mg kg}^{-1}$ [32] and $65.8 \pm 4.7 \text{ mg kg}^{-1}$ [40]. No certified value for this SRM was provided by NIST. The average value of $34.7 \pm 2.7 \text{ mg kg}^{-1}$ of three measurements obtained in this work for the NIST SRM 1573 tomato leaves agrees with the literature value of $38.3 \pm 0.7 \text{ mg kg}^{-1}$ [32] and information value of 30 mg kg^{-1} . The detection limit was 0.7 mg kg^{-1} for 1,000 s irradiation times for both of the SRMs. The limit for the vegetables with low sodium content was around 0.5 mg kg^{-1} .

The reproducibility of the PGAA method was evaluated by analyzing two Canadian food samples, namely whole milk (A01) and baked beans (G01). Three portions of each sample were irradiated for two different times. The average values are presented in Table 2. It is evident that the values agree well within the experimental errors.

The PGAA method was applied to a small selection of Canadian and Japanese food samples. Boron levels in Canadian and Japanese vegetables are presented in Tables 3 and 4, respectively. These values are comparable to those published by Anderson et al. [36] for the U.S. vegetables. A few Canadian and Japanese spice samples were also analyzed for boron by the PGAA method; the results given in Table 5 show that

Table 6 Mass fractions of boron and sodium in select Canadian foods by PGAA (mg kg^{-1})

Code	Material	B, this work (wet weight)	B, reference [36] wet weight	Na, this work (wet weight)
A01	Milk, whole	0.62 ± 0.26	0.13 ± 0.05	153 ± 209
A02	Milk, 2 %	0.45 ± 0.22	0.23 ± 0.01	<66.0
B01	Beef, steak	0.97 ± 0.68	0.10 ± 0.01	<638
C02	Poultry, chicken, turkey	1.15 ± 0.73	–	<847
D03	Fish, canned	1.61 ± 0.69	–	$4,040 \pm 425$
F12	Flour, wheat	1.83 ± 1.40	–	<1820
F14	Pancakes	2.16 ± 0.90	0.36 ± 0.02	$6,290 \pm 524$
J07	Puddings	2.46 ± 0.64	0.21 ± 0.06 (custard)	$3,550 \pm 335$
M06	Frozen dinner, beef + vegetable + dessert	1.10 ± 0.80	–	$6,250 \pm 575$
N02	French fries	0.80 ± 0.57	0.95 ± 0.10	$3,530 \pm 466$

the levels are low in general. A selection of items from various food groups are presented in Table 6. Sodium content of the foods analyzed is also given in Tables 3, 4, 5 and 6 to show the extent of correction needed to obtain boron values. It is evident that low levels of boron in these samples can be reliably measured by the PGAA method.

Conclusions

The PGAA method was found to be suitable for the determination of low levels of boron in presence of sodium in the Canadian and Japanese food samples analyzed. The method is applicable to solid samples without any pre-treatment. The precision and accuracy of the method were good. The detection limit was around 0.5 mg kg^{-1} . Since the feasibility project was completed, the disastrous earthquake and Tsunami on 3/11 in North East Japan has forced the reactor facility to shut down. No resumption of the facility has yet been announced.

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