Determination of Boron Isotopic Ratio by Using an Alpha Track Technique

Yong Joon Park,* Hyung Yeal Pyo, Kyuseok Song, Byoung Chul Song, Kwang Yong Jee, and Won-Ho Kim

*Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, P.O. Box 105, Yusung, Daejeon 305-600, Korea. *E-mail: jparky@kaeri.re.kr*
Received June 21, 2006

The determination of the boron isotopic ratio in solutions was achieved by means of a solid state track detector by using an alpha track. The neutron flux was optimized by using a Cd-foil to find the optimum conditions for counting the number of alpha tracks on the selected solid detector caused by the (n, α) nuclear reaction of boron. The home-made multi-dot detector plate was utilized in this study to increase the reproducibility of the measurement by uniformly drying the boron solution within the marked circle area on the detector plate. The experimental results of this study verified that the $^{11}B/^{10}B$ isotopic ratio can be measured by observing the number of alpha tracks for different concentrated standard solutions with various isotopic compositions. This technique was applied to the determination of ^{10}B enrichment factor in a biological sample for a boron neutron capture therapy.

Key Words : Alpha track analysis, Boron, Isotopic ratio, Enrichment, Multi-dot plate

Introduction

Boron is an important element in various fields of researches, such as nuclear science, astronomy and medical sciences due to the $^{10}B(n, \alpha)^{7}Li$ neutron capture reaction. Boron plays a crucial role in the nuclear power industry because of its high neutron absorption cross-section. More precisely, boron is used in a primary coolant system in pressurized water reactors (PWRs) in the form of boric acid to control the reactivity in the core. Boron is also used as a source for the short range α particles in a cancer treatment by a boron neutron capture therapy (BNCT)[1] which is a novel technique for treating cancer by using ^{10}B-labeled compounds and a neutron radiation to kill the cancerous cells. The significance of the B compounds stems from a high neutron cross section or a capture probability of the ^{10}B atom when compared to other biologically ubiquitous atoms such as carbon, hydrogen, nitrogen and oxygen atoms.

The precise determination of the isotopic composition of natural boron is of great interest in geochemistry,[2,3] nuclear industry,[4] and environmental studies.[5] Naturally occurring materials may vary enormously in their boron isotope proportion. Boron is actually a mixture of two stable isotopes ^{10}B and ^{11}B. One of the stable isotopes of boron, ^{10}B, is involved in an (n, α) nuclear reaction while the ^{11}B stable isotope is not. The natural boron isotopic ratio ($^{11}B/^{10}B$) varies from 3.8 to 4.2 depending on the source and the nature of the materials. Moreover, a measurement of the $^{11}B/^{10}B$ ratio in BNCT compounds becomes very important since the production of charged particles, ^{7}Li and ^{4}He, which kill tumor cells, depends on the concentration of ^{10}B in the capture agent. As a result, there is currently a strong demand for the determination of the boron isotopic ratio at all levels. The low atomic number of boron makes it difficult to determine its precise concentration with conventional analytical techniques such as XRF, PIXE, etc. Furthermore, its nuclear property makes it difficult to determine its concentration by a thermal neutron activation analysis.[6] Analytical techniques for a boron determination in solid or aqueous samples include spectrophotometry,[7] ICP-AES and an isotope dilution mass spectrometry by using TIMS.[8,9] These techniques require a tedious and time-consuming separation of the boron from the samples. Therefore, the development of a simple, convenient and sensitive analytical method for boron is of great interest in various fields of boron research.

Alpha track technology has been recognized as one of the highly sensitive analytical methods for the determination of boron.[10] The alpha track analysis is based on the detection of tracks on a alpha-sensitive solid state detector from (n, α) reactions. In this paper, a correlation of the alpha track count against various boron concentrations was studied by adopting the multiple regression curve technique. The slope of the correlation curve was used to determine ^{10}B enrichments.

Experimental Section

Reagents and materials. The solid state track detectors used in the study were Lexan (GE-Plastic, Korea), CR-39 (TASTRACK, UK), and CN-85 (DOSIRAD, France). All of these detectors were first checked for their sensitivity to alpha particles by an exposure to an alpha multi-radioisotope source (^{239}Pu, ^{241}Am, ^{244}Cm mixed alpha standard B 860, 1.67×10^{5} alpha particles per minute, Amersham) followed by an etching.

Boron standard solutions in various concentrations (1-100 mg/L) were prepared by diluting the ICP-AES standard solution (SPEX, 1,000 mg/L, ^{10}B content = 19.8%). Collodion solution was prepared by mixing Collodion and ethyl alcohol at a 1 : 1 ratio, while 0.1 mL of the concentrated boron stock solution was added into 2 mL of the mixed solution of Collodion to make 1.0, 5.0, 10.0, 25.0 mg/L of a standard boron solution.

Sample preparation and neutron irradiation. In this study, a multi-dot plate has been utilized to provide a good reproducibility for the sample preparation. The multi-dot plate provides a fixed standard shape of the sample solution which remains inside of the printed circle, and consequently increases the reproducibility of the boron analysis. The details of the procedure for preparing a multi-dot plate are described in a previous paper.[11] A short description is included in this paper.

Sample solution was placed inside a printed circle (3 mm id.) on the surface of a solid track detector. The circles, which served as a boundary wall on the Lexan detector for the sample solution to remain inside the circle area, were drawn by a printing using a copier. Normally, there are 10 or more circles on the 30 × 100 mm Lexan detector plate. An additional Lexan detector was mounted onto the plate on which the samples were loaded. The Lexan detectors were then inserted into a 1 mm thick Cd box as shown in Figure 1 and placed in the thermal column of the HANARO research reactor in the Korea Atomic Energy Research Institute, and irradiated to a thermal flux of 2×10^{14} n/cm^2·sec for 30 seconds. The irradiated sample was then left standing for a week for a cooling at room temperature.

Etching procedure. Following the irradiation, the solid detector was etched using a solution of 2.5 M NaOH at a temperature of 60 °C and then washed with distilled water several times and dried in air for a microscopic observation. The number of tracks was counted from an area of 1.22 ± 0.03 mm^2/detector by using a digital image analyzer system with an optical microscopy. This procedure was repeated for 7 times for each sample and the highest and lowest data were eliminated.

Calibration and analytical method. The standard solutions were prepared by diluting 1000 ppm of a boric acid solution which was made from boron enriched to 95 at % in ^{10}B. The boron concentration of the sample was calculated from a calibration curve of a number of tracks as a function of the ^{10}B concentration derived from a set of standard solutions containing a range of known ^{10}B concentrations which were processed and irradiated on the same solid detector plate. The concentration of ^{10}B was determined by comparing the slope of the detector response for the sample with that of a calibration curve of the detector response obtained with known concentrations of ^{10}B in a standard solution.

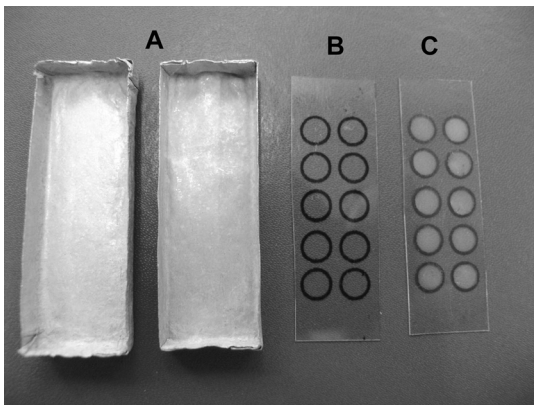

Figure 1. Photos of a Cd-foil box and a dropped B sample for a neutron irradiation. A is a Cd-foil box, B is a plain CN-85 multi-dot plate, and C is a CN-85 multi-dot plate with a sample.

Results and Discussion

Optimal conditions for the nuclear track detectors. The detection sensitivities of various solid track detectors were evaluated by exposing them to a mixed alpha radio-isotope source of ^{239}Pu, ^{241}Am and ^{244}Cm to establish the optimum conditions for an alpha track measurement. Polycarbonates (Lexan and CR-39) and cellulose nitrate (CN-85) were tested to establish a proper solid track detector for providing a good alpha track efficiency. It was found that it took more than 3 hours of an etching time to observe the alpha tracks on the polycarbonate detector with 2.5 M NaOH solution at 60 °C. However, the CN-85 detector showed good alpha track efficiency between 10 to 40 minutes of etching time as shown in Figure 1 under the same etching conditions.

Optimization of the neutron flux by using Cd-foil. Determination of boron in an aqueous solution can be achieved by counting the number of alpha tracks on the selected solid detector caused by the (n, α) nuclear reaction of boron. Therefore, the number of alpha tracks should also be optimized within the optically countable range. Since too many tracks were observed after an irradiation to a thermal neutron flux of 2×10^{14} n/cm^2·sec for 2 minutes, various thickness of the cadmium foils (0.1, 0.25, 0.5 and 1 mm) were used to reduce the thermal neutron flux. The calculated thermal flux with the cadmium foils were 3.2×10^{12}, 6.0×10^{11}, 3.4×10^{10}, 1.2×10^{8} n/cm^2·sec, respectively.

Boron standard solutions in the concentration range of 0 to 25 mg/L were prepared by an addition of the Collodion solution which was used for a better dispersion of the sample solution on the surface of the track detector. Several Cd-foil boxes were constructed with various thicknesses of the cadmium foils in order to cover the CN-85 solid detector as shown in Figure 1. The measured numbers of alpha tracks after an irradiation in the HANARO reactor for 30 seconds using various thicknesses of the cadmium foils are listed in Table 1. When using the Cd-foil of a 1 mm thickness, the CN-85 detector was strongly damaged by the heat production from the nuclear reaction between the Cd-foil and the neutrons. It seemed that the use of the Cd-foil of 0.25 mm provided the optimum countable tracks for the boron concentration in the range of 0 to 25 mg/L.

Enhancement of the reproducibility for the alpha track measurements. In the quantitative analysis of boron by using the alpha track analysis, the shape or area of a sample on the solid track detector becomes very important especially for the analysis of liquid samples. In this study, a multi-dot plate has been developed for this purpose. The multi-dot plate provides a fixed standard shape of the sample solution which remains inside the printed circle, and consequently increases the reproducibility of the boron analysis. In

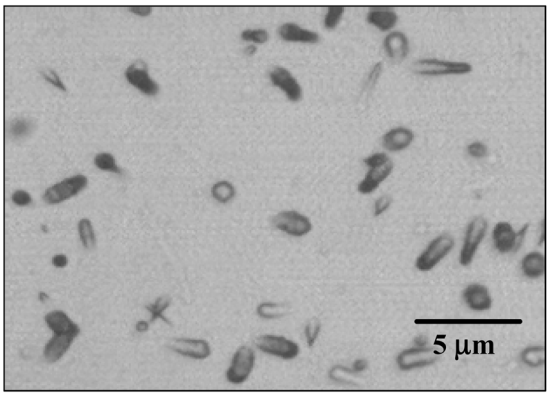

Figure 2. Alpha tracks on the CN-85 detector with an etching time of 20 minutes. Etching was done with 2.5 M NaOH at 60 °C. The magnification of the figure is × 200.

addition to this, the amount of dispersing agent (Collodion) can also influence the reproducibility. Since, Collodion did not mixed well with aqueous samples, ethyl alcohol was added to the sample solution to help the mixing of the Collodion and the aqueous samples. Figure 2 shows the shape of the dried sample on the surface of the multi-dot plates. Mixing ratio of the Collodion, ethyl alcohol and the aqueous sample was 6.4 : 12.6 : 1 which provided a good dispersion of the sample solution.

Determination of the ^{10}B enrichments and the total B by an alpha track analysis. Various ^{10}B enrichment (10% to 50%) stock solutions were prepared using the ^{10}B (99 atom%, Aldrich) and ^{11}B (99 atom%, Aldrich) standard solutions. The reference solutions with various total B concentrations were prepared by diluting the stock solution to determine the correlation between the number of alpha tracks and the B concentration as well as the ^{10}B enrichment. Figure 3 shows the changes in the number of alpha tracks on the CN-85 detector with increasing B concentrations from 0 to 25 mg/L (^{10}B enrichment = 20%). The number of alpha tracks was measured in an area of 60 × 40 μm^2 under a digital image analyzer system with a × 1000 magnification.

Figure 4 is a graph of the detector response versus the total boron concentration in various ^{10}B enrichment standard reference solutions, plotted with a least squares fit of the straight lines. The number of alpha tracks for each ^{10}B enrichment (10-50%) was also linear to the various total boron concentrations (1-15 mg/L). Note that each calibration line of the various ^{10}B enrichments shows the different slope.

Table 1. Alpha tracks depend on the Cd-foil thickness

Boron concentration (mg/L)	Cd-foil thickness (mm)			
	0.1	0.25	0.5	1.0
0	131	65	44	
1	341	152	82	The sample was deformed after the irradiation
5	585	183	104	
10	604	229	144	
25	626	360	60	

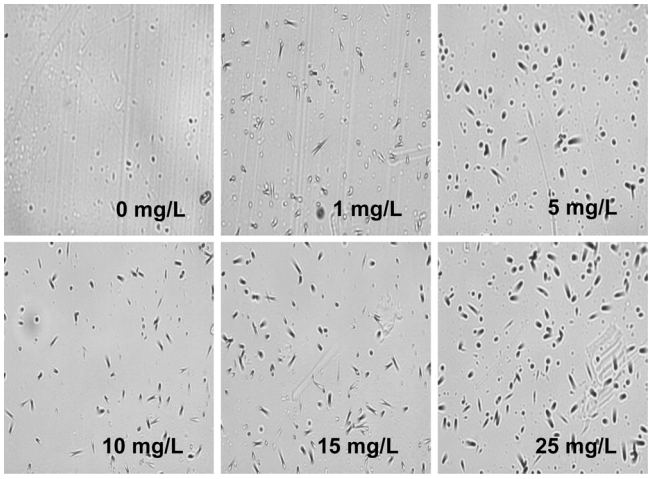

Figure 3. Alpha tracks on the CN-85 detector with various B concentrations. Etching was done with 2.5 M NaOH at 40 °C. The magnification of picture is × 200.

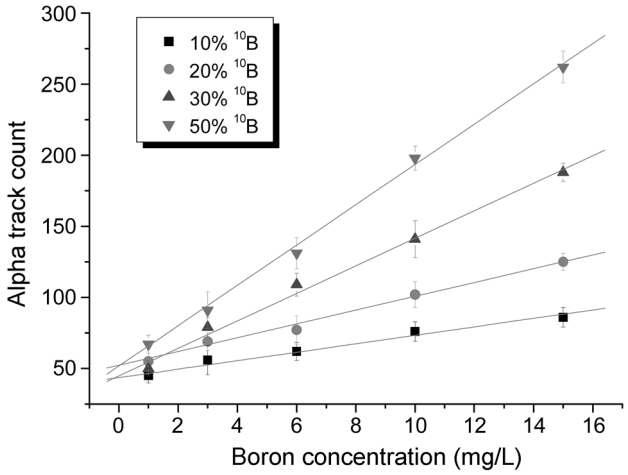

Figure 4. Correlation of the alpha track counts with various boron enrichments and concentrations.

The slope of the calibration curve increases with ^{10}B enrichment as shown in Table 2. The concentration of boron in an unknown sample can be determined from this calibration curve. The slopes of the regression line in the calibration curves were plotted against the ^{10}B enrichment in Figure 5. The ^{10}B enrichment for an unknown sample can be obtained from this regression equation.

The detection limit of this analytical method was determined from the calibration curves shown in Figure 4 by using a fundamental assumption of the unweighted least-squares method where each point on the plot has a normally

Table 2. Results of the alpha track counts according to the boron concentration

^{10}B enrichment (%)	Slope	Intercept	Corr. coeff. (R)
10	2.97 ± 0.57	43.6 ± 4.8	0.9915
20	4.86 ± 0.60	52.2 ± 5.8	0.9970
30	9.62 ± 0.86	44.7 ± 4.5	0.9967
50	14.2 ± 0.81	51.8 ± 6.2	0.9989

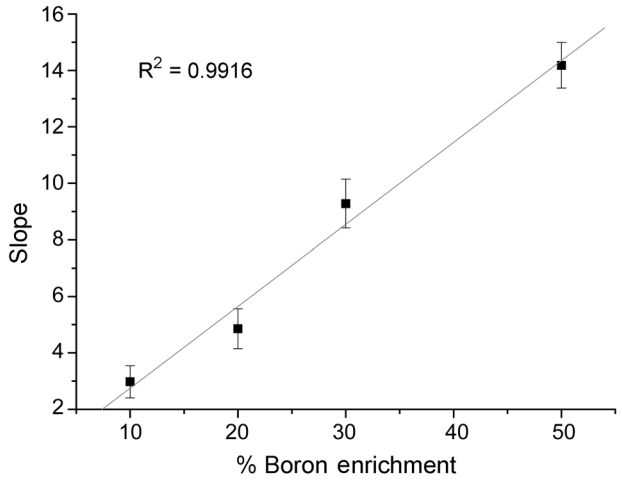

Figure 5. Standard calibration curve for the determination of the boron enrichment.

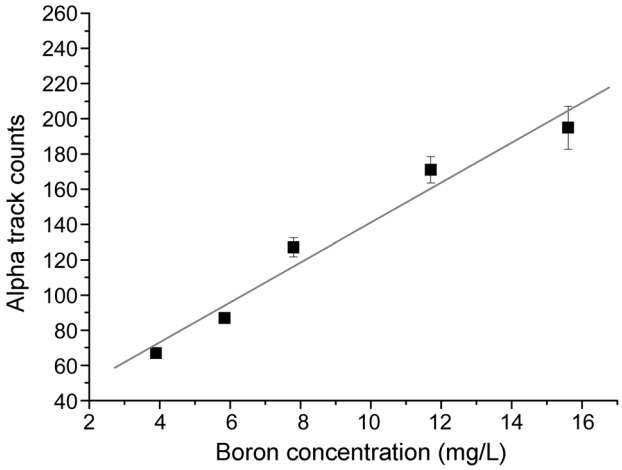

Figure 6. Correlation of the alpha track counts with various boron concentrations for an unknown biological BNCT sample.

distributed variation with a standard deviation estimated by the errors in the slope and the intercept of the regression line.[12] Use of the regression equations yielded detection limits of 6.8, 2.5, 2.4, 6.8 ng for the ^{10}B enrichments of 10, 20, 30, 50%, respectively.

Application to the biological BNCT sample. The alpha track technique was evaluated by applying it to the analysis of ^{10}B in a biological sample used for a BNCT experiment. The ^{10}B containing biological sample was prepared by the injection of a dose of 750 mg/kg body weight in a mouse for the BNCT experiment in the HANARO BNCT facility at KAERI. A freeze dried tumor cell sample (200 mg) was used in this work. The ^{10}B concentration of this sample is expected to be in the range of 50 to 120 μg/g.

The analysis of total boron content in the sample was performed by using the ICP-AES technique after a dissolution process with a mixture of nitric acid and hydroperoxide by using a microwave digestion system (Milestone MLS-1200). The isotopic ratio (^{10}B/^{11}B) of boron was measured by using the negative ions TIMS method with $^{10}BO_2^-$ and $^{11}BO_2^-$ as described elsewhere.[8] The enrichment factor of ^{10}B was found to be 42.0 ± 2.9%.

As shown in Table 3, the total boron concentration of the biological sample was found to be 80.0 ± 6.0 μg/g by ICP-AES. The sample solution was diluted to the range of 2 to 16 μm/L prior to the alpha track measurement. The number of alpha tracks were counted and plotted against the boron concentration as shown in Figure 6. From the slope of the regression curve (11.33 ± 1.22, R^2 = 0.983) for the unknown sample, the enrichment factor of ^{10}B was calculated as 39.6 ± 4.8. This result agrees well with that measured by TIMS within a 10% relative error.

Table 3. Comparison of the analytical results measured by different methods

	Track method	TIMS	ICP-AES
Total boron	–	–	80.0 ± 6.0
^{10}B enrichment (%)	39.6 ± 4.8	42.0 ± 2.9	–

Conclusion

The enrichment factor of ^{10}B of boron containing solution sample has been determined by using an alpha track technique. The home-made multi-dot detector plate was utilized in this study to increase the reproducibility of the measurement. This alpha track technique was applied to a BNCT sample and its result agrees well with that measured by TIMS within 10% relative error. Consequently, the isotopic ratio measurement technique by using the alpha track technique can be used for a cross-checking of the PGNAA results for the BNCT samples and also can be applied to the determination of the boron isotopic ratio of the primary cooling water in nuclear power plants.

Acknowledgement. This work has been accomplished under the fund of the Mid- and Long-term Nuclear Research & Development Program of the Ministry of Science and Technology, Korea.

References

1. Probst, T. U. *Fresenius J. Anal. Chem.* **1999**, *364*, 391.
2. You, C. F.; Spivack, A. J.; Gieskes, J. M.; Rosenbauer, R.; Bischoff, J. L. *Geochimica et Cosmochimica Acta* **1995**, *59*, 2435.
3. Palmer, M. R.; Helvaci, C. *Geochimica et Cosmochimica Acta* **1957**, *61/15*, 3161.
4. May, P. W.; Rosser, K. N.; Fox, N. A.; Younes, C. M.; Beardmore, G. *Diamond and Related Materials* **1997**, *6*, 450.
5. Jiang, S.; Palmer, M. R.; Peng, Q.; Yang, J. *Chemical Geology* **1997**, *135*, 189.
6. Pillay, A. E.; Peisach, M. *J. Radioanal. Nucl. Chem.* **1991**, *151*, 379.
7. Sekerka, I.; Lechner, J. F. *Analytica Chimica Acta* **1990**, *234*, 199.
8. Jeon, Y. S.; Cho, K. S.; Han, S. H.; Park, Y. J.; Jee, K. Y. *Analytical Science and Technology* **2005**, *18*, 27.
9. Hemming, N. G.; Hanson, G. N. *Chem. Geol.* **1994**, *114*, 147.
10. Yanagie, H.; Ogura, K.; Matsumoto, T.; Eriguchi, M.; Kobayashi, H. *Nucl. Instr. Met. Phys. Res. A* **1999**, *424/1*, 122.
11. Park, Y. J.; Pyo, H. Y.; Song, B. C.; Jee, K. Y. *Analytical Science and Technology* **2004**, *17*, 434.
12. Miller, J. C.; Miller, J. N. *Statistics for Analytical Chemistry*, 2nd ed.; Ellis Horwood Limited: 1988; p 115.