

Determination of the mass fraction of ^{10}B in boric acid by the measurement of thermal neutron flux depression

Andrzej Bolewski Jr,
Marek Ciechanowski,
Andrzej Kreft

Abstract. A thermal neutron absorption technique has been improved with the aid of Monte Carlo N-particle (MCNP) modelling and used for the determination of the mass fraction of ^{10}B in boric acid. A relative standard deviation of that determination has been estimated to be below 0.12%. Owing to the good precision and simplicity, the presented technique could be helpful in nuclear plants with pressurized water reactors, where boric acid is added to the primary circuit coolant to control the chain reaction. Possible applications include the checking of the actual mass fraction of ^{10}B in lots of boric acid delivered to nuclear power plants as well as calibration of instruments used for on-line monitoring the content of ^{10}B in reactor coolants.

Key words: ^{10}B • boric acid • ^{252}Cf neutron source • Monte Carlo N-particle (MCNP) • reactor coolant • thermal neutron absorption

Introduction

Boron and its compounds are extensively used in nuclear industry as strong thermal neutron absorbers. In particular, in nuclear power plants with pressurized water reactors (PWR), boric acid (H_3BO_3) is added to the primary circuit coolant with the aim of controlling the chain reaction. Owing to the application of the neutron-absorbing coolant, the irregularities in the power density distribution and fuel consumption within the reactor core can be avoided. Thereby, performance of nuclear power plants can be improved. Concentration of the neutron absorber in the coolant should be reduced commensurably with increasing fuel burn-up. Uncontrolled increase or reduction of its content would lead to an operational upset, so the continuous monitoring of its concentration in the reactor coolant is of great significance. As is known, natural boron is a mixture of ^{10}B and ^{11}B isotopes with abundances of about 20 and 80%, respectively. Thermal neutron absorption cross-sections of ^{10}B and ^{11}B are 3843 b and 0.0055 b, respectively. In this connection, the actual factor affecting the reactor performance is the content of ^{10}B isotope in the coolant. It is also known that the isotopic composition of natural boron is not fixed and varies depending on its origin. Besides, boric acid enriched in ^{10}B is increasingly used [14]. In practice, the content of ^{10}B in boric acid is frequently not known at the moment of purchasing the material [16]. Furthermore, ^{10}B added to the reactor coolant is constantly burnt out during the

A. Bolewski Jr, M. Ciechanowski, A. Kreft[✉]
AGH University of Science and Technology,
Faculty of Physics and Applied Computer Science,
Department of Applied Nuclear Physics,
al. A. Mickiewicza 30, 30-059 Krakow, Poland,
Tel.: +48 12 617 4153, Fax: +48 12 634 0010,
E-mail: Andrzej.Kreft@fis.agh.edu.pl

Received: 30 January 2012
Accepted: 13 March 2012

reactor operation. For those reasons, chemical methods are not adequate for determining the content of ^{10}B of in the reactor coolant. The above facts resulted in the development of measurement systems sensitive specifically to ^{10}B isotope. Techniques based on the thermal neutron absorption, i.e. on the same physical principle that is applied to the reactor control, appeared to be especially suitable for this purpose. Different versions of such devices designed for continuous on-line or off-line monitoring of the concentration of ^{10}B in the reactor coolant have been developed and perfected since the beginning of the PWR technology [1, 6, 9, 10, 14, 16, 17]. All instruments of this type require calibration which may be a quite complex task, especially in the case of instruments designed for on-line monitoring of ^{10}B content in technological circuits of nuclear power plants. Every calibration procedure is based on the use of proper calibration solutions of boric acid. The most direct, but costly way, is to make calibration solutions using an isotopic reference material for ^{10}B assays. Calibration solutions can be also prepared of boric acid taken from the same lot that is added to the reactor coolant as long as the content of ^{10}B in calibration solutions is accurately determined. As mentioned by Shul *et al.* [16], it can be done using inductively coupled plasma mass spectrometry (ICP-MS). It seems that this goal could be also attained with the aid of thermal neutron absorption techniques, like those developed by Bolewski *et al.* [4], Brooke *et al.* [8], Gogitdze [11] or Herzog and Smolen [12]. For the sake of metrological traceability of the measurement system, any calibration should finally refer to the certified boric acid isotopic reference material like those available from NIST (USA) or IRMM (Belgium).

The aim of this work was to improve the thermal neutron absorption technique developed earlier [3–5] and to examine its capability for determining the mass fraction of ^{10}B in boric acid through the measurement of the mass fraction of ^{10}B in the purposely prepared water solution of this compound. The idea of measuring the mass fraction of ^{10}B directly in boric acid powder was considered but was abandoned because of difficulties concerning the preparation of homogeneous samples.

A good deal of attention was given to improve the measurement device and to optimize the measurement procedure in order to increase the sensitivity of the technique and reduce the uncertainty of assays.

Experimental set-up and methodology

Figure 1 shows in outline the geometry of measurements and Monte Carlo (MC) simulations presented in this paper. This measurement device is designed in accordance with the conclusions drawn from previous works [3–5]. All its vital elements are placed in a large solid polyethylene rectangular prism. A sample of analysed liquid is poured into a container in the shape of double-walled tube. A ^{252}Cf neutron source and a thermal neutron detector are inserted axially into the inner tube of the sample container.

The neutron source is mounted in a 15 cm long Teflon rod (Fig. 1) which is connected coaxially with a 40 cm long steel screw bolt. A rotary motion of the

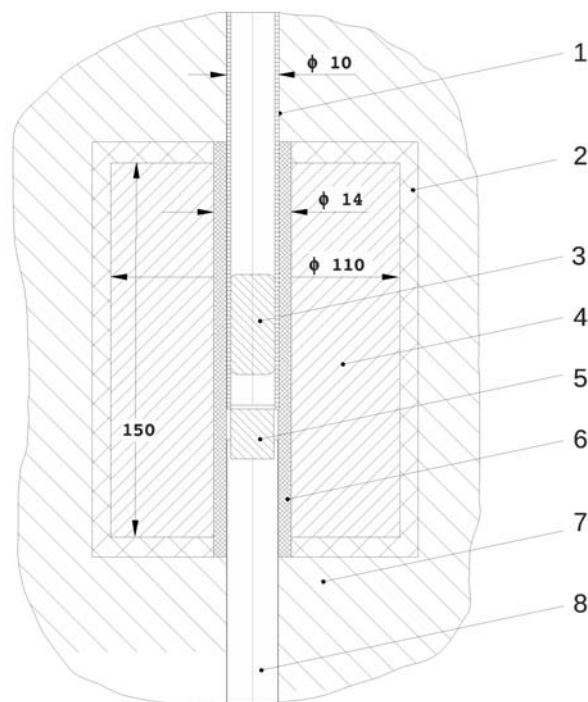


Fig. 1. Geometry of measurements and Monte Carlo simulations: 1 – stainless steel cathode of BF_3 proportional counter; 2 – sample container (polyethylene); 3 – active volume of BF_3 counter; 4 – sample; 5 – ^{252}Cf neutron source in stainless steel capsule; 6 – inner tube of the sample container (polyethylene or Teflon); 7 – polyethylene prism; 8 – Teflon rod. All dimension are given in millimetres.

screw bolt is blocked. A screw nut mating with the screw bolt is joined coaxially with the driven gear of a mitre gear. A driving gear of the mitre gear is fastened to a horizontal shaft which extends from the measurement device body. A small crank and a tachometer are attached to that shaft. With the use of the above described mechanism a rotary motion of the screw nut (driven by the crank and the mitre gear) is converted to an endwise movement of the screw bolt. In this way the neutron source can be safely shifted from the shielded position to the desired position on the axis of the sample container with reproducibility of 0.1 mm.

A slim proportional counter filled with BF_3 was chosen as the thermal neutron detector because of its relatively low efficiency for epithermal neutrons as compared to modern high-pressure ^3He counters [5]. Specifications of that counter are given in Table 1. The

Table 1. Specifications of BF_3 -filled proportional counter shown in Fig. 1

Parameter	Value
Overall length	300 mm
Maximum diameter	10 mm
Effective length	30 mm
Effective diameter	8 mm
Effective volume	1.5 cm ³
Neutron sensitive material	BF_3 enriched to 92% in ^{10}B
Fill pressure	0.092 MPa (700 mmHg)
Cathode material	Stainless steel
Operating voltage	1300 V
Thermal neutron sensitivity	0.07 cps/nv

detector is placed directly on the ^{252}Cf neutron source. The reproducibility of positioning the detector and neutron source in relation to the sample is a key issue because the detector response is sensitive to changes of the source-sample-detector configuration [3].

The present work was aimed, among other things, to attain the highest possible sensitivity of the technique. For this reason, the volume of the sample has been increased many times as compared to that in a previous study [4]. The capacity of the sample container shown in Fig. 1 is of 1370 ml. It has been decided to use samples of that size in consideration of the diffusion length of thermal neutrons (L) in water solution of boric acid. The value of L decreases with mass fraction of ^{10}B . For pure water $L = 2.755$ cm [2]. The radius of the sample shown in Fig. 1 is roughly twice as much. The maximum range of thermal neutrons is about $3L$. Therefore, neutrons being thermalized outside the sample have a little prospect of reaching the detector and influencing its response. The use of samples even much larger than 1370 ml would result in some small increase of the sensitivity, however at the expense of the handiness of the technique.

The main purpose of measurements was the validation of Monte Carlo modelling. Samples used for calibration of the investigated system were water solutions of boric acid standard (isotopic reference material). The solution with the highest mass fraction of boric acid standard (referred to as primary solution) was prepared first. Other calibration solutions were obtained by diluting the primary solution with pure water. Mass fractions of ^{10}B in calibration solutions were calculated from mass fractions of boric acid standard in its water solution and isotopic composition of boron specified for that standard. As a principle, measurements (and computer simulations) were performed using samples of the same mass. Every weighing related to the sample preparation was made with the required accuracy. To avoid any possible temperature effects, measurements were carried out at a constant temperature of 20°C .

Monte Carlo simulations were carried out to compare features of two versions of the measurement device shown in Fig. 1 which differ in construction of the sample container. The sample container made wholly of polyethylene (PE) and another one with the inner tube (element number 6 in Fig. 1) made of polytetrafluoroethylene (Teflon) were modelled. Real measurements were simulated with the use of the MCNP-4C code [7] and ENDF/B-VI.8 nuclear data library. Computations were performed in a general source mode. The ^{252}Cf source was specified as a point isotropic neutron source with Watt fission spectrum encased in a cylindrical stainless steel capsule 7.8 mm in diameter, 10 mm high and 1.6 mm thick. Calculations were aimed at determining the number of counts, i.e. number of $^{10}\text{B}(\text{n},\alpha)^7\text{Li}$ events within the sensitive volume of the BF_3 counter, per source neutron and its relative standard deviation. The total number of source neutron histories for each simulated case was 2 million. The resulting relative standard deviation of the number of counts varied with the mass fraction of ^{10}B in the modelled solution of boric acid. For instance, in the case of the sample container made wholly of polyethylene, the relative standard deviation of simulated number of counts was 0.66% for pure

water and 1.34% for the ^{10}B mass fraction of 550.8 $\mu\text{g/g}$ (ppm), respectively.

Results and discussion

Results of measurements and Monte Carlo simulations

Both experiments and Monte Carlo simulations dealt with the calibration of the measurement device described in the foregoing section. In this case the calibration consisted in relating the detector counting rate as the experimental value to the known mass fraction of ^{10}B in the water solution of boric acid. According to the experience resulting from the previous works [3–5] the following linear formula was chosen to describe the calibration curve:

$$(1) \quad \frac{1-x}{x} = S \cdot W$$

where W is the mass fraction of ^{10}B in water solution of boric acid, S is a constant to be determined by calibration and $x = I/I_0$ is the ratio of detector counting rates obtained from measurements made with the samples of water solution of boric acid (I) and pure water (I_0), respectively.

Results of experiments and MC simulations are shown in Fig. 2. Measured and calculated values of the quantity $(1-x)/x$ are related to the known mass fractions of ^{10}B in the calibration solutions, respectively. Experimental values of the counting rate ratio, $x = I/I_0$, were determined with the relative standard deviation of 0.05%. Numerical results of measurements and MCNP calculations obtained in the case of the sample container made wholly of polyethylene are given in Table 2. Comparison of those two data sets has been carried out with the use of the χ^2 (chi-square) test [13]. The resulting value of χ^2 for the analysed data sample is 18.09. For the significance level $\alpha = 0.05$ and 10 degrees of freedom, the percentile $\chi^2_{0.95}$ of χ^2 distribution is 18.31. Since the resulting χ^2 is not larger than $\chi^2_{0.95}$, we have no reason to discard the hypothesis that results of MCNP calculations are in agreement with results of measurements. It means that the measurements validate the MCNP simulations.

Both experiments and MC simulations show that in the case of the sample container made wholly of polyethylene the linearity of the calibration curve, i.e. the validity of Eq. (1), is limited to the mass fractions of ^{10}B smaller than 250 $\mu\text{g/g}$.

Results of MC simulations obtained for the sample container with the inner tube made of Teflon are much more favourable. In this case the calibration curve appears to be linear in a considerably extended range of ^{10}B mass fraction, at least up to 750 $\mu\text{g/g}$. The slope of the straight line fitted to the results of those simulations, i.e. the value of the constant S in Eq. (1), is: $S = 0.0060463 \pm 0.0000272$ ($\mu\text{g/g}$) $^{-1}$ (the estimated uncertainty means 1 standard deviation). The constant S is the sensitivity of the technique to the mass fraction of ^{10}B . It is proper to add that the sensitivity obtained with the use of 6 ml sample was 0.0004089 ($\mu\text{g/g}$) $^{-1}$ [4], i.e. about 15 times smaller.

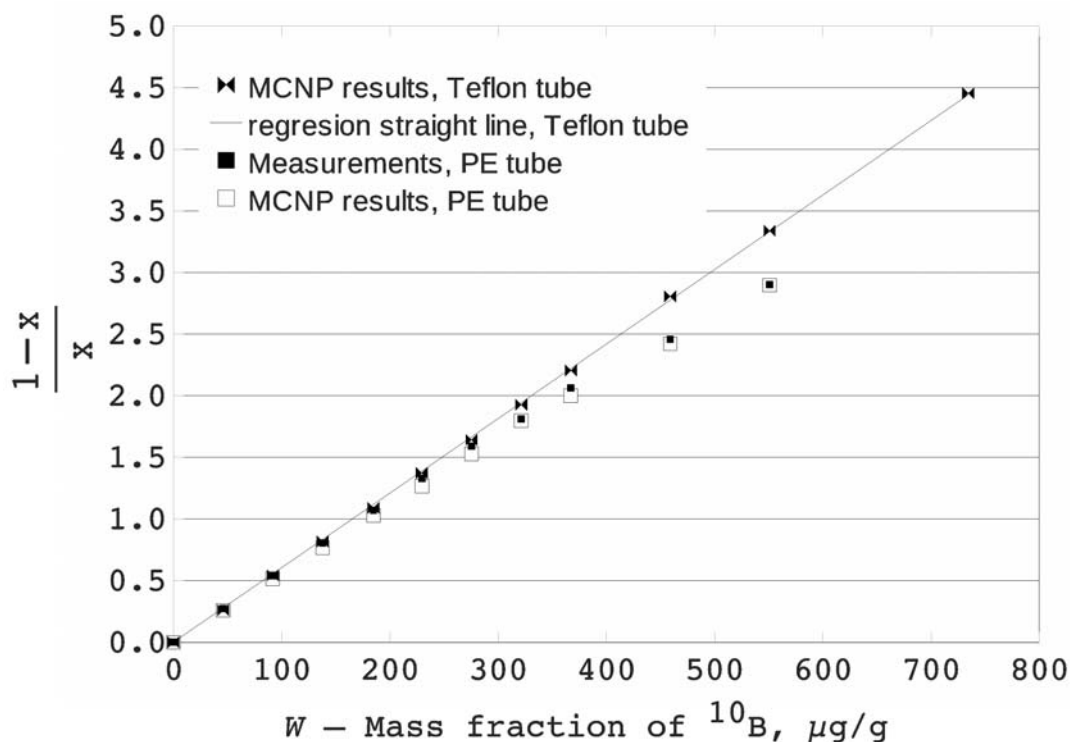


Fig. 2. Results of measurements and Monte Carlo simulations.

Table 2. Comparison of numerical results of measurements and MCNP simulations obtained in the case of the sample container made wholly of polyethylene

Mass fraction of ^{10}B ($\mu\text{g/g}$)	Measurements			MCNP simulations			$\frac{(\text{EXP} - \text{SIM})^2}{\sigma_{\text{EXP}}^2 + \sigma_{\text{SIM}}^2}$
	x_{exp}	$\text{EXP} = \frac{1 - x_{\text{exp}}}{x_{\text{exp}}}$	σ_{EXP}^a	x_{sim}	$\text{SIM} = \frac{1 - x_{\text{sim}}}{x_{\text{sim}}}$	σ_{SIM}^b	
0.0	0.999600	0.000400	0.000500	0.99850	0.00150	0.00935	0.0138
45.9	0.784917	0.274020	0.000637	0.79477	0.25826	0.0126	1.5605
91.8	0.648989	0.540858	0.000770	0.65998	0.51520	0.0161	2.5340
137.7	0.556539	0.796819	0.000898	0.56599	0.76682	0.0197	2.3142
184.7	0.482827	1.07114	0.00104	0.49263	1.0299	0.0238	2.9968
229.5	0.434558	1.30119	0.00115	0.44145	1.2653	0.0277	1.6759
275.4	0.385912	1.59126	0.00130	0.39551	1.5284	0.0322	3.8048
321.3	0.355541	1.81262	0.00141	0.35725	1.7992	0.0369	0.1320
367.2	0.326296	2.06470	0.00153	0.33328	2.0005	0.0406	2.4969
459.0	0.289090	2.45913	0.00173	0.29215	2.4229	0.0490	0.5460
550.8	0.256162	2.90378	0.00195	0.25659	2.8973	0.0582	0.0124

$$\chi^2 = 18.0873$$

^a σ_{EXP} denotes the standard deviation of EXP.

^b σ_{SIM} denotes the standard deviation of SIM.

Table 3 includes numerical results of MCNP calculations obtained in the case of the sample container with the inner tube made of Teflon and values of the quantity $(1-x)/x$ given by Eq. (1) fitted to results of MCNP calculations, respectively. The χ^2 test has been carried out to compare those two data sets. The resulting value of χ^2 for the tested data sample is 6.0185. For the significance level $\alpha = 0.1$ and 11 degrees of freedom, the percentile $\chi^2_{0.9}$ of χ^2 distribution is 17.28. Since the resulting value of χ^2 is smaller than $\chi^2_{0.9}$, we have no reason to discard hypothesis that the calibration curve of the measurement device is in the shape of Eq. (1).

There is a good physical foundation for a supposition that the difference between results of MCNP calculation obtained for two above-mentioned sample containers

is due to different impacts of polyethylene and Teflon tubes on the neutron spectrum inside the BF_3 counter. In an infinite medium a shape of the thermal neutron spectrum depends on the ratio $\Sigma_a/\xi\Sigma_s$, where Σ_a is the macroscopic thermal neutron absorption cross-section and $\xi\Sigma_s$ is the slowing down power [2]. The 1370 ml sample of water solution of boric acid is large enough to harden the neutron spectrum, to an extent depending on its Σ_a , as compared to that in the polyethylene block. Interactions of neutrons with the polyethylene shield of the detector cause a partial softening of the hardened spectrum which results in the increase of the detector response (because of its $1/v$ efficiency characteristics) and finally in the deviation of the calibration curve from the straight line. As the slowing down power of Teflon

Table 3. Validation of the calibration curve (1) by the χ^2 test carried out with the use of results of MCNP simulations obtained in the case of the sample container with the inner tube made of Teflon

Mass fraction of ¹⁰ B (µg/g)	Results of MCNP simulations			S·W (according to Eq. (1) fitted to results of MCNP simulations) ^b	$\frac{(SIM - S \cdot W)^2}{\sigma_{SIM}^2}$
	x_{sim}	$SIM = \frac{1 - x_{sim}}{x_{sim}}$	σ_{SIM}^a		
0.0	1.0000	0.0000	0.0089	0.0000	0.0000
45.9	0.7936	0.2600	0.0121	0.2775	2.1066
91.8	0.6482	0.5428	0.0157	0.5551	0.6095
137.7	0.5504	0.8169	0.0195	0.8326	0.6454
184.7	0.4784	1.0904	0.0237	1.1168	1.2386
229.5	0.4216	1.3716	0.0280	1.3876	0.3251
275.4	0.3784	1.6426	0.0326	1.6652	0.4811
321.3	0.3416	1.9273	0.0376	1.9427	0.1680
367.2	0.3121	2.2039	0.0581	2.2202	0.0783
459.0	0.2628	2.8051	0.0533	2.7753	0.3141
550.8	0.2304	3.3409	0.0643	3.3303	0.0271
734.4	0.1833	4.4544	0.0887	4.4404	0.0248
					$\chi^2 = 6.0185$

^a σ_{SIM} denotes the standard deviation of SIM.

^b Values of $(1 - x)/x$ given by formula (1) with substitution $S = 0.0060463$ (µg/g)⁻¹.

is incomparably smaller than that of polyethylene, the impact of the Teflon tube on the thermal neutron spectrum is negligible.

The impact of the polyethylene shield on the response of BF₃ counter placed in neutron-absorbing media was studied experimentally by Kreft *et al.* [15]. The measured counting rate of the shielded detector (I_{sh}) was always greater than that of the bare detector (I_b). It was ascertained that the ratio I_{sh}/I_b kept increasing with Σ_a of the medium and the thickness of the PE shield.

In spite of the use of sample containers made wholly of polyethylene no deviation from Eq. (1) was observed in previous implementations of the technique [3–5]. Reasons for that are threefold: much smaller samples, much lower Σ_a of the analysed materials and a thinner tube surrounding the detector.

Determination of the mass fraction of ¹⁰B in water solution of boric acid

As long as the linear Eq. (1) is valid, the determination of ¹⁰B mass fraction in water solution of boric acid will be very simple. Only one calibration solution is needed. Combining Eq. (1) written twice, for the analysed solution and for the standard solution, one finally obtains:

$$(2) \quad W = \frac{(1 - x)y}{(1 - y)x} W_s$$

where W_s is the known mass fraction of ¹⁰B in the water solution of the boric acid standard, whereas $y = I_s/I_{0s}$ is the ratio of detector counting rates obtained from measurements carried out for the calibration solution (I_s) and pure water (I_{0s}), respectively. To avoid correlation between ratios $x = I/I_0$ and $y = I_s/I_{0s}$ two independent measurements of the counting rates I_0 and I_{0s} should be done with pure water sample to obtain x and y values.

The applicability of Eq. (2) is strongly related to the validity of Eq. (1). Many efforts have been made to get calibration curve in the shape of Eq. (1). Nevertheless, in

order to minimize a bias caused by any deviation of the actual calibration curve from formula (1) the value of W_s should be chosen close to the measured value of W .

Determination of the mass fraction of ¹⁰B in boric acid

The mass fraction of ¹⁰B in the boric acid (W_{B10}) can be easily derived from W . Namely,

$$(3) \quad W_{B10} = \frac{W}{W_{BA}}$$

where W_{BA} is the mass fraction of boric acid in the purposely prepared water solution (the ratio of the boric acid mass to the total mass of the solution).

If boric acid is of stoichiometric purity, the isotopic composition of boron can be derived from the W_{B10} value.

Optimization of the procedures

Provided that uncertainty of every weighing related to the sample preparation is negligible and there is no deviation of the actual calibration curve from Eq. (1), the uncertainty of determination of the mass fraction of ¹⁰B in water solution of boric acid depends only on the counting statistics, and the quality of the boric acid standard. According to Eq. (2) and the law of error propagation, the relative standard deviation of the ¹⁰B mass fraction W may be estimated using the following formula:

$$(4) \quad \delta_x^2 = \frac{1}{It} + \frac{1}{I_0(t - t)}$$

where δ_x , δ_y and δ_{W_s} denote relative standard deviations of x , y and W_s , respectively.

It follows from the law of error propagation that $\delta_x^2 = \delta_I^2 + \delta_{I_0}^2$, where δ_I and δ_{I_0} are relative standard deviations of counting rates I and I_0 , respectively. According to counting statistics δ_I^2 and $\delta_{I_0}^2$ are equal to reciprocals of relevant total counts. Thus, the relative standard deviation δ_x can be expressed through the counting

rates I and I_0 conjointly with time intervals spent on measuring them.

$$(5) \quad \delta_w^2 = \frac{\delta_x^2}{(1-x)^2} + \frac{\delta_y^2}{(1-y)^2} + \delta_{W_S}^2$$

where t_t denotes the fixed total time available to carry out both I and I_0 measurements, t denotes the time interval allotted to measure the counting rate I whereas $(t_t - t)$ is the time interval allotted to measure the counting rate I_0 .

One can easily show that δ_x^2 , a function of t reaches its minimum at

$$(6) \quad t = t_t (1 + \sqrt{x})^{-1}$$

The optimum partition of the total available time t_t becomes especially important in cases of long-lasting counting experiments. In connection with Eq. (6) a question arises how to use it prior to measuring counting rates I_0 and I ? The answer is the following: values of I and I_0 can be obtained from brief counting experiments.

In the light of Eqs. (5) and (6) the first term in Eq. (4) reads:

$$(7) \quad \frac{\delta_x^2}{(1-x)^2} = \frac{1}{I_0 t_t} (\sqrt{x} - x)^{-2}$$

Analogically to Eq. (7), the optimum partition of the total time t_t allotted to measure the ratio $y = I_S/I_{0S}$ results in the following shape of the second term in Eq. (4):

$$(8) \quad \frac{\delta_y^2}{(1-y)^2} = \frac{1}{I_{0S} t_t} (\sqrt{y} - y)^{-2}$$

The right side of Eq. (8) reaches its minimum value equal to $16/(I_{0S} t_t)$ at $y = 0.25$. Using Eq. (1) one can substitute $y = 1/(S \cdot W_S + 1)$ and express the right side of Eq. (8) as the function of W_S :

$$(9) \quad \frac{\delta_y^2}{(1-y)^2} = \frac{1}{I_{0S} t_t} \left(\frac{1 + S \cdot W_S}{\sqrt{1 + S \cdot W_S} - 1} \right)^2$$

As the mass fraction W_S of ^{10}B in the calibration solution of the boric acid standard is chosen freely by the experimenter, its value is a subject for optimization. With the constant $S = 0.0060463 \text{ (}\mu\text{g/g)}^{-1}$ the right side of Eq. (9) reaches its minimum at $W_S = 496.2 \text{ }\mu\text{g/g}$. In practice, it is not necessary to use the calibration solution with W_S equal exactly to $496.2 \text{ }\mu\text{g/g}$ because that minimum is quite shallow. In the wide range of W_S between $250 \text{ }\mu\text{g/g}$ and $750 \text{ }\mu\text{g/g}$ the value of the second term in Eq. (4) does not exceed $18.5/(I_{0S} t_t)$. For any mass fraction of ^{10}B in the calibration solution falling within that range, the following inequality can be written:

$$(10) \quad \frac{\delta_y^2}{(1-y)^2} \leq \frac{18.5}{I_{0S} t_t}$$

With regard to the high cost of the boric acid isotopic reference material the choice of value of W_S close to $250 \text{ }\mu\text{g/g}$ seems to be reasonable.

The third term in Eq. (4) depends on the quality of the used boric acid standard. Provided that the calibration solution is prepared with accuracy, the relative standard deviation of W_S is equal to the relative standard

deviation ($\delta_{W_{B10S}}$) of the ^{10}B mass fraction in the boric acid standard (W_{B10S}). Hence $\delta_{W_S} = \delta_{W_{B10S}}$. In the case of high quality boric acid isotopic reference materials, like those distributed by NIST (USA) or IRMM (Belgium), the relative standard deviation $\delta_{W_{B10S}}$ does not exceed the value of 0.05%.

To sum up, under the above-mentioned conditions and an additional assumption $I_{0S} \cong I_0$, the attainable relative standard deviation of ^{10}B mass fraction in water solution of boric acid reads:

$$(11) \quad \delta_w \leq \left\{ \frac{1}{I_0 t_t} \left[(\sqrt{x} - x)^{-2} + 18.5 \right] + \delta_{W_{B10S}}^2 \right\}^{\frac{1}{2}}$$

Using again Eq. (1) one can substitute $x = 1/(S \cdot W + 1)$ and express δ_w as a function of W :

$$(12) \quad \delta_w \leq \left\{ \frac{1}{I_0 t_t} \left[\left(\frac{1 + S \cdot W}{\sqrt{1 + S \cdot W} - 1} \right)^2 + 18.5 \right] + \delta_{W_{B10S}}^2 \right\}^{\frac{1}{2}}$$

Formula (12) gives hints how to achieve a further reduction of δ_w . In order to attain a possibly high counting rate I_0 an adequate neutron source should be used. A practical limit set to the counting rate of the counting equipment used in this experiment was about 10^4 counts/s. In the case of the measurement system shown in Fig. 1 this limit can be reached with the use of ^{252}Cf neutron source emitting about 2×10^7 neutrons/s. As regards the total time t_t allotted to measurements of I and I_0 , the value of 1 h seems to be a reasonable assumption. The use of a weaker neutron source resulting in the lower counting rates can be counterbalanced by longer counting times.

Figure 3 shows a plot of the dependence of δ_w upon W given by the right side of formula (12) with substitutions: $I_0 t_t = 36 \times 10^6$, $S = 0.0060463 \text{ (}\mu\text{g/g)}^{-1}$ and $\delta_{W_{B10S}} = 0.05\%$.

If the actual goal of the measurement is to determine the mass fraction of ^{10}B in the given boric acid, the content of ^{10}B in the purposely prepared water solution of that boric acid solution should be optimized. According to formula (12) and Fig. 3, the relative standard deviation δ_w reaches its minimum of 0.11% at $W = 496.2 \text{ }\mu\text{g/g}$ (it corresponds to $x = 0.25$). On the other hand, the use of the solution with the mass fraction of ^{10}B close to that

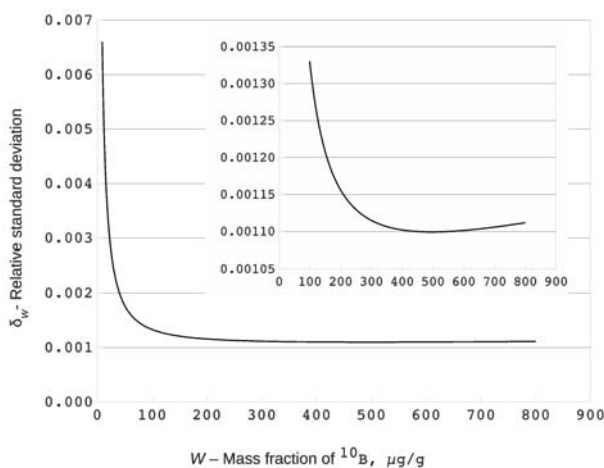


Fig. 3. Dependence of the attainable relative standard deviation δ_w on W as given by Eq. (12) with substitutions: $I_0 t_t = 36 \times 10^6$, $S = 0.0060463 \text{ (}\mu\text{g/g)}^{-1}$ and $\delta_{W_{B10S}} = 0.05\%$.

optimal value is not critical because within the wide range $160 \mu\text{g/g} < W < 750 \mu\text{g/g}$ the relative standard deviation δ_W does not vary significantly and does not exceed 0.12%. Therefore, to attain $\delta_W \leq 0.12\%$ it is sufficient to prepare the solution with the mass fraction of ^{10}B between 160 and 750 $\mu\text{g/g}$.

Assuming that the uncertainty of W_{BA} (the mass fraction of boric acid in its purposely prepared water solution) may be neglected, the relative standard deviations of W_{B10} (the mass fraction of ^{10}B in boric acid) is $\delta_{W_{B10}} = \delta_W$.

According to the above presented considerations, the optimized procedure for determining the mass fraction of ^{10}B in some water solution of boric acid includes the following steps.

Step 1. Carry out a brief counting experiment with the sample container filled with pure water to estimate roughly the counting rate I_0 . This step concerns only the very first use of the measurement device or the first use after its modification. Afterwards the value of I_0 is known from earlier assays.

Step 2. Carry out a brief counting experiment with the sample container filled with a given water solution of boric acid to estimate the counting rate I . Then estimate the ratio $x = I/I_0$.

Step 3. Determine the total time t_i available to carry out both measurements of counting rates I and I_0 (hint: to attain the relative standard deviation δ_W as shown in Fig. 3, a condition $I_0 t_i = 36 \times 10^6$ should be fulfilled). Then use the estimated value of x and Eq. (6) to divide in the best possible manner the total time t_i into time intervals t and $(t_i - t)$ allocated to determine the counting rates I and I_0 , respectively.

Step 4. Carry out the counting experiment over the time interval t with the sample of investigated water solution of boric acid and determine the counting rate I .

Step 5. Carry out the counting experiment over the time interval $(t_i - t)$ with the sample of pure water, determine the counting rate I_0 and calculate $x = I/I_0$.

Step 6. Use the boric acid standard to prepare its water solution with exactly known mass fraction of ^{10}B (W_s) within the range between 250 $\mu\text{g/g}$ and 750 $\mu\text{g/g}$, preferably close to 250 $\mu\text{g/g}$. Then use the calibration curve to estimate the ratio $y = I_s/I_{0s}$ corresponding to the value of W_s and employ Eq. (6) to make the optimum partition of the total time t_i into time intervals t and $(t_i - t)$ allotted to determine the counting rates I_s and I_{0s} , respectively.

Step 7. Carry out the counting experiment over the time interval t with the sample of the water solution of the boric acid standard and determine the counting rate I_s .

Step 8. Carry out the counting experiment over the time interval $(t_i - t)$ with the sample of pure water, determine the counting rate I_{0s} and calculate $y = I_s/I_{0s}$.

Step 9. Determine the mass fraction of ^{10}B (W) in the investigated water solution of boric acid with the use of Eq. (2). Then estimate the relative standard deviation δ_W using formula (12).

The procedure for determination of the mass fraction of ^{10}B in some lots of boric acid starts with the careful preparation of the water solution of that boric acid. The mass fraction of ^{10}B in this purposely prepared solution should fall between 160 $\mu\text{g/g}$ and 750 $\mu\text{g/g}$. The procedure

is then continued through steps 1–9 and finally the mass fraction of ^{10}B in the given boric acid (W_{B10}) is determined from Eq. (3). The relative standard deviation $\delta_{W_{B10}}$ is close to the value of δ_W estimated in Step 9.

Conclusions

An improved thermal neutron absorption technique to measure the mass fraction of ^{10}B in water solution of boric acid has been elaborated. Its performance has been verified experimentally and by the Monte Carlo modelling with the use of MCNP-4C code and ENDF/B-VI.8.2 nuclear data library. An agreement between results of experiments and computer simulations has been achieved.

MCNP modelling proved to be useful to optimize the measurement system. Computer simulations revealed that the polyethylene sample container in the shape of double-walled tube with the internal tube made of Teflon offered a distinct advantage over the sample container made wholly of polyethylene. With the use of the former one the mass fraction of ^{10}B can be measured within a considerably wider range, at least up to 750 $\mu\text{g/g}$.

The difference between results of MCNP calculation obtained for two versions of the measurement device appears to be consistent with the experimental evidence coming from earlier works.

The measurement procedure for determination of the mass fraction of ^{10}B in water solution of boric acid has been optimized both in respect of selecting the calibration standard and partition of the total time available to measure the ratio of two counting rates.

The measurement aimed at determining the mass fraction of ^{10}B in some boric acid should be carried out with the use of the purposely prepared water solution of that boric acid. In order to minimize the uncertainty of the assay the mass fraction of ^{10}B in this solution should be chosen between 160 and 750 $\mu\text{g/g}$. If the analysed boric acid is of stoichiometric purity, the isotopic composition of boron can be derived from the mass fraction of ^{10}B in this compound.

The main advantages of the presented measurement technique are its simplicity and good precision. With the use of 1370 ml sample, ^{252}Cf neutron source emitting about 2×10^7 neutrons/s and assuming 1 hour allotted to measure two counting rates, the relative standard deviation below 0.12% can be achieved for determination of the mass fraction of ^{10}B in water solution of boric acid. The relative standard deviation of determining the mass fraction of ^{10}B in boric acid has been estimated to be also below 0.12%.

The presented technique could facilitate the control of ^{10}B content in primary circuit coolants of nuclear reactors. In particular, it could be used for checking the actual mass fraction of ^{10}B in lots of boric acid being delivered to nuclear power plants. In consideration of good precision and reliability the presented technique is suitable for preparing secondary standards for calibration of instruments designed for on-line monitoring the content of ^{10}B in reactor coolants. Other possible applications include determining the content of ^{10}B in different compounds containing boron.

Acknowledgment. This work was supported by the Polish Ministry of Science and Higher Education and its grants for scientific research.

References

1. Bauer H, Nopitsch K, Gehring E (2002) Measurement device for determining boron concentration. US Patent no. US 6,345,080 B1
2. Beckurts KH, Wirtz K (1964) Neutron physics. Springer, Berlin
3. Bolewski Jr A, Ciechanowski M, Dydejczyk A, Kreft A (2005) A practical method for measuring the boron equivalent of graphite impurity. Nucl Instrum Methods B 237:602–612
4. Bolewski Jr A, Ciechanowski M, Dydejczyk A, Kreft A (2005) The measurement of thermal neutron flux depression for determining the concentration of boron in blood – suggestions as to further development of the method. Phys Med Biol 50:L21–L24
5. Bolewski Jr A, Ciechanowski M, Dydejczyk A, Kreft A (2008) On the optimization of the isotopic neutron source method for measuring the thermal neutron absorption cross section: Advantages and disadvantages of BF_3 and ^3He counters. Appl Radiat Isot 66:4:457–462
6. Bovin VP, Chulkin VL, Shagov SV (1975) Neutron-absorption analyzer of boron in the coolant of the primary circuit of water-cooled water-moderated power reactors. At Energ 38;5:283–286 (in Russian)
7. Briesmeister JF (ed) (2000) MCNPTM – A general Monte Carlo N-Particle Transport Code. Version 4C, LA-13709-M
8. Brooke SL, Green S, Charles MW, Beddoe AH (2001) The measurement of thermal neutron flux depression for determining the concentration of boron in blood. Phys Med Biol 46:707–715
9. Fährmann K, Jäpel F (1967) Eine Meßvorrichtung zur Überwachung der Borsäurekonzentration in Reaktor-anlagen. Kernenergie 10;11:337–340
10. Fährmann K, Westphal D (1975) Eine verbesserte Meßeinrichtung zur Überwachung der Borkonzentration in Reaktor-anlagen. Kernenergie 18;7:216–220
11. Gogitidze OA (1971) Determination of B-10 concentrations in compounds containing boron by means of thermal neutron absorption measurement technique. Kernenergie 14;3:87–89 (in Russian)
12. Herzog W, Smolen D (1982) Eine neue Methode der Qualitätskontrolle von Spezialbeton zur Neutronenabschirmung. Materialprüfung 24;1:10–12
13. Himmelblau DM (1970) Process analysis by statistical methods. Wiley, New York
14. IAEA (2002) High temperature on-line monitoring of water chemistry and corrosion control in water cooled power reactors. IAEA-TECDOC-1303. International Atomic Energy Agency, Vienna
15. Kreft A, Maloszewski P, Morstin K (1983) New concept of measuring the neutron absorption properties of bulk media. In: Böckhoff KH (ed) Nuclear data for science and technology. ECSC, EEC, EAEC, Brussels and Luxembourg, pp 900–901
16. Shul R, Klimes J, Rypar V, Novak E (2007) System for boron concentration measuring. In: Materials of IAEA Technical Meeting on Increasing Power Output and Performance of Nuclear Power Plants (NPPs) by Improved Instrumentation and Control (I&C) Systems, 29–31 May 2007, Prague. http://entrac.iaea.org/I-and-C/TM_PRAGUE_2007_05/CD/Papers/Klimes_paper.pdf (Last accessed on March 8, 2012)
17. Zaoui A, Bede G, Gacs I (1975) Borkonzentrationsmessung in 1. Kreislauf von Druckwasserreaktoren. Kernenergie 18;2:47–49