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Invited Article

Precise Determination of Silicon in Ceramic Reference Materials by Prompt Gamma Activation Analysis at JRR-3

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ABSTRACT

Prompt gamma activation analysis using a thermal neutron-guided beam at Japan Atomic Energy Agency JRR-3M was applied for the precise determination of Si in silicon nitride ceramic reference materials [Japan Ceramic Reference Material (JCRM) R 003]. In this study, the standard addition method coupled with internal standard was used for the nondestructive determination of Si in the sample. Cadmium was used as internal standard to obtain the linear calibration curves and to compensate for the neutron beam variability. The analytical result of determining Si in JCRM R 003 silicon nitride fine powder ceramic reference materials using prompt gamma activation analysis was in good agreement with that obtained by classical gravimetric analysis. The relative expanded measurement uncertainty ($k = 2$) associated with the determined value was 2.4%.

1. Introduction

The National Metrology Institute of Japan (NMIJ) is responsible for developing certified reference materials and establishing traceability to SI (International System of Units) for chemistry metrology in Japan. To realize SI traceability, the primary methods of measurement should be applied to characterize the reference materials. First of all, coulometry, gravimetric analysis, titration, isotope dilution mass spectrometry, and depression of the freezing-point method are recognized as potential primary methods of measurement in Consultative Committee for Amount of Substance-Metrology in Chemistry/the International Committee of Weights and Measures (CCQM/CIPM) under the Meter Convention. In addition, neutron activation analysis using the comparator standard is regarded as a potential primary method of measurement, and its analytical capability is discussed in CCQM [1]. Neutron activation analysis, which is well known as a nondestructive analytical method, can determine most elements without any chemical treatments—that is, neutron activation analysis is

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basically free from a potential risk of loss and contamination during the sample preparation and measurement procedure. The characteristics of prompt gamma activation analysis (PGAA) irradiated by neutron-guided beam are similar to those observed in neutron activation analysis. PGAA is also useful for the nondestructive determination of light elements such as hydrogen, boron, silicon, and sulfur in metal, biological, and geological samples [2–5]. PGAA, in particular, is a powerful analytical method for silicon and boron in refractory materials, such as silicon carbide and silicon nitride. Considerable skill is required for determination of Si in these ceramic materials with gravimetric analysis, because it is very difficult to decompose a sample completely. In general, a long irradiation and counting time is required to sufficiently measure the γ-ray spectrum by conventional straight neutron beam irradiation. A neutron beam focusing unit was developed to increase neutron flux in neutron-guided beam in JRR-3 of Japan Atomic Energy Agency (JAEA). The neutron beam flux (5.7×10^8 n/cm^2/s) is three times the conventional straight neutron beam [6]. The use of the focused neutron-guided beam enhances the count rate of prompt γ-ray. However, the profile of the focused neutron guided beam is commonly less homogeneous when compared with the straight neutron beam. Appropriate internal standards are required to correct the neutron beam profile for precise and accurate determination. Miura et al [7] determined boron in refractory ceramic samples by PGAA using focused neutron-guided beam coupled with the internal standard method [7]. The analytical sensitivity can be improved by using the focused neutron-guided beam; however, the variability of the analytical value increases. It assumes that the inhomogeneous profile of the focused neutron beam has resulted in an increase of the variability of the determined value. Therefore, the conventional straight neutron beam is suitable for the highly precise elemental analysis of PGAA.

The aim of this study was to evaluate the analytical performance of PGAA using the straight neutron-guided beam at JRR-3. PGAA was applied to the determination of Si in ceramics, and the effect of an internal standard and the measurement uncertainty in PGAA were investigated. The analytical result and measurement uncertainty of Si using an internal standard were compared with those obtained by the relative calibration method.

2. Materials and methods

2.1. Reagents and materials

Si metal (purity: 99.99%, powder, Lot No. 711W2251) purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) was used as additional standard in calibration for ceramic samples. NIST SRM (National Institute of Standards and Technology Standard Reference Material) 912a urea was used as a standard for nitrogen. The cadmium solution was prepared from the NMIJ primary standard of metal. The purity was 100.000 ± 0.001% and was determined by trace analysis. An aliquot of the primary cadmium metal (1.00 g) was weighed, dissolved with HNO_3 (1 + 9), and finally diluted to 1 kg with 0.05 mol/dm^3 in high-density polyethylene bottle to prepare the cadmium stock solution (approx. 1 g/kg). The cadmium working solution (mass fraction of Cd, 123.6 mg/kg) was prepared by diluting the cadmium stock solution with 0.05 mol/dm^3 HNO_3. The cadmium working solution was used as an internal standard for the samples.

Pure water used throughout the experiment was prepared with Milli-Q SP ICP-MS (Japan Millipore Ltd., Shinagawa, Japan). A perfluoroalkoxy alkane (PFA) microcentrifuge tube vial [PFA vial; volume, 1.5 mL; 11 mm (Φ) × 39 mm, 3.8 g] was used as a sample container for the PGAA experiment.

2.2. Sample

The Ceramic Society of Japan JCRM (Japan Ceramic Reference Material) fine silicon nitride fine powder reference material JCRM R 003 was analyzed using PGAA. The certified value of Si in JCRM R 003 is 59.55 ± 0.55% based on 10 gravimetric analytical data obtained from the round robin test by Japanese laboratories [8]. The certified value of nitrogen of the other main components in JCRM R 003 is 39.00 ± 0.10% based on titration after sample decomposition obtained from the above-mentioned round robin test [8].

2.3. Preparation of samples and standard addition samples

Four 300-mg aliquots of JCRM R 003 and three 300-mg aliquots of Si metal were weighed in the PFA vials. Six 300-mg aliquots of JCRM R 003 were weighed in the PFA vials for the standard addition method. An aliquot amount of the Si metal was added into the six PFA vials to prepare the standard addition samples. The levels of standard addition series were 0.27, 0.34, 0.54, 0.82, 0.68, and 1.12 g/g of added Si metal to the sample, respectively. Then approximately 300 mg of the Cd working solution was added into each PFA vial.

A 1.0822-g aliquot of NIST SRM 912a urea was weighed in another PFA vial, which was then used to measure the correction factor to correct the spectral interference of ^{14}N 3,532 keV peak for ^{28}Si 3,539 keV peak. In addition, a blank PFA vial was prepared that later used to measure the correction factor to correct the spectral interference of ^{19}F 556 keV peak for ^{131}Cd 558 keV [9].

2.4. PGAA system at JRR-3

The PGAA system at the JRR-3 research reactor of JAEA Tokai Research and Development Center was used for this study. The PGAA system consisted of a thermal neutron guide tube, a neutron beam shutter (Pb and B_4C), a neutron beam collimator (LiF), a sample box [polytetrafluoroethylene (PTFE)], a neutron beam stopper (Pb and B_4C), a neutron and γ-ray shield, and multimode γ-ray spectrometer. The PGAA system was set at the thermal neutron beam port (T1-4-1), and the flux was 1.6×10^8 n/cm^2/s with the peak neutron energy at 42 meV (0.14 nm). The thermal neutron beam was collimated in a 20 × 20 mm area by LiF collimator. The multimode γ-ray spectrometer consisted of a high-purity Ge detector (ORTEC GMX-2019-Plus-S, energy resolution at 1,332 keV; 1.75 keV, relative detection efficiency; 23.5%), $Bi_4Ge_3O_{12}$ (BGO) shielding

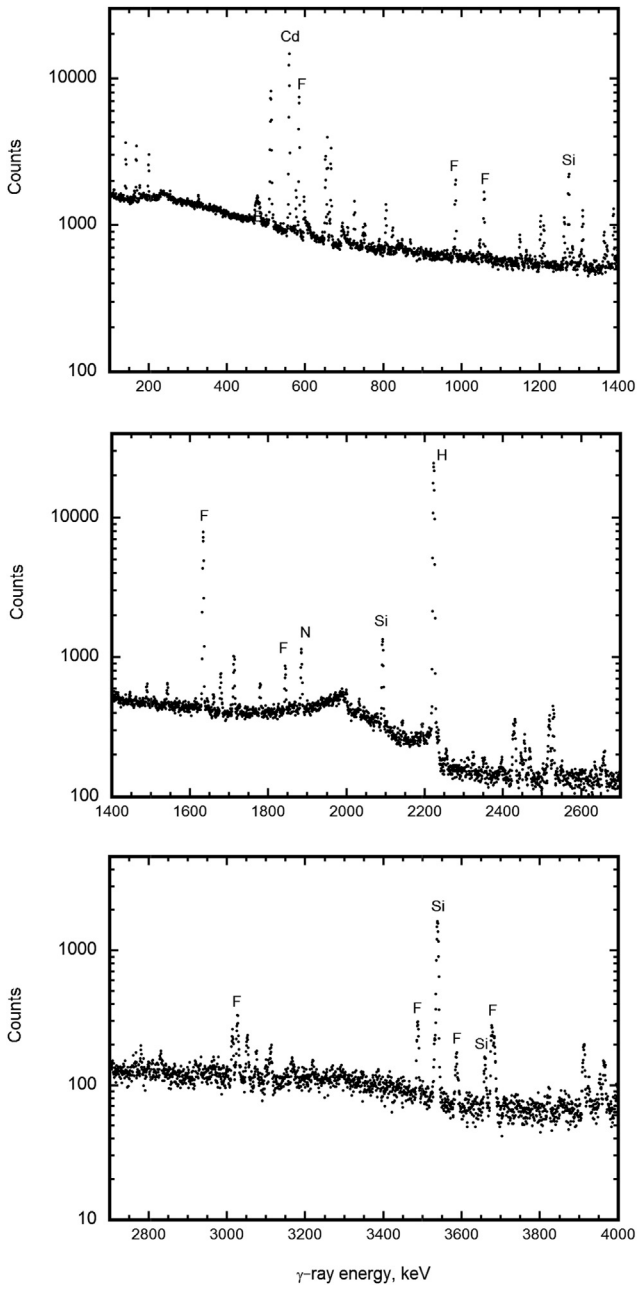

Fig. 1 – Typical prompt γ-ray spectrum of silicon nitride sample. Silicon nitride, 0.27 g; Cd, 36 μg; counting time, 7,229 seconds.

detectors, and a multichannel analyzer system controlled by a personal computer. The details of the PGAA system have already been described by Yonezawa et al [10] and Matue and Yonezawa [11]. The γ-ray detection efficiency curve of the γ-ray spectrometer for the sample to the detector distance of 24.5 cm was determined by Raman et al [12]. They measured the radioactivity standard source (^{60}Co, ^{75}Se, ^{88}Y, ^{133}Ba, ^{152}Eu, ^{207}Bi, ^{226}Ra, and ^{228}Th), radioactivity secondary source (^{24}Na, ^{46}Sc, ^{56}Mn, ^{75}Se, and ^{110m}Ag), and prompt γ-rays of nitrogen, carbon, and chlorine. The determined γ-ray detection efficiency curve of the γ-ray spectrometer was reported in the above article [12].

2.5. *Prompt gamma-ray measurement*

The samples were set on a PTFE sample holder using a 25-μm-thick fluorinated ethylene propylene resin film bag and 0.3-mm-diameter PTFE strings, and then the sample holder was mounted at a 45° angle to the neutron beam direction in the PTFE sample box. The samples were irradiated by the straight thermal neutron beam at JRR-3. The prompt γ-ray spectrum was measured with the Compton suppression PGAA system for 3,000–6,000 seconds according to the spectrum intensity. The measured prompt γ-rays were 559 keV (^{131}Cd), 1,273 keV (^{28}Si), 1,633 keV (^{19}F), 1,884 keV (^{14}N), 2,093 keV (^{28}Si), and 3,539 keV (^{28}Si). The irradiation of thermal neutron guided beam and the measurement of γ-ray spectrum were performed under He gas flow (1,000 mL/min) in the sample box to reduce the background γ-ray emitted from atmospheric N_2. The count rates of the γ-ray peaks were analyzed by SEIKO EG&G DS-P100/W32. The typical prompt γ-ray spectrum of the silicon nitride sample (0.27 g) including Cd (36 μg) as internal standard is shown as Fig. 1. The energy calibration of the spectrometer was performed using the γ-ray spectrum of 0.53 g of Si metal sample.

3. Results

3.1. *Interference correction*

The analytical sensitivity (cps/mg) of the measured element and interference of elements for measured prompt γ-ray are shown in Table 1. The certified value of nitrogen in JCRM R 003 is 39.00 ± 0.10%. Therefore, the amount of nitrogen in JCRM R 003 could not be negligible. The prompt γ-ray peak of ^{14}N 3,532 keV may interfere with ^{28}Si 3,539 keV prompt γ-ray peak. In the same way, ^{19}F 556 keV peak may interfere with ^{131}Cd 558 keV peak. In this study, the interferences of these peaks were investigated by measuring the γ-ray spectrum of the urea sample and the blank PFA vial. As a result, ^{14}N 3,532 keV peak interfered with Si 3,539 keV peak, and similarly ^{19}F 556 keV peak interfered with ^{131}Cd 558 keV peak. The interference of ^{14}N 3,532 keV was corrected by using a correcting factor method in which the count rate of ^{14}N 3,532 keV was calculated from the ratio to 1,885 keV peaks. In addition, the

Table 1 – Analytical sensitivities of measured element and interference of elements for measured prompt γ-ray.

Element	Eγ (keV)[a]	Analytical sensitivity[b] (cps/mg)	Interference element: prompt γ-ray energy[a] (relative intensity)
^{113}Cd	559	159	^{19}F: 556 keV (5.6%)
^{28}Si	1,273	6.11×10^{-3}	^{14}N: 3,532 keV (30%)
^{28}Si	2,093	5.02×10^{-3}	
^{28}Si	3,539	1.15×10^{-2}	

[a] Web database, National Nuclear Data Center, Thermal Neutron Capture γ's (CapGam; http://www.nndc.gov/capgam/).
[b] Analytical sensitivity was calculated from the mean value of more than three samples.

interference of ^{19}F 556 keV peak was corrected by using the count rate ratio of ^{19}F 556 to 1,633 keV.

4. Discussion

4.1. *Effects of internal standardization*

The previous researchers [4,10,13] presented the application of PGAA for the determination of Si in environmental and geological reference materials. The reported relative standard deviations (RSDs) of the determined values ranged from 5.2% to 6.9%. Using the internal standard can help reduce the variability of analytical results. For example, the RSD of the specific count rate of ^{28}Si 3,539 keV peak (cps/g) was improved to 2.7% ($n = 3$) from 3.6%, when the specific count rate of ^{131}Cd 558 keV peak (cps/g) was used as the internal standard. It is necessary to apply an internal standard in order to carry out precise measurements, for example, when Si is determined using PGAA [7]. In this study, the Cd solution was added to the measured samples as internal standard.

The determination of Si was performed with the standard addition method, as the detection efficiency of the spectrometer is not necessary. In the standard addition method, the measured signal is plotted on the y axis; the x axis is graduated in terms of the amounts of analyte added. The linear standard addition calibration curve is calculated, but space is provided for it to be extrapolated to the point on the x axis at which $y = 0$. The negative intercept of the calibration curve on the x axis corresponds to the amount of the analyte in the test sample [14]. The linear standard addition calibration curves for Si were obtained when ^{131}Cd (cps/mg) was used as internal standard. The correlation coefficient of the calibration curves was at least 0.999. The typical linear calibration curve of the standard addition method for Si determination is shown Fig. 2.

The RSDs of ^{28}Si 3,539 keV specific count rates (cps/g) of JCRM R 003 were 1.5% and 2.1% when Cd 558 keV and no peak were used as internal standard, respectively. These results suggest that use of an internal standard is essential for PGAA with the thermal neutron beam to carry out precise measurements. They also showed that the Cd 558 keV peak is very useful to compensate for the variability of the neutron beam irradiation.

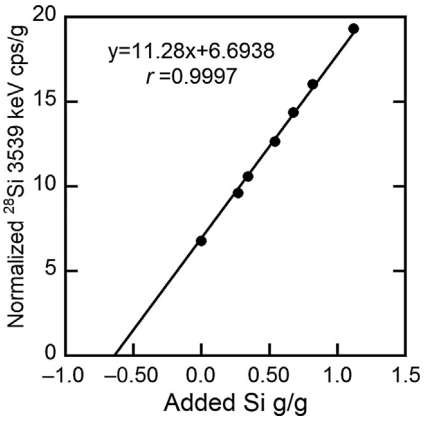

Fig. 2 – Calibration of Si in JCRM R 003 by PGAA using standard addition method with internal standard. JCRM, Japan Ceramic Reference Material; PGAA, prompt gamma activation analysis.

Table 2 – Analytical results of silicon in JCRM R 003 by PGAA using standard addition method with internal standard.

Run no.	1,273 keV Si (%)	2,092 keV Si (%)	3,539 keV Si (%)	Mean Si (%)
1	58.81	60.75	60.62	60.06
2	58.93	61.24	59.75	59.97
3	58.22	60.32	58.92	59.15
4	58.23	59.94	59.34	59.17
			Mean ± SD	59.59 ± 0.495
			RSD	0.83%
Analytical result of Si: Si (g/g) ± U (g/g)[a]		59.59% ± 1.4% (2.4% relative)		

JCRM, Japan Ceramic Reference Material; PGAA, prompt gamma activation analysis; RSD, relative standard deviation; SD, standard deviation.
[a] Expanded uncertainty (coverage factor, $k = 2$).

4.2. *Determination of Si in ceramic CRMs and estimation of measurements uncertainty*

The determination of Si in ceramic CRM was carried out via linear calibration curves of the standard addition method using an internal standard. Cd 559 keV peaks in the samples were used as internal standard. The analytical results are shown in Table 2. The analytical result of determining Si in JCRM R 003 silicon nitride powder (59.59% ± 1.4%, $k = 2$) is in good agreement with the certified value (59.55% ± 0.10%, $k = 2$), which was characterized by the analytical results obtained by classical gravimetric analysis. The RSD of sample measurement replication is 0.83% ($n = 4$), which was realized in a highly precise determination. In contrast, the analytical results of Si in the same sample using the conventional relative calibration method is 60.18% ± 2.4%, $k = 2$.

The measurement uncertainty budget is shown in Table 3, where the typical uncertainty components are listed. The

Table 3 – Uncertainty budget for analytical results of JCRM R 003.

Component	Relative standard uncertainty (%)
Preparation of sample	
Sample weighing	0.005
Internal standard addition	0.020
Metallic silicon purity	0.010
Internal standard weighing	0.03
Calibration by standard addition method	1.14
Sample measurement repeatability	0.41
Combined standard uncertainty(u_c)	1.2
Coverage factor	2
Expanded uncertainty ($k = 2$)	2.4

JCRM, Japan Ceramic Reference Material.

main component of the standard uncertainty was the calibration by standard addition method for JCRM R 003. The relative expanded uncertainty associated with the determined value was 2.4% (coverage factor, $k = 2$).

In this study, PGAA using the straight thermal neutron beam was applied to the precise determination of Si in silicon nitride ceramic CRM JCRM R003. The internal standard method was found to be useful in reducing measurement repeatability. The analytical result of Si in JCRM R 003 was in good agreement with the certified value. The relative expanded uncertainty (coverage factor, $k = 2$) was 2.4%. Using the standard addition method with internal standard, the relative expanded uncertainty fell to 2.4% from 4.0% (result obtained using the relative method). PGAA using the thermal neutron beam can successfully determine the main component of refractory ceramics without any sample dissolution.

Conflicts of interest

The authors declare no conflicts of interest.

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