Nuclear Engineering and Technology 48 (2016) 299–303

Available online at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Invited Article

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

Tsutomu Miura [a,*] *and Hideaki Matsue* [b]

[a] *National Metrology Institute of Japan-AIST, Tsukuba Central 3, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8563, Japan*

[b] *Quantum Beam Science Directorate, Japan Atomic Energy Agency, Shirane 2-4, Tokai, Ibaraki 319-1195, Japan*

ARTICLE INFO

Article history:
Received 10 February 2016
Accepted 18 February 2016
Available online 27 February 2016

Keywords:
Ceramics
Internal Standard
Neutron Guided Beam
Prompt Gamma Activation Analysis
Silicon
Standard Addition Method
Uncertainty

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

* *Corresponding author.*
E-mail address: t.miura@aist.go.jp (T. Miura).

http://dx.doi.org/10.1016/j.net.2016.02.005

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