# ANALYSIS OF RADIOACTIVE IMPURITIES IN ALUMINA AND SILICA USED FOR ELECTRONIC MATERIALS

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A developed neutron activation analysis(NAA) and gamma-spectrometry were applied to improve the analytical sensitivity and precision of impurities in electronic-circuit raw materials. It is well known that soft errors in high precision electronic circuits can be induced by alpha particles emitted from naturally occurring radioactive impurities such as U and Th. As electronic circuits have recently become smaller in dimension and higher in density, these alpha-particle emitting radioactive impurities must be strictly controlled. Therefore, new NAA methods have been established using a HTS(Hydraulic Transfer System) irradiation facility and a background reduction method. For eliminating or stabilizing fluctuated background caused by Rn-222 and its progeny nuclides in air, a nitrogen purging system is used. Using the developed NAA and gamma-spectrometry, ultra trace amounts of U(0.1ng/g) and Th(0.01ng/g) in an alumina ball and high purity silica used for an epoxy molding compound (EMC) could be determined.

**KEYWORDS** : NAA, Alumina, Silica, Uranium, Thorium, Soft Error

## 1. INTRODUCTION

The electric, electronic, mechanical and thermal characteristics of high density electronic devices can be affected by the physico-chemical characteristics of base materials as well as by trace impurities. It is well known that soft errors caused by trace $\alpha$-emitting impurities are one cause of the faulty operation of electronic devices. This phenomenon was initially reported in May[1] in the 1970s. Recently, a number of studies concentrating on the solving and preventing of soft errors have progressed in the military and airplane industries, as high precision electronic devices such as VLSI, DRAM, SRAM, are rapidly developing[2-6]. Neutron activation analysis(NAA) is known to be a useful technique for the determination of metallic elements in insoluble materials such as alumina and silica, due to its capabilities of nondestructive and absolute analyzable characteristics of a high sensitivity for most metallic elements[7-9]. Various conducting elements such as Na, Mg, Fe, Cu and Ti may decrease the conductance of alumina, and soft errors can occur as a result of $\alpha$-emitting elements such as U and Th. For these reasons, high purity alumina is required for use in electronic device materials. Alumina is also used in a ball form in industries that produce fine powders. The produced powder can be contaminated by metallic impurities in alumina balls due to their abrasion; therefore, strict quality control is required.

The aim of this work is the development of simple, accurate and sensitive NAA procedures for the determination of trace and ultra-trace metallic elements, particularly U and Th, in high purity silica and alumina materials. In order to achieve this aim, optimum NAA procedures were investigated, and a low background counting system was set up using a nitrogen purging system.

## 2. EXPERIMENTAL

Major and controlled impurities in silica and alumina have been determined using general NAA procedures. Neutron flux densities of PTS(Pneumatic Transfer System) and HTS facilities in HANARO have been measured by using Au(Au/Al alloy wire: 0.1274 % of gold, R/X, USA) and Co(Co/Al alloy wire: 1 % of cobalt, Degussa, FRG) flux monitors. For the determination of trace impurities in high purity silica, 5 g of Si powder was sealed in a high purity quartz tube, which was cleaned with hot nitric acid

and deionized water, using a high purity quartz torch. In addition, samples were irradiated in an HTS facility for 72 hours with a flux monitor. After five days of cooling, the irradiated samples were transferred to counting vials, and the medium half-lived nuclides were counted using a HPGe detector system(relative efficiency 30 %, FWHM 1.9 keV at 1.33 MeV, EG&G, USA). After 21 days of cooling, the samples were recounted for the long half-lived nuclides analysis. For the analysis of the alumina ball, 1 g of the sample was sealed in a polyethylene vial and irradiated in the PTS facility for 20 minutes with the flux monitor. After three days of cooling, the sample was transferred to a counting vial and the medium half-lived nuclides were counted. Long half-lived nuclides also were counted after 20 days of cooling. The contents of each element were calculated using a U-fission effect corrected by a SCM-UF program.

A low background gamma-spectrometry was established using a simple nitrogen purging system[10]. This system could be used to minimize and stabilize the background spectrum due to natural radioactive nuclides, especially Rn-222, and its progenies in the atmosphere of the counting room and chamber.

## 3. RESULTS AND DISCUSSION

Nuclear data of the controlled impurities in silica and alumina can be found at Table 1.

For the determination of ultra trace impurities in the high purity silica, the neutron flux densities of each irradiation facility of HANARO were measured, and the results are shown in Table 2. From these results, it is clear that PTS and HTS-2 have the lowest and highest thermal neutron flux, respectively. High purity silica was irradiated in each irradiation facility, and the lower limit of detections(LLD) of six impurities are shown in Fig. 1, where the values are compared to those for PTS. The thermal neutron flux is the highest at HTS-2, and the epithermal neutron flux is different. The $\Phi_{th}/\Phi_{epi}$ ratio was highest at PTS and lowest at HTS-2. This value reflects the sensitivity difference of each element. As each element has a different thermal and epithermal neutron cross section value, a differing amounts of the radionuclide were produced by the (n,$\gamma$) reaction. The HTS-2 facility has the highest thermal and epithermal neutron flux, thus the highest amount of radionuclide will be produced. From the sensitivity comparison results, the lowest LLD(Low Limit of Detection) value of each element

**Table 2.** The Neutron Flux of Each Irradiation Facility (Unit ; n · cm$^{-2}$ · s$^{-1}$)

| Facility | $\Phi_{th}$* | $\Phi_{epi}$** | $\Phi_{th}/\Phi_{epi}$ |
|---|---|---|---|
| PTS | $2.28 \times 10^{13}$ | $1.85 \times 10^{10}$ | 1232.4 |
| HTS-1 | $8.37 \times 10^{13}$ | $3.61 \times 10^{12}$ | 23.2 |
| HTS-2 | $1.32 \times 10^{14}$ | $1.57 \times 10^{13}$ | 8.4 |
| HTS-3 | $4.88 \times 10^{13}$ | $8.75 \times 10^{10}$ | 557.7 |

* $\Phi_{th}$ : Thermal neutron flux

** $\Phi_{epi}$ : Epithermal neutron flux

**Table 1.** Nuclear Data of the Controlled Impurities in High Purity Silica and Alumina

| *$E_a$ | $N_p$ | $\theta$ | $\sigma_t$ | $\sigma_e$ | $T_{1/2}$ | $E_\gamma$ |
|---|---|---|---|---|---|---|
| Na | $^{24}$Na | 100 | 0.53 | 0.34 | 15 | 1368 |
| Fe | $^{59}$Fe | 0.31 | 1.15 | 1.7 | 1070 | 1092 |
| U | $^{239}$Np** | 99.3 | 2.7 | 275 | 56.4 | 278 |
| Th | $^{233}$Pa** | 100 | 7.4 | 72.4 | 648 | 311 |

* $E_a$ : Element.
$N_p$ : Product nuclide.
$\theta$ : Natural abundance, %.
$\sigma_t$ : Thermal neutron cross-section, barn.
$\sigma_e$ : Epithermal neutron cross-section, barn.
$T_{1/2}$ : Half life, h.
$E_\gamma$ : Emitted $\gamma$ energy, keV.

** $^{238}$U(n,$\gamma$) $^{239}$U ($\beta$-decay) $^{239}$Np.
$^{232}$Th(n,$\gamma$) $^{233}$Th ($\beta$-decay) $^{233}$Pa.

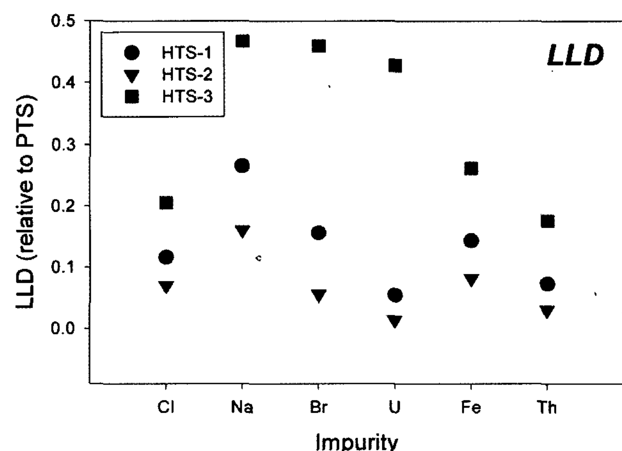


Fig. 1. Sensitivity Comparison of Each Impurity Elements in High Purity Silica at Each Irradiation Facility Based on PTS

was achieved at HTS-2, and these values varied from 0.1 to 0.5 at HTS-3 and HTS-1.

As Np-239 and Pa-233 from U-238 and Th-232 by (n, $\gamma$) reactions respectively have different nuclear properties such as half-lives, and neutron cross-sections, different NAA procedures must be applied to analyze them with high sensitivity. In addition, other NAA procedures have been investigated for analyzing major impurities, such as Na, Cl, Br and Fe, at the HTS-2 irradiation facility. The optimum NAA procedures and detection limits of important impurities in high purity silica are shown in Table 3.

High purity silica may be contaminated during the powdering process through the use of alumina balls. Various metallic impurities may result from the abrasion of the alumina. For this reason, a strict quality control is required. The impurities in alumina balls can be determined by PTS-NAA due to their high concentrations. However, low-level impurities in high purity silica must be analyzed by HTS-NAA. Table 4 shows the impurity concentrations of high purity silica and an alumina ball.

Fig. 2 shows the atmospheric background radioactivity of Pb-214(295 keV), which is a progeny nuclide of Rn-222. In an ultra-trace radioactivity measurement, a background influenced by radon progeny nuclides can contribute to an analytical deviation. In the present study, the atmospheric background radioactivity could be minimized and stabilized through the use of a nitrogen purging system.

**Table 3.** The Optimum NAA Procedures and Detection Limits of the Important Impurities in High Purity Silica

| Impurity | Irradiation | $T_I$* | $T_C$** | LLD($\mu$g/kg) | |
|---|---|---|---|---|---|
| | | | | This | Demand |
| Na | PTS | 18m | 18m | 600 | 1,000 |
| Fe | HTS-2 | 72h | 360h | 500 | 1,000 |
| U | HTS-2 | 72h | 120h | 0.1 | 0.5 |
| Th | HTS-2 | 72h | 360h | 0.01 | 0.2 |

* $T_I$ : Irradiation time, ** $T_C$ : Cooling time

**Table 4.** Concentration of Important Impurities in High Purity Silica and an Alumina Ball (Unit: mg/kg)

| Element | silica | alumina |
|---|---|---|
| U | 0.5 | 5 |
| Th | 0.01 | 10 |
| Na | 100 | 200 |
| Cl | 50 | 500 |
| Fe | 50 | 500 |

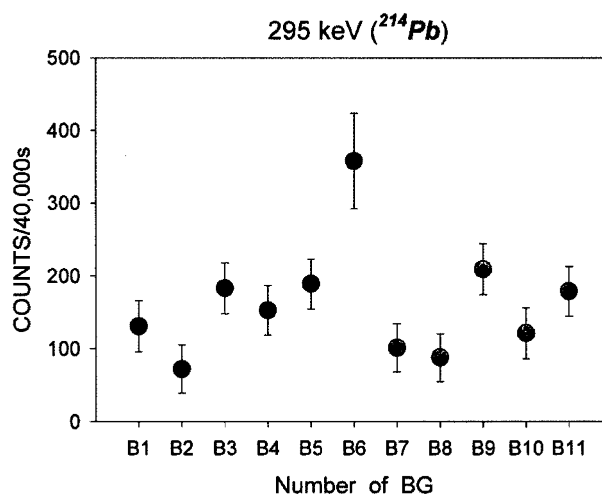


Fig. 2. Count Rates of a 295 keV Gamma-Ray Emitted by PB-214, a Natural Radioactive Nuclide

## 4. CONCLUSIONS

NAA procedures for analyzing major impurities and ultra-trace U and Th in high purity silica and alumina were optimized using different neutron irradiation facilities of HANARO. By using a HTS-2 NAA procedure, ng/g level impurities could be determined. An unstable background could be stabilized and minimized by an $N_2$ flushing method. Using a HTS-2/NAA procedure and the $N_2$ flushing method, NAA is a very useful tool for the determination of ultratrace U, Th and other elements in high purity materials.

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