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Prompt gamma-ray analysis of archaeological bronze

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Prompt γ-ray analysis using the internal monostandard method was applied to voluminous archaeological bronze mirrors produced in ancient China. Sn/Cu content ratios were determined nondestructively by this method. Furthermore, Au/Cu, As/Cu, and Sb/Cu content ratios were determined by means of measuring decay γ-rays emitted from radioactive nuclides produced within samples via (n,γ) reactions. It is clear that the Sn/Cu content ratios in bronze mirrors produced in the Sung era is smaller than in ones produced in between the Han and the Tung era.

Introduction

Knowledge and techniques of natural science have been contributing to the study of archaeology especially in the fields of fluoroscopy, chemical analysis, preservation methods, and so on. For example, various methods for elemental analysis have been applied to samples for estimating the producing area and/or for classification of samples. In many cases archaeological samples are so invaluable that their analytical method has to be nondestructive and/or it should require only a small amount of the sample. In order to achieve this requirement, X-ray fluorescence analysis, β-ray back scattering, etc. are used for nondestructive analysis and neutron activation analysis, ICP-emission spectrochemical analysis, ICP-MS, and so on are used for analysis of very small quantities of samples.

Recently the nondestructive method of neutron capture prompt γ-ray activation analysis (PGAA) which employs neutron beams extended from a research reactor through a guide tube has developed. This analytical method has a great advantage for determinations of some elements (H, B, N, Si, Ca, Cd, and Gd) that are barely or not at all determined by instrumental neutron activation analysis (INAA). As the analytical sensitivities of PGAA for the stated elements are remarkably high, this method of simultaneous multielement analysis has often been utilized complementarily to INAA which allows the determination of a large number of minor elements. In addition, the fact that PGAA imposes less restriction on the shapes and sizes of samples to be analyzed is another big advantage. So it is possible to analyze quite voluminous invaluable samples. This fact is very convenient for analyzing archaeological samples nondestructively.

For analyzing voluminous samples by PGAA, we have developed an internal monostandard method to reduce the influences of neutron absoption and scattering and γ-ray absorption within the analyzed sample itself.[1] In Reference 2, this method was applied to analyze major element concentration ratios of Mn, K, Na, Ti, Fe, Al, and Ca with repect to Si and minor ones of B, Sm, and Gd to Si in archaeological pottery bowls produced in the late 18th century. As a result, PGAA using the internal monostandard method was found very useful for classifying pottery bowls by means of, in particular, $(K_2O+Na_2O)/SiO_2$ and B/Si content ratios.

In this paper, another example of applying PGAA to archaeological bronze mirrors is reported. Furthermore, a new method is proposed which is essentially a combination of PGAA and INAA by a single neutron irradiation, which we propose to call Neutron Beam Activation Analysis (NBAA). After irradiation with neutrons for PGAA, decay γ-rays emitted from radioactive nuclides produced within a sample are measured off-line. The major element content ratio of Sn to Cu and the minor element content ratios of Au, As, and Sb to Cu in archaeological bronze samples could be measured by the internal monostandard method of NBAA. These content ratios in bronze mirrors are reported.

Experimental

Samples

Archaeological bronze mirrors were used as samples. Bronze mirrors consist mainly of Cu, Sn, and Pb. In addition, some other elements like As, Sb, Ni, Fe, and Zn are reported as minor or trace constituents.[3,4]

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Table 1. Selected γ-ray energies and $\sigma_x b_x/\sigma_{Cu} b_{Cu}$ and $\sigma_x b_x/\sigma_{Cu} br_{Cu}$ values using thermal neutrons

(a) For PGAA

Element (x)	Gamma-ray energy,* keV	$\sigma_x b_x/\sigma_{Cu} b_{Cu}$**
Sn	1171.3	0.0871±0.0017
Sn	1293.3	0.129±0.002

* The γ-ray enegy selected for Cu was 278.2 keV.
** The ratios were evaluated from the analysis of standard samples prepared with a known amount of CuO and SnO.

(b) For INAA

Element (x)	Gamma-ray energy,* keV	$\sigma_x br_x/\sigma_{Cu} br_{Cu}$**
Au	411.8	4448
As	559.1	92.12
Sb	564.2	192.1

* The γ-ray enegy selected for Cu was 1345.8 keV.
** The ratio were calculated with σ and br in Ref. 8.

The chemical analysis of bronze mirrors have been performed since the1930s sporadically by the wet method or more recently, by X-ray fluorescence analysis.

100 archaeological bronze mirrors, which had been excavated in China at one time and belong to Japanese collectors today, were prepared in cooperation with Osaka prefecture board of education. Most of them are disk-shaped with a diameter of 5 cm to 21 cm and a weight of 18 g to 1700 g. Some mirrors are hexagons like petals. On the back side (an opposite side of the smooth face which functions as mirror), various artistic pictures of geometric patterns, imaginary gods and animals, and/or plants are engraved.

From their designs on the back side, mirrors were judged as the products of ancient China and classified into 6 groups according to the producing era, that is, the Former Han (B.C.206 - A.D.8), the Later Han (A.D.25 - A.D.220), Sankuo-Liu-chao (A.D.220 - A.D.589), Tang (A.D.618 - A.D.907), Sung (A.D.1127 - A.D.1279), and the present. The designs of the mirrors classified as "products in Sung era" are considered as imitations of those produced in the former era (Han, Sankuo-Liu-chao, and Tang). The mirrors classified as "products in the present" are fakes.

The mirrors have various external appearances; surface is wholly or partly rusted: in a few samples, broken parts are bonded by a bonding agent: in some other samples, rusts are apparently removed from the surface.

Method

The samples fixed by PTFE strings in the sample box were irradiated at the prompt γ-ray analyzing system[5] from the front side for about 1 hour in He gas atmosphere by the thermal-neutron beam guided out from a research reactor, JRR-3M, at the Japan Atomic Energy Research Institute (JAERI). The neutron beam is collimated to the size of 20 mm×30 mm at the entrance of the sample box . The prompt γ-rays were detected by a high-purity Ge detector surrounded with BGO detectors coupled with 8 K pulse-height analyzer under a Compton suppression mode.

At about 5~7 hours after the end of irradiation, decay γ-rays emitted from residual radioactive nuclides produced via (n,γ) reactions within the irradiated sample were measured for about 2~3 hours with a high-purity Ge detector coupled with 4K pulse-height analyzer.

The photopeak assignment and the evaluation of the area under a photopeak were performed with an automatic peaksearch program system, "SPECanal" by HAMAJIMA.[6]

Results and discussion

49 mirrors were analyzed by only PGAA and 38 mirrors were analyzed by NBAA.

Most of the observed prompt γ-rays in the whole energy region could be assigned to Cu with a few γ-rays from Sn. Unfortunately no γ-ray from Pb was observed. The content ratio of Sn to Cu was calculated from the following equation:[1]

$$\frac{A_{Sn}}{A_{Cu}} = \frac{n_{Sn}}{n_{Cu}} \cdot \frac{\sigma_{Sn} b_{Sn}(E_\gamma^{Sn})}{\sigma_{Cu} b_{Cu}(E_\gamma^{Cu})} \cdot \frac{\int W_{Sn}(\vec{r})\eta(E_\gamma^{Sn},\vec{r})d\vec{r}}{\int W_{Cu}(\vec{r})\eta(E_\gamma^{Cu},\vec{r})d\vec{r}} \qquad (1)$$

where A is the photopeak area, n is the number of atoms, b is the number of photons emitted per neutron capture, σ is the effective neutron capture cross section, W is the normalized spacial density distribution of the prompt γ-ray source, η is the γ-ray detection efficiency, E_γ is the γ-ray energy, and $\vec{r}$ is the position vector from the origin in the γ-ray detector to the point where neutron capture reactions occur. The second term of the right hand side, $\sigma_{Sn} b_{Sn}(E_\gamma^{Sn})/\sigma_{Cu} b_{Cu}(E_\gamma^{Cu})$, was determined from the analysis of the standard samples prepared with a known amount of CuO and SnO. The measured $\sigma_{Sn} b_{Sn}/\sigma_{Cu} b_{Cu}$ values are shown in Table 1(a). The last term of the right hand site, $\int W_{Sn}(\vec{r})\eta(E_\gamma^{Sn},\vec{r})d\vec{r}/\int W_{Cu}(\vec{r})\eta(E_\gamma^{Cu},\vec{r})d\vec{r}$, corresponds to a relative counting efficiency, which was determined for each irradiation position of the target sample against the incident neutron beam. The relative counting efficiency curve was calculated by dividing photopeak areas of the prompt γ-rays from Cu by the b_{Cu} values. Because some b_{Cu} values in Reference 7 were found incorrect, we determined relative b_{Cu} values by measuring the prompt γ-rays from a Cu foil (99.9% of purity and 0.020 mm of thickness) using the Ge detector with known relative detection efficiencies. The obtained relative b_{Cu} values normalized to unity one at 278.24 keV are shown in Table 2.

The following decay γ-rays were detected by γ-ray spectrometry of irradiated samples for NBAA; 511 and 1345.8 keV from ^{64}Cu ($T_{1/2}$ = 12.7 h), 559.1, 657.1 and 1216.1 keV from ^{76}As ($T_{1/2}$ = 76.32 h), 564.2 keV from ^{122}Sb ($T_{1/2}$ = 2.70 d), and 411.8 keV from ^{198g}Au ($T_{1/2}$ = 2.695 d). The Au/Cu, As/Cu, and Sb/Cu ratios were calculated by the following equation in a similar manner with PGAA;

$$\frac{A_x}{A_{Cu}} = \frac{n_x}{n_{Cu}} \cdot \frac{\sigma_x br_x(E_\gamma^x)}{\sigma_{Cu} br_{Cu}(E_\gamma^{Cu})} \cdot \frac{1-e^{-\lambda_x t_{irrd}}}{1-e^{-\lambda_{Cu} t_{irrd}}} \cdot \frac{e^{-\lambda_x t_{mes}}}{e^{-\lambda_{Cu} t_{mes}}} \cdot \frac{\varepsilon_x(E_\gamma^x)}{\varepsilon_{Cu}(E_\gamma^{Cu})} \qquad (2)$$

where br is the fractional abundance of the decay γ-ray, λ is the decay constant, t_{irrd} is the irradiation time, t_{mes} is the time from the end of irradiation, and ε is the counting efficiency . The last term of the right hand side, $\varepsilon_x(E_\gamma^x)/\varepsilon_{Cu}(E_\gamma^{Cu})$, which corresponds to the relative counting efficiency, was determined using 3 γ-rays emitted from ^{76}As for each sample. The second term of the right hand side, $\sigma_x br_x(E_\gamma^x)/\sigma_{Cu} br_{Cu}(E_\gamma^{Cu})$, values need to be experimentally determined for the energy spectrum of the neutron beam used, but they were tentatively calculated in this presentation using literature values[8] and are shown in Table 1(b). Thus obtained values are only preliminary ones although they are correct as long as their relative difference among various samples is considered.

Table 2. Measured relative prompt γ-ray intensities, b_{Cu}, for Cu using thermal neutrons

Energy, keV	Relative intensity	Energy, keV	Relative intensity
159.28	0.711 ± 0.009	494.85	0.0260 ± 0.0022
186.01	0.273 ± 0.005	503.65	0.0605 ± 0.0038
202.95	0.216 ± 0.004	534.11	0.0314 ± 0.0020
212.39	0.0431 ± 0.0018	543.85	0.0261 ± 0.0020
237.82	0.0267 ± 0.0019	579.80	0.0927 ± 0.0034
264.88	0.0320 ± 0.0017	608.75	0.271 ± 0.0058
278.24	1	648.80	0.107 ± 0.0033
315.71	0.0255 ± 0.0021	663.06	0.0697 ± 0.0033
343.94	0.236 ± 0.005	822.68	0.0274 ± 0.0021
376.85	0.264 ± 0.002	831.20	0.0158 ± 0.0017
384.74	0.223 ± 0.006	878.28	0.0423 ± 0.0027
436.91	0.0147 ± 0.0011	1039.42	0.0553 ± 0.0031
449.51	0.0408 ± 0.0019	1138.82	0.0244 ± 0.0024
465.15	0.148 ± 0.004	1320.31	0.0239 ± 0.0024
467.99	0.0682 ± 0.0023	1559.36	0.0288 ± 0.0027

These values were used for calculating relative counting efficiencies for each sample.

Before analyzing the bronze mirrors, 11 bronze blocks (c.a. 20 mm×40 mm×7 mm) made of raw materials of known contents of Cu, Sn, and Pb were analyzed to confirm the validity of the present method proposed for voluminous samples. The measured content ratios of Sn/Cu are plotted as a function of those in the raw materials in Fig. 1. Only 1171.3 keV of the prompt γ-ray for Sn was used for calculating the content ratios since Cu emits the prompt γ-ray with an energy of 1293.9 keV which is very close to 1293.3 keV emitted from Sn. The errors of the relative contents are those associated with the counting statistics. The counting statistic of the 1171.3 keV photopeak mainly contributed to the final error. All measured values except for 3 values lie on the 1:1 correlation line within the errors in the region of 10–50% of Sn/Cu ratios. The 3 values are about 13% smaller than raw material's values but the cause of the deviation is unknown. As a result, it was found that our internal monostandard method of PGAA can be used for analyzing Sn/Cu content ratio in bronzes.

Measured Sn/Cu, Au/Cu, As/Cu, and Sb/Cu content ratios in the bronze mirrors are plotted in Fig. 2 by open circles for the Former Han, open squares for the Later Han, diamonds for Sankuo-Liu-chao, open triangles for Tang, reverse open triangles for Sung, and dot open circles for fakes. The values of Au/Cu, As/Cu, and Sb/Cu ratios are tentative results but they are correct for comparison among samples as pointed out previously. Sn/Cu values reported by Komatsu and Yamauchi in 1937 and 1940[3,4] are also plotted in Fig. 3 for comparison by crosses for Shin, open circles for Han, open diamonds for Sankuo, cross open squares for Sui, open triangles for Tang, and reverse open triangles for Sung. They analyzed a few grams of mirror samples using the conventional wet chemistry procedure. It is noted that our mirror samples are different from theirs.

Sn/Cu values in this work varied from about 5% to 40%. The distribution is visually classified to three groups; Han-Tang, Sung, and fakes. Sn/Cu values in Han-Tang groups are roughly constant, 30% on the average, for about 1100 years. This trend is obviously apparent also in Fig. 3, but the average is 35%, slightly higher than ours. But in the Sung era, the content ratio of Sn/Cu becomes lower; 13% on the average. The feature that Sn contents in bronze mirrors produced in Sung era and the later era are lower than the former era was pointed out in some articles rather qualitatively but it has been more quantitatibly demonstrated in this work.

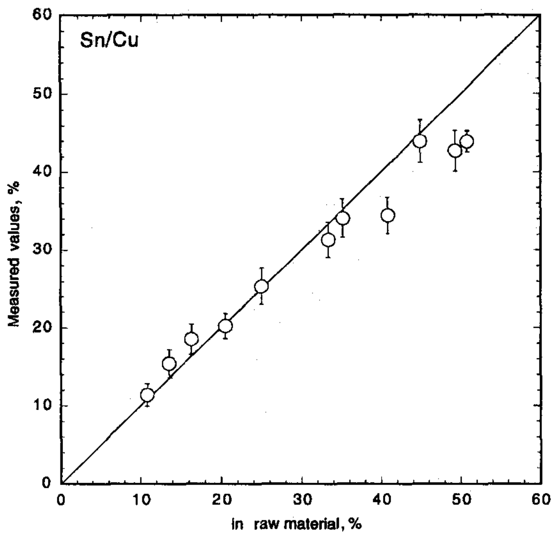

Fig. 1. Comparison of analytical results of Sn/Cu ratios and contents of raw materials

In nondestructive PGAA of a voluminous sample, if only a fraction of the whole sample is irradiated by neutrons, the results may not represent the contents of the bulk. In this work, neutron beam irradiation positions were varied within a same sample to study the uniformity of the sample. First, the neutron beam was oriented from the front and the back side of the same mirror. This check was performed for two different mirrors, A and B. In mirror B, the whole back side surface is rusted and turned brown and green, and the front side is kept silvery with no apparent rust. The obtained values were 30.7± 1.5% and 30.6±1.4% for irradiation from the front side and from the back side, respectively for mirror A, and 31.9±4.6% and 29.2±2.5% for mirror B. Both values of the front side and back side are in agreement within errors. Secondly, three different areas, that is, upper, center, and bottom areas of the same mirror were irradiated from the front side. The values of 25.8±2.4%, 28.0±2.7%, and 26.9±1.8% were obtained, respectively. These values are also consistent within errors. As a result, we assumed for the present bronze mirror samples that the obtained value was representative of values of a bulk wherever the irradiation was performed.

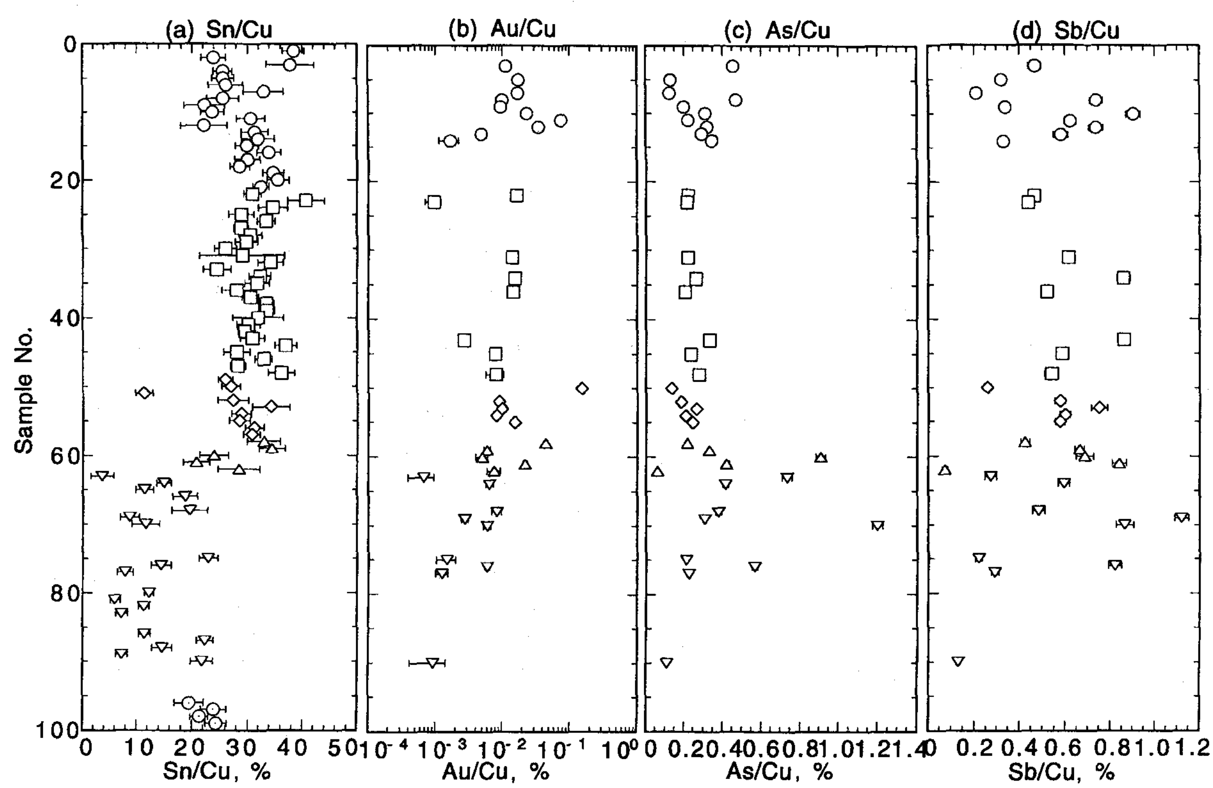

Fig. 2. Measured content ratios of Sn, Au, As, and Sb to Cu in archaeological bronze mirrors. The values of mirrors produced in the Formar Han, in the Later Han, in Sankuo-Liu-chao, in Tang, in Sung, and in Present (fakes) are shown by open circles, open squares, open diamonds, open triangles, reverse open triangles, and dot open circles, respectively. The scale of x-axis in (b), (c), and (d) are arbitrary (see text for details) and the data are depicted from the top of the figure in the order of the sample number which is labeled from the oldest

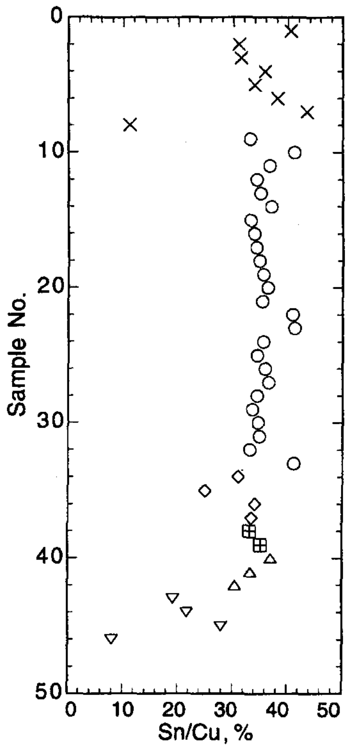

Fig. 3. Reported content ratios of Sn, Pb, As, and Sb to Cu in archaeological bronze mirrors.[3,4] The values of mirrors produced in Ch'in, in Han, in Sankuo, in Sui, in Tang, and in Sung are shown by crosses, open circles, open diamonds, cross open squares, open triangles, and reverse open triangles, respectively

The residual radioactivity is a critical factor when the analysis of invaluable samples is performed by neutron irradiation. The residual activities within one irradiated bronze mirror (55 g of weight and 8.4 cm of diameter) irradiated by thermal neutrons for about 3000 seconds were 0.070 Bq of ^{124}Sb ($T_{1/2}$=60.2 d), 0.49 Bq of ^{46}Sc ($T_{1/2}$=83.8 d), 0.20 Bq of ^{59}Fe ($T_{1/2}$=44.5 d), and 0.05 Bq of ^{60}Co ($T_{1/2}$=5.27 y) at 36 days after the end of irradiation. The maximum radioactivity of a substance that is allowed to be taken outside the controlled area in many countries is 74 Bq/g, so it is obvious that the radioactivity remaining in the sample was negligibly small. As a consequence, it was found that the sample could be removed from restricted areas with minimal cooling time after the irradiation.

Conclusions

As a practical application of PGAA, the internal monostandard method proposed by SUEKI et al.[1] was for the first time tested in nondestructive manner with archaeological bronze mirrors. Furthermore, a nondestructive INAA method combined with PGAA (called NBAA) was also applied to them. 89 mirrors which were already classified by archaeologists, were chosen as samples for the analysis.

By NBAA, Sn/Cu, Au/Cu, As/Cu, and Sb/Cu content ratios were determined. It was clear that Sn/Cu ratios in mirrors produced in Sung era were smaller than those produced in between the Han and Tang era. The NBAA has proved very useful for voluminous samples because elemental contents of not only major elements but also some minor elements can be obtained without further treatments. It is also to be noted that as the residual radioactivity produced by neutron irradiation is negligibly small even an invaluable sample can be taken out of the radiation controlled area after a few weeks.

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