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Determination of As and Sb in iron and steel by neutron activation analysis with multiple gamma-ray detection

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Recycled steel products demands a new technique for determining tramp elements in steel. In this paper, As and Sb in iron certified reference materials were determined by neutron activation analysis with the multiple gamma-ray detection method. The determined values are in good agreement with certified and reference values. The lower determination limits (LDL) for As and Sb in high purity iron are 0.012 and 0.0025 ppm, respectively. As the demanded LDL for As and Sb is 0.1 ppm, the method described in this work is suitable for determining As and Sb in recycled steel.

Introduction

For the effective usage of resources and the restraint of CO_2 emission, the recycling of steels is promoted. When steel scrap is recycled, impurity elements increase. They has big influence on the characteristic of the recycled steel. Especially, some elements such as As, Sb, and Zn do not seem to influence the characteristics of the recycled steel and it is difficult to refine away these, so-called tramp elements in the iron recycling process. For this reason, in order to recycle the increasing amount of scrap iron and at the same time to maintain the competitive power of steel related products, such as cars and other industrial products, we have to develop not only the technology of removing impurities but also the way of determining trace elements.

Atomic absorption spectrometric determination,[1,2] ICP-AES,[3–5] and ICP-MS[6,7] are widely used for the quantitative analysis of the trace elements. However, these techniques require preliminary chemical separation, involving sophisticated techniques that deteriorate the accuracy. Therefore, a new determination technique must be established.

Neutron activation analysis (NAA) has the disadvantage of needing a reactor and facilities for handling radioactivity. NAA is based on the nuclear reactions, and differs widely from other techniques. For some elements, NAA has a better sensitivity than other analytical methods. Especially, instrumental neutron activation analysis (INAA) without chemical separation has a high measurement precision.[8–11] Because of these advantages, NAA is used as microanalytical method in some special fields like materials, environmental, and biological sciences, etc.

In recent years, we have developed a highly sensitive determination method combining NAA with multiple gamma-ray detection method used in experimental nuclear physics. The tramp elements, As and Sb, in iron certified reference materials were determined by neutron activation analysis with the multiple gamma-ray detection method.

Experimental

Neutron activation analysis with the multiple gamma-ray detection method

Normally, in NAA, a single detector is used to measure gamma-ray emitted from a neutron activated sample. When many elements are contained in the sample, the signal-to-noise ratio is reduced by background due to Compton scattering, and the LDL becomes worse.

To overcome this problem, radiochemical NAA (RNAA) is used. By removing the background elements by chemical separation, the Compton scattering decreases, LDL is attained.[12,13] In RNAA, the influence of contaminations whose activity interferes with the measurement are separated chemically. As a result, the precision of RNAA is higher than with other analytical methods. However, there are many problems. The most important ones are that the chemical separation introduces errors in the yield determination, a special facility to deal with unsealed radioactivity is necessary, nuclides with short half-lives cannot be measured, and the worker who is doing the chemical separations is exposed to radiation.

In order to achieve good detection limits without chemical separations, we developed a neutron activation analysis with the multiple gamma-ray detection method. Figure 1 shows a schematic diagram of the method using ^{55}Mn as an example. Many neutron-activated nuclides emit more than two gamma-rays in a β-decay. In the case of ^{55}Mn, ^{56}Mn that is formed by the ^{55}Mn(n,γ)^{56}Mn reaction decays with a half-life of 2.6 hours, and emits gamma-rays. In the β-decay process, it

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falls onto the level at 2.658 MeV in 27.9% and emits 2 gamma-rays of 2113 keV and 847 keV in 27.2%. In the same way, the nuclide falls onto the level at 2.960 MeV in 14.6% and emits 2 gamma-rays of 1811 keV and 847 keV in 14.3%. Because the lifetime of the middle level (847 keV) is very short (6.1 ps), the gamma-rays of these combinations are regarded as coincident when Ge detectors are used.

In this method, we measure γ-γ coincidences by using an array of gamma-ray detectors. One event of this measurement comprises two energy informations. Thus, by taking the two gamma-ray energies in the *X* and *Y* axes, and the counts in the *Z* axis, a two-dimensional matrix is obtained as shown in Fig. 2. The main background counts which are caused by the coincident events of Compton scattering and photo-peak form in lines. The other background counts which are caused by the coincident events of Compton scatterings or accidental counts, spread out to the wide area. However, the counts of the coincident photo-peaks concentrate as peaks on the matrix. Unless the coincident peaks pile up with the background lines which were caused by the matrix elements, the signal-to-noise ratio improves dramatically, and detection sensitivity improves drastically in comparison to standard NAA. As a result, the trace elements that could not be observed in the standard NAA can be analyzed rapidly without chemical separation. Therefore, this method is expected to become a powerful quantitative method of analysis.

The experimental setup

In this paper, the tramp elements As and Sb in iron certified reference materials were determined by neutron activation analysis combined with the multiple gamma-ray detection method.

The level scheme of Sb and As is shown in Figs 3 and 4. ^{124}Sb that is formed by ^{123}Sb(n,γ)^{124}Sb reaction decays with a half-life of 60.2 days, and becomes ^{124}Te. By β-decay, 47.5% of the ^{124}Sb emits 1691 keV and 602 keV gamma-rays. ^{76}As that is formed by ^{75}As(n,γ)^{76}As reaction decays with a half-life of 26.3 hours. By β-decay, 6.2% of it emits 2 gamma-rays of 559 keV and 657 keV in 6.2%. We measured the coincidence of these gamma-rays.

As there is a big difference between the half-lives of ^{124}Sb and ^{76}As, the experiments of Sb and As were done separately in this paper.

For Sb, 8 samples (Japanese Iron and Steel Certified Reference Materials (JSS): JSS001-5: 114.2 mg, JSS003-2: 103.9 mg, JSS003-4: 103.2 mg, JSS168-7: 96.1 mg, JSS172-7: 112.6 mg, JSS175-7: 106.0 mg, and NIST1763: 116.9 mg, NIST 1765: 95.6 mg) were enclosed in silica tubes. These samples were irradiated by thermal neutrons in the JRR-3 HR-1 pipe (thermal neutron flux: $9.6 \cdot 10^{17}$ n·m^{-2}·s^{-1}) for 5 hours and the gamma-rays were measured with the gamma-ray detector array GEMINI-II[12,13] after cooling for 21 days.

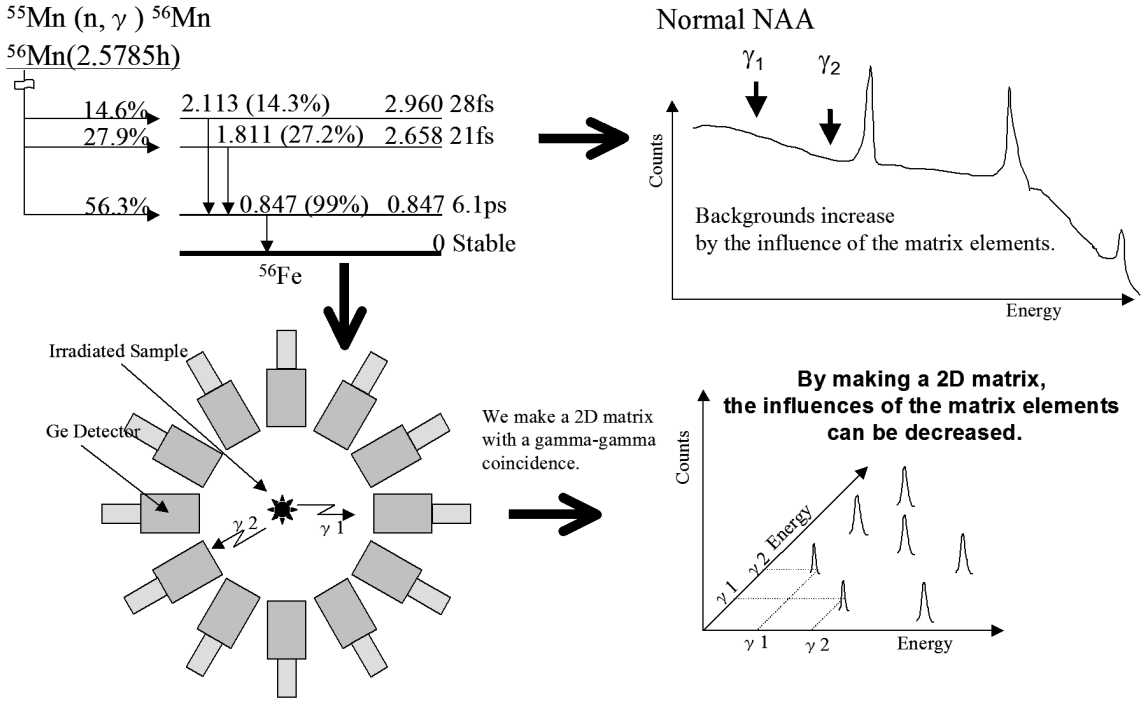

Fig. 1. Schematic diagram of neutron activation analysis with the multiple gamma-ray detection method

GEMINI-II consists of 16 Ge detectors with BGO anti Compton suppressor. The energy resolution (FWHM) of GEMINI-II is 2.3 keV at 1.33 MeV gamma-rays. As GEMINI-II is designed for nuclear physics, detection efficiency is not good, and the detection efficiency at 1.33 MeV is 1.5%. Therefore, the measuring time was long, and each sample was measured for 24 hours.

For As, 3 samples (JSS001-5: 53.2 mg, JSS168-7: 50.0 mg, JSS169-7: 51.2 mg) were enclosed in silica tubes. These samples were irradiated in the JRR-3 PN-1 pipe (thermal neutron flux: $5.2 \cdot 10^{17}$ n·m^{-2}·s^{-1}) for 10 minutes and the gamma-rays were measured by GEMINI-II for 12 hours after cooling for 8 hours.

To calculate the dispersion of this method, we prepared five sets of JSS001-5 sample (50.0–56.2 mg) and JSS169-7 sample (51.2–54.8 mg) and each set of the samples were irradiated in the JRR-3 PN-1 pipe for 10 minutes and measured by GEMINI-II for 12 hours after cooling for 8 hours.

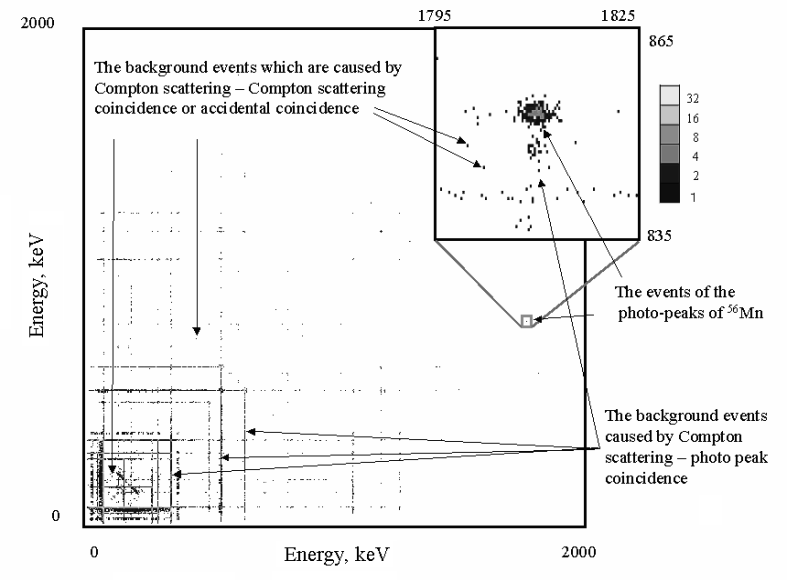

Fig. 2. The sample of the 2D matrix and the peak of Mn

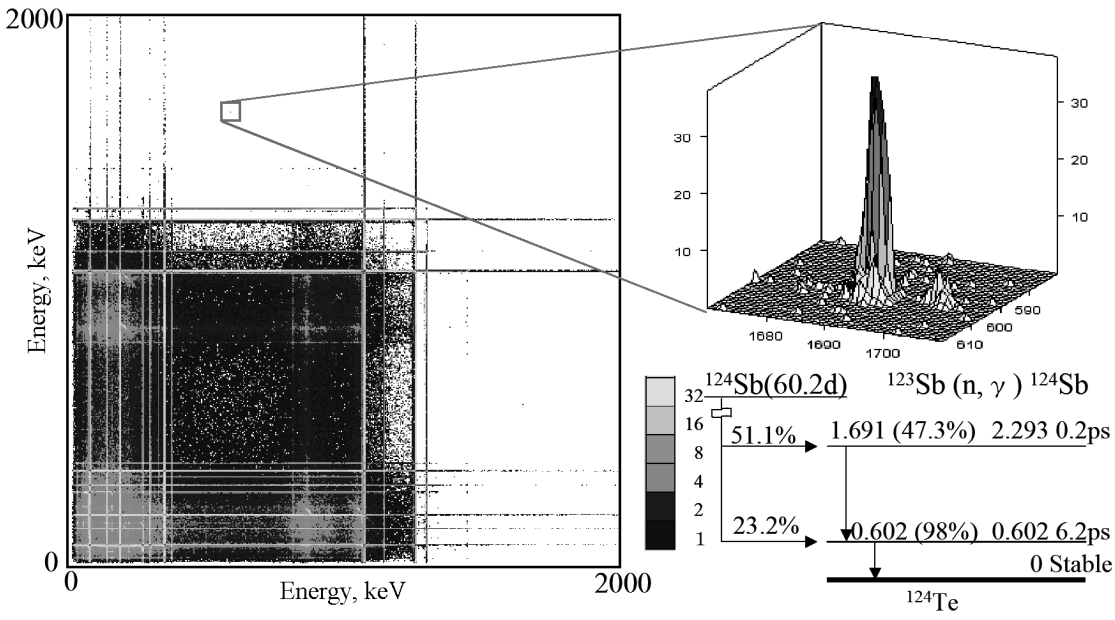

Fig. 3. The 2D matrix of the JSS003-2 sample around the peak of Sb (1691 keV and 602 keV) and the level scheme of ^{124}Sb. The JSS003-2 sample, which is one of the pure iron standard samples, was irradiated in the JRR-3 HR-1 pipe (thermal neutron flux: $9.6 \cdot 10^{17}$ n·m^{-2}·s^{-1}) for 5 hours and measured by GEMINI-II for 24 hours after cooling for 21 days

Results and discussion

The two-dimensional matrix of the JSS003-2 around the coincident peak of Sb (1691 keV and 602 keV), and that of the JSS001-5 sample around the coincident peak of As (657 keV and 559 keV) are shown in Fig. 3. The backgrounds caused by Compton scattering are very low in the vicinity of the peaks and good signal-to-noise ratio is achieved.

With Sb, the comparison method is applied using JSS172-7 (Sb: 21.8±0.8 $\mu g \cdot g^{-1}$) as a reference material. The same method was used for As, but with JSS169-7 (As: 50.5±1.9 $\mu g \cdot g^{-1}$) as a reference material. The determined, certified and reference values for As and Sb are shown in Table 1. The experimental values are in good agreement with the certified and reference values.[14] The uncertainties of the determined values in Table 1 contain statistics errors (two times of the standard deviation) and the uncertainties of the certified values of reference materials.

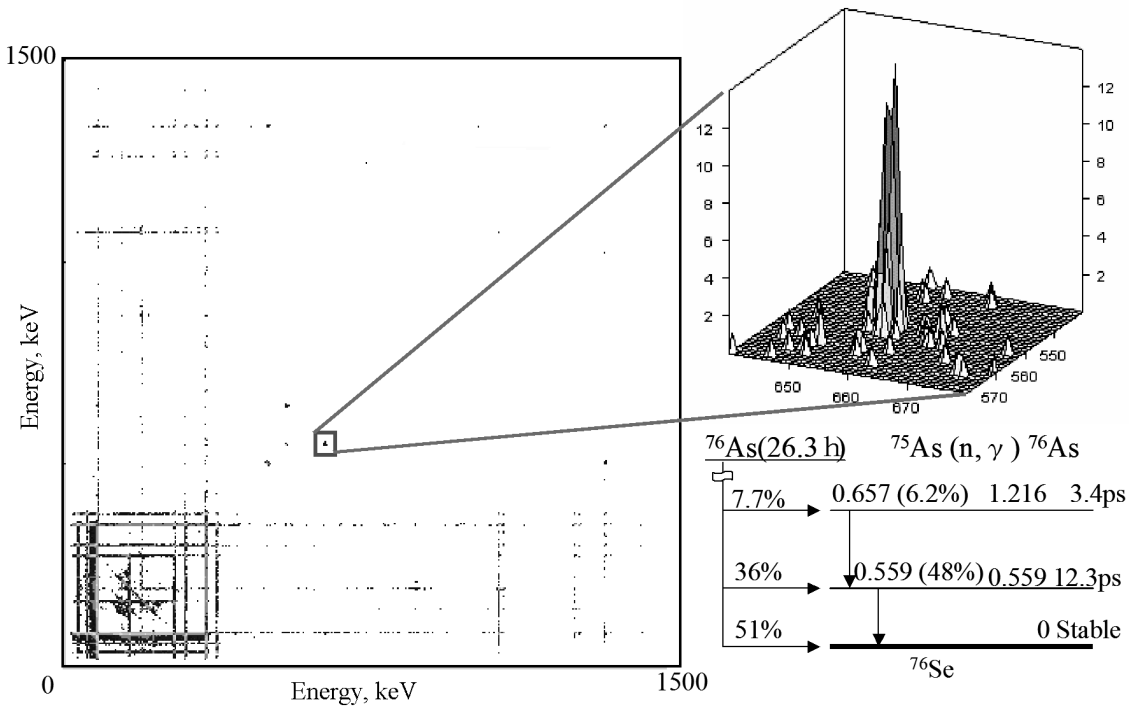

Fig. 4. The 2D matrix of the JSS001-5 sample around the peak of As (559 keV and 657 keV) and the level scheme of ^{76}As. The JSS001-5 sample, which is also one of the pure iron standard samples, was irradiated in the JRR-3 PN-1 pipe (thermal neutron flux: $5.2 \cdot 10^{17}$ $n \cdot m^{-2} \cdot s^{-1}$) for 10 minutes and measured by GEMINI-II for 12 hours after cooling for 8 hours

Table 1. Determined, certified and reference values for As and Sb in JSS and NIST standard materials

Sample	This work,* $\mu g \cdot g^{-1}$		Certified value, $\mu g \cdot g^{-1}$	
	Sb	As	Sb	As
JSS001-5	0.010 ± 0.003	2.20 ± 0.21	No data	2.1 ± 0.5
JSS003-2	0.051 ± 0.005		0.039 ± 0.006[14]	
JSS003-4	0.033 ± 0.004		0.029 ± 0.002[14]	
JSS175-7	210 ± 7		200 ± 7	
JSS168-7	1.22 ± 0.04	111.0 ± 1.1	No data	120 ± 10
NIST 1765	9.53 ± 0.33		10	
NIST 1763	98.9 ± 3.3		(110)**	

* The uncertainties of the determined values contain statistics errors: two times of the standard deviation, and the uncertainties of the certified and reference values of reference materials.
** Reference value.

The good signal-to-noise ratios are greatly improved the LDLs. In this paper, it is supposed that the 20 counts was the identification limit of the peak (in the case of these experiments, top counts of coincident peak was 3), and the LDLs were calculated. Of course, these values are influenced by the matrix elements and the conditions of the irradiation. The values of the LDLs for As and Sb in high purity iron JSS001-5 were 0.008 and 0.0025 $\mu g \cdot g^{-1}$, respectively. The demanded LDL for both As and Sb is 0.1 $\mu g \cdot g^{-1}$, and these values achieved by this method satisfy the requirement.

The results of the five set samples are 2.20±0.21, 2.14±0.22, 2.50±0.23, 2.36±0.22, 2.36±0.22 $\mu g \cdot g^{-1}$. These uncertainties contain statistics errors and the uncertainties of the certified values of the JSS169-7. The dispersion of these values was 2.31±0.14 $\mu g \cdot g^{-1}$. This value satisfies the demand for material science.[15]

Conclusions

In this paper the tramp elements, As and Sb, in iron certified reference materials were determined by neutron activation analysis combined with the multiple gamma-ray detection method.

The determined values are in good agreement with the certified and reference values.

The values of the LDLs for As and Sb in high purity iron were 0.008 and 0.0025 $\mu g \cdot g^{-1}$. As the demanded LDL for both As and Sb is 0.1 $\mu g \cdot g^{-1}$, and the values attained by this method satisfy the requirement. The LDLs of this method is greatly smaller than the conventional INAA (As: 0.08 $\mu g \cdot g^{-1}$ Sb: 0.01 $\mu g \cdot g^{-1}$).[14]

The dispersion of this method is enough small to satisfy the demand from materials science.[15]

From the results obtained by this method proves to be useful for determining As and Sb in recycled steel.

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