Proton Activation Analysis of Several Trace Impurities in Standard Steel Samples

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It is well known that proton activation has been populaly used in charged particle activation analysis, especially for the analysis of trace impurities in various materials [1]. However, there are only a few reports dealing with iron and steel sample, because of an intense radioactivity induced in their matrices. As an example, Fig. 1 shows a gamma-ray spectrum of the standard steel sample, JSS trace element series No. 174-6 bombarded with 13 MeV proton for 2 hours and cooled for 3 days after bombardment. In this spectrum, all photopeaks were identified as ^{56}Co from ^{56}Fe(p, n) reaction and any gamma-rays emitted from trace elements in this sample were not able to detect. Therefore, in order to improve the detection limit of trace elements, it is necessary to remove iron before irradiation or ^{56}Co after irradiation, or to isolate trace elements selectively from matrix.

In this work, the methylisobutylketone (MIBK) extraction method was applied to remove iron and the internal standard method coupled with the standard addition method (ISM-SAM) [2,3] has been first applied to proton activation analysis using with prechemical separation. The JSS standard samples of trace element series and low alloy series were selected as test samples. Traces of Ti, V, Cr, As and Zr were determined by using Y as an internal standard element.

Two portions of 500-mg of precleaned sample were spiked with 100 μg of Y and dissolved into aqua regia in a Teflon crucible. Accurate amounts of elements, such as Ti, V, Cr, As and Zr were added to one of the pair, for preparation of standard addition sample. Then, iron was extracted twice into MIBK from sample solution conditioned to 6N HCl. Residual solution was dried and dissolved into 5 ml of 4N HNO_3. After adding same volume of tetraethylsilicate, sample solution was mixed mechanically until gelification. Silica-gel was dried and powdered in a microwave oven for several minutes and in an electric furnace for one hour at 400°C. Three portions of powdered sample (250 mg) was pressed into a disk of 10 mm in diameter with enough thickness to stop incident proton and wrapped doubly in a pure aluminum foil with thickness of 10 μm, respectively. All irradiations were done under the condition of 2-4 μA for 2 hours by using the rotating target assembly which

can assure to irradiate 12 samples simultaneously. In 13 MeV-proton bombardment, all radioisotopes used for determination were produced by the (p, n) reaction. Induced radioactivities from samples and standard addition samples were measured by the automatic gamma-ray spectrometer equipped with a small-robot for sample changing [4].

The chemical recovery of Ti, Cr, As, Zr and Y were almost 100 %, and that of V was 70-80 %. Although, Nb, Mo, Sn and Sb were extracted into MIBK along with Fe. In order to demonstrate the effect of MIBK extraction, Fig. 2 shows the gamma-ray spectrum of JSS 174-6 measured under the same condition as Fig. 1 after chemical separation. Comparing with Fig. 1, the gamma-ray peaks of ^{56}Co from Fe could be reduced effectively and the gamma-ray peaks of ^{51}Cr, ^{90}Nb, ^{92m}Nb and ^{89}Zr from V, Zr and Y could be observed clearly.

In the case of ISM-SAM [2], when yg of element A is added in the sample, unknown amount (xg) of element A in sample can be calculated by the following simple equation without any corrections of range and beam intensity; that is, $x = y / [(R^*/R) - 1]$, where R is the peak area ratio of gamma-ray emitted from a nuclide produced from element A to 909 keV gamma-ray of ^{89}Zr from Y in the sample and R* is the ratio in the standard addition sample as above. The analytical results of the JSS trace element series No. 169-6, 170-6, 174-6 and 175-6 were shown in Table 1 along with sensitivities and certified values. All analytical data were averaged over the values obtained by using three samples and three standard addition samples. For comparison, the results of 20-MeV photon activation analysis (PAA) were also shown. The results of the JSS low alloy series of No. 152-9 and 154-9 were shown in Table 2. These results show good reproducibility and sensitivity and agree with the standard values and PAA results.

In the case of steel sample, Y is one of the most suitable element as the internal standard elements. Because, Y is hardly present in steel and give only one radioisotope (^{89}Zr) by the (p, n) reaction. The product isotope ^{89}Zr has very useful nuclear characteristics, that is, simple decay scheme, no interfering gamma-rays for determination, suitable half-life for measurement from one day to two weeks.

This report is the first experiment of the combined use of chemical separation and ISM-SAM. It has been shown that ISM-SAM is available to the case of which an internal standard and elements to be determined behave together during chemical separation.

Reference

1) Vandecasteele C., Activation analysis with charged particles, (Ellis Horwood Ltd., Chichester, (1988), p. 111.
2) Masumoto K. and Yagi M., J. Radioanal. Chem. **78**(1983)233.
3) Yagi M. and Masumoto K., J. Radioanal. Nucl. Chem. **111**(1987)359.
4) Masumoto K. et al., Anal. Sci. **7**(1991) suppl. p.743.

Table 1. Analytical results of JSS Trace Element Series No.169-6, 170-6, 174-6 and 175-6.

Sample	Element	This work Average	D. L.#	Std. Value	PAA* Average	D. L.#
JSS 169-6		(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)
	Ti	100 ± 1	3	120	117 ± 4	5
	Cr	959 ± 41	11	960	995 ± 27	17
	As	54 ± 6	10	50	53 ± 5	1
JSS 170-6						
	Ti	998 ± 14	3	1030	1116 ± 5	13
	Cr	417 ± 14	12	420	479 ± 26	30
	As	316 ± 22	11	310	317 ± 4	3
JSS 174-6						
	V	629 ± 18	5	590	ND	
	Zr	201 ± 7	2	200	206 ± 5	1
JSS 175-6						
	V	999 ± 15	8	920	ND	
	Zr	398 ± 9	2	390	422 ± 17	2

*; The results of photon activation analysis with 20MeV bremsstrahlung irradiation.
#; Detection limit ($3\sqrt{BG}$).

Table 2. Analytical results of JSS Low Alloy Steel Series No.152-9 and 154-9.

Sample	Element	This work Average	D. L.#	Std. Value	PAA* Average	D. L.#
JSS 152-9		(μg/g)	(μg/g)	(μg/g)	(μg/g)	(μg/g)
	Ti	ND	10	-	33 ± 4	6
	V	962 ± 31	12	970	ND	
	Cr	5000 ± 150	20	5000	5000 ± 210	120
	As	186 ± 7	14	-	168 ± 5	4
JSS 154-9						
	Ti	ND	10	-	43 ± 5	8
	V	2920 ± 90	26	3000	ND	
	As	40 ± 7	12	-	39 ± 1	3

*; The results of photon activation analysis with 20MeV bremsstrahlung irradiation.
#; Detection limit ($3\sqrt{BG}$).

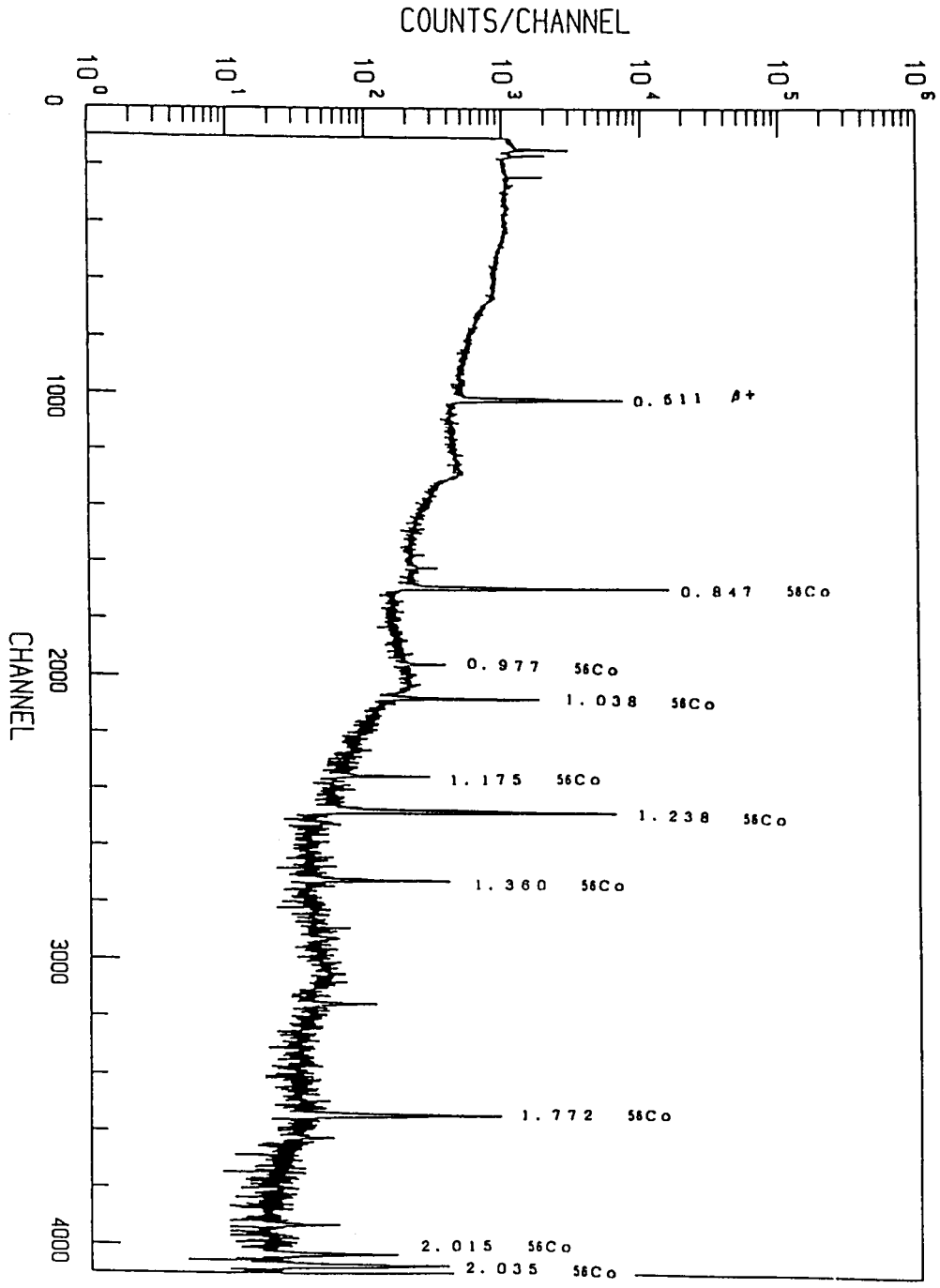

Fig. 1. Gamma-ray spectrum of JSS trace element series No. 174-6.

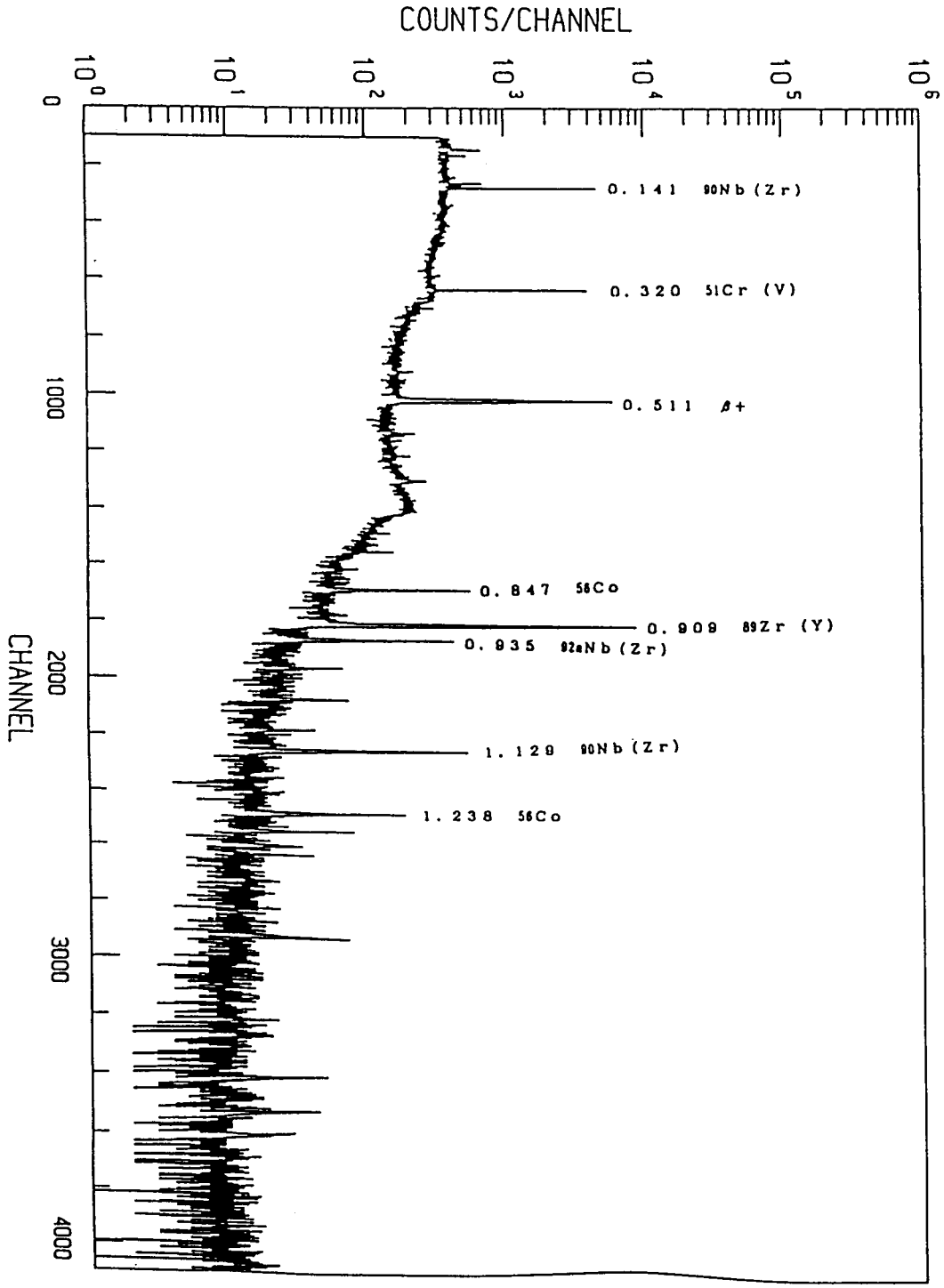

Fig. 2. Gamma-ray spectrum of JSS trace element series No. 174-6 after MIBK extraction.