Preparation and Quality Testing of Minor Element Series B of Japanese Standard Samples for Iron and Steel Analysis*

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I. Introduction

Advances of manufactural technique have given high-quality and variety of steel. Corresponding to this situation, much effort has been made for the expansion of kinds of standard samples, by taking the order of the importance and popularization of steels into consideration, at the Committee on Iron and Steel Standard Samples for Analysis.

The activities of the committee have been described in the booklet *Progress of Japanese Standard Samples of Iron and Steel*, published in commemoration of the 50th Convention.¹⁾

The history and actual results of the committee have been mentioned in the Special Issue on Iron and Steel Analysis of *Tetsu-to-Hagané*.^{2)***} Annual reports and technical comments have also appeared in the pages of Committee News in *Tetsu-to-Hagané*.***

In this report, the production method and the technical inspection of production process are presented about the standard samples of Minor Element Series B, which have recently been produced.

II. Standard Sample of Minor Element Series B

This series has been produced for the purpose of expansion of kinds of Japanese Standard Samples for Iron and Steel Analysis and for control of quality of steel.

Four of the standard samples contain nickel, chromium, molybdenum, arsenic, tin, titanium and calcium with gradational concentrations, and other four contain vanadium, cobalt, aluminum, boron, zirconium, niobium and antimony. Those are the first standard samples for calcium and antimony in Japan.

Chip samples are applicable for chemical analyses and disc samples (35 mmφ×20 mm), which constitute one set with the eight kinds, are for instrumental analyses. The chemical compositions of the samples for instrumental analyses are shown in Table 1.

The chemical compositions of samples for chemical analyses are different from those of the samples for instrumental analyses. (Refer to *Tetsu-to-Hagané*, **60** (1974), N245).

Table 1. Chemical composition of Minor Element Series B (%)

Element	JSS 168-1	JSS 169-1	JSS 170-1	JSS 171-1	JSS 172-1	JSS 173-1	JSS 174-1	JSS 175-1
C	0.055	0.054	0.062	0.081	0.081	0.079	0.071	0.083
Si	(0.24)	(0.21)	(0.20)	(0.20)	(0.21)	(0.21)	(0.21)	(0.21)
Mn	(0.41)	(0.41)	(0.42)	(0.42)	(0.42)	(0.42)	(0.41)	(0.41)
P	(0.005)	(0.005)	(0.005)	(0.003)	(0.004)	(0.003)	(0.003)	(0.003)
S	(0.013)	(0.010)	(0.009)	(0.009)	(0.008)	(0.009)	(0.009)	(0.009)
Ni	0.013	0.038	0.070	0.100				
Cr	0.012	0.094	0.037	0.067				
Mo	0.095	0.067	0.011	0.038				
V					0.010	0.035	0.062	0.093
Co					0.055	0.030	0.020	0.010
Ti	0.065	0.013	0.097	0.038				
Al	0.047	0.046	0.049	0.052	0.015	0.024	0.032	0.054
As	0.010	0.005	0.028	0.046				
Sn	0.005	0.011	0.053	0.032				
B					0.0021	0.0031	0.0052	0.0085
Nb					0.053	0.032	0.021	0.011
Zr					0.009	0.019	0.028	0.048
Sb					0.0019	0.0047	0.0100	0.019
Ca	0.0007	0.0013	0.0017	0.0027				
Fe	(99.0)	(99.0)	(98.9)	(98.9)	(99.1)	(99.1)	(99.1)	(99.0)

(): Uncertified value

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III. Production Method

The outline of the production process of the standard samples is shown in Fig. 1. Ingots containing objective elements were melted to product from electrolytic iron in a vacuum melting furnace. The ingots were forged into the scraps of 120 mm cube (the primary sample).

The top and bottom of the primary sample were then cut off and ground to remove the decarbonized layer and forging cracks.

The suitable parts for standard samples were selected through the results of segregation tests, *i.e.*,

Cut the top and bottom of ingot sample, and grind or peel the surface layer.

Sulfur print.
Macroscopic test.
Analysis of main elements.

sulfur print, microscopic test and chemical analysis.

The chips for chemical analysis were prepared from the primary sample by removing the segregation part.

The segregation part of a disc for instrumental

Fig. 1. Preparation process of Minor Element Series B

Table 2. Chemical composition of NBS and BAS standards (%)

Element	NBS 1161	NBS 1162	NBS 1163	NBS 1164	NBS 1166	NBS 1167	NBS 1168	BAS SS-50	BAS SS-59	BAS SS-432	Range
C	0.15	[0.40]	0.19	[0.54]	0.065	0.11	[0.26]	(0.22)	(0.16)	0.093	0.065~0.19
Si	0.047	0.28	0.41	0.48	0.025	0.26	0.075	(0.024)	(0.15)	0.042	
Mn	0.36	0.94	1.15	1.32	0.113	0.275	0.47	(0.19)	0.12	1.10	
P	0.053	0.045	0.031	0.017	0.012	0.033	0.023	(0.019)	(0.029)	0.016	
S	(0.02)	(0.02)	(0.02)	(0.02)	(0.01)	(0.01)	(0.02)	(0.009)	(0.021)	0.053	
Ni	[1.73]	[0.70]	[0.39]	0.135	0.051	0.088	[1.03]	0.022		[0.24]	0.022~0.135
Cr	0.13	[0.74]	[0.26]	0.078	[0.011]	0.036	[0.54]	0.131		[0.21]	0.036~0.131
Mo	[0.30]	0.080	0.12	0.029	0.011	0.021	[0.20]	[0.22]		0.039	0.011~0.120
V	0.024	0.058	0.10	[0.295]	0.007	0.041	[0.17]		0.083		0.007~0.10
Co	[0.26]	[0.11]	0.013	0.028	0.046	0.074	[0.16]		0.070		0.013~0.074
Ti	(0.01)	0.037	0.010	0.004	0.057	[0.26]	0.011	0.021			0.004~0.057
Al	0.005	0.023	0.027	0.005	0.015	[0.16]	0.042	0.013	0.058	0.020	0.005~0.058
As	0.028	0.046	[0.10]	0.018	0.014	[0.14]	0.008	0.031			0.008~0.046
Sn	0.022	0.066	0.013	0.043	0.005	0.10	0.009	0.085		0.016	0.005~0.085
B	0.0002	0.0005	0.0012	0.005	(0.0002)	(0.0002)	[0.009]		[0.008]		0.0002~0.005
Nb	0.011	0.096	[0.195]	0.037	0.005	[0.29]	0.006			0.029	0.005~0.096
Zr	(<0.005)	0.063	0.20	0.010	(<0.005)	0.094	(<0.005)				0.005~0.094

(): Uncertified value []: Standard value, not used for the calculation in this work

analysis causes difference between standard samples. So the disc was prepared according to Fig. 1; the segregation parts were cut and rejected and then the steel samples remained were forged into round stick (35 mmφ) samples (the secondary sample). Test portions quarried from them were checked by emission spectroscopy and it was certified that the samples had good precision.

This series has been produced at Research Laboratories of Kawasaki Steel Corp. in Japan.

IV. Results of Segregation Test

The procedure is established as follows as the rules of the Committee on Iron and Steel Standard Samples for Analysis about the examination of constituent segregation within and between samples:

“Uniformity of standard samples for instrumental analysis should be confirmed by an appropriate instrumental analysis for one-tenth of whole samples at a laboratory in charge of production.”

So, the following examination of segregation within and between samples was performed according to the method³⁾ established cooperatively by the Photoelectric Emission Spectroscopic Analysis Subcommittee in the Iron and Steel Analysis Committee, the Joint Research Society of the Iron and Steel Institute of Japan.

Ten samples from NBS and BAS standards within the range of the content of Minor Element Series B (hereinafter indicate ‘comparative samples’) were used to compare with the Japanese samples. Chemical compositions of the comparative samples are shown in Table 2. The non-standardized values are in parentheses and the standard values which are out of the range of the content of this series and not used for calculation in this work, in brackets.

Apparatus and analytical conditions are listed in Table 3 and analytical lines in Table 4.

Table 3. Apparatus and analytical conditions

Spectrometer and excitation source	Shimadzu Co. Vacuum Quantorecorder GVM 100	
	Shimadzu Co. High speed unit SG-400 low voltage spark	
	Capacitance	5 μF
	Inductance	5 μH
	Resistance	2 Ω
Electronic console	Output voltage 420 V	
	Shimadzu Co. Recording console 241 000	
Electrode	Silver	6 mmφ
Analytical gap	5 mm	
Ar gas flow and exposure condition	Initial flush	1.5 l/min × 4 sec
	Preburn period	2.5 l/min × 7 sec
	Integration period	2.5 l/min × 5 sec
Abrasive*	AA	#60

* Preparation of Sample: The surface of the sample for the determination of aluminum is finished with a dry silicon carbide abrasive belt of 80 grit.

Table 4. Analytical lines

Element	Wave length (Å)	Element	Wave length (Å)
Carbon	C I 1 930.9	Arsenic	As 1 972.6
Nickel	Ni II 2 316.0	Tin	Sn II 1 899.9
Chromium	Cr II 2 677.2	Boron	B I 1 826.4
Molybdenum	Mo 2 020.3	Niobium	Nb II 3 195.0
Vanadium	V II 3 110.7	Zirconium	Zr II 3 392.0
Cobalt	Co I 3 453.5	Calcium	Ca II 3 933.7
Titanium	Ti II 3 372.8	Iron	Fe II 2 714.4
Aluminum	Al I 3 961.5		

1. Segregation within Sample

Firstly, each element in the comparative samples was determined by emission spectroscopic method with a daily-work calibration curve. The emission was detected from four points on one analyzing surface.

The average (A_N) and standard deviation (σ_{wN}) were calculated from obtained values. The simple regression equation for the relation between σ_{wN} and the corresponding analytical value was obtained. Standard deviation ($\sqrt{V_{yx}}$) representing fluctuation from the regression curve was obtained. The results are shown in Table 5 with the regression equations.

Then, ten pieces picked up at random from each eight prepared samples were analyzed by the same method as for the comparative samples and average (A_J) and standard deviation (σ_{wJ}), as shown in Table 6, were calculated. σ_{wcJ} was calculated by substituting a standard value of prepared sample into the

equation in Table 5.

The result of the comparison between σ_{wJ} and σ_{wcJ} is expressed as the mark of *a*, *b* or *c* at right shoulder of σ_{wJ} in Table 6. Values marked with *a*, *b* and *c* are respectively for the case of $\sigma_{wJ} \leq \sigma_{wcJ} + \sqrt{V_{yx}}$, $\sigma_{wcJ} + \sqrt{V_{yx}} < \sigma_{wJ} \leq \sigma_{wcJ} + 2\sqrt{V_{yx}}$ and $\sigma_{wJ} > \sigma_{wcJ} + 2\sqrt{V_{yx}}$. Most of them were marked with *a*. So, the samples of Minor Element Series B were confirmed to be excellent as standard samples for spectroscopic analysis.

σ_{wN} for calcium was not obtained because no indication of the standard value was given for the comparative sample and the determination of antimony was impossible for low sensitivity at measurement.

σ_{wJ} for calcium was calculated from the results of the prepared samples, and is added to Table 6.

Samples without a mark in Table 6 could not be compared with the comparative samples because the content was beyond that of the comparative samples.

Table 6. Test results on segregation within

Element	JSS No.	Standard value (%)	Repeatability [σ_{wJ}] (10^{-3} %)									
			I	II	III	IV	V	VI	VII	VIII	IX	X
C	168-1	0.055	2.0	1.0	3.3	1.1	1.5	1.4	1.6	1.4	3.3	0.7
	169-1	0.054	2.5	3.1	3.3	1.4	0.7	1.4	2.9	1.4	0.9	2.3
	170-1	0.062	1.4	3.9	0.8	2.5	2.8	2.7	1.5	1.7	2.6	1.2
	171-1	0.081	3.9 ^a	1.3 ^a	3.7 ^a	3.2 ^a	0.9 ^a	1.4 ^a	1.1 ^a	1.9 ^a	3.5 ^a	2.8 ^a
	172-1	0.081	2.6 ^a	4.0 ^a	2.0 ^a	1.2 ^a	2.1 ^a	2.6 ^a	4.3 ^a	2.5 ^a	2.6 ^a	2.4 ^a
	173-1	0.079	1.4 ^a	2.6 ^a	2.7 ^a	2.4 ^a	2.8 ^a	4.4 ^a	2.7 ^a	2.7 ^a	2.3 ^a	4.8 ^b
	174-1	0.071	4.2 ^a	2.8 ^a	3.4 ^a	4.0 ^a	4.9 ^b	2.9 ^a	2.2 ^a	2.1 ^a	2.5 ^a	0.6 ^a
	175-1	0.083	3.4 ^a	4.6 ^b	2.2 ^a	2.2 ^a	4.0 ^a	4.3 ^a	2.1 ^a	2.7 ^a	2.6 ^a	2.9 ^a
Ni	168-1	0.013	0	0.4	0.5	0.8	0.4	0.5	0.4	0.8	0.9	0.8
	169-1	0.038	1.5 ^a	0.8 ^a	0	0.5 ^a	0	0.8 ^a	0.8 ^a	0.9 ^a	1.1 ^a	0.5 ^a
	170-1	0.070	0.9 ^a	0.8 ^a	1.3 ^a	0.5 ^a	1.8 ^a	2.1 ^b	0.8 ^a	1.2 ^a	1.5 ^a	1.5 ^a
	171-1	0.100	3.1 ^b	2.0 ^a	2.1 ^a	1.1 ^a	1.7 ^a	0.5 ^a	1.3 ^a	1.1 ^a	3.4 ^b	0.9 ^a
Cr	168-1	0.012	0.1	0.2	0.4	0.3	0.2	0.2	0.3	0.4	0.4	0.2
	169-1	0.094	1.4 ^b	0.5 ^a	0.4 ^a	0.7 ^a	0.5 ^a	0.8 ^a	1.1 ^a	0.8 ^a	0.8 ^a	0.5 ^a
	170-1	0.037	0.4 ^a	0.2 ^a	0.4 ^a	0.2 ^a	0.6 ^a	0.6 ^a	0.3 ^a	0.2 ^a	0.4 ^a	0.5 ^a
	171-1	0.067	0.9 ^a	0.6 ^a	0.5 ^a	0.5 ^a	1.0 ^a	0.2 ^a	0.5 ^a	0.4 ^a	1.0 ^a	0.4 ^a
Mo	168-1	0.095	0.5 ^a	0.7 ^a	0.8 ^a	1.1 ^a	0.9 ^a	0.9 ^a	0.8 ^a	0.9 ^a	1.5 ^a	1.0 ^a
	169-1	0.067	1.2 ^a	0.6 ^a	0.4 ^a	0.8 ^a	0.2 ^a	0.5 ^a	0.8 ^a	0.9 ^a	0.9 ^a	0.3 ^a
	170-1	0.011	0.3	0.2	0.4	0.1	0.5	0.6	0.2	0.4	0.5	0.5
	171-1	0.038	0.8 ^a	0.6 ^a	0.6 ^a	0.3 ^a	0.8 ^a	0.1 ^a	0.5 ^a	0.3 ^a	1.1 ^a	0.3 ^a
V	172-1	0.010	0.2 ^a	0.2 ^a	0.2 ^a	0.2 ^a	0.3 ^a	0.2 ^a	0.1 ^a	0.1 ^a	0.2 ^a	0.3 ^a
	173-1	0.035	0.4 ^a	0.3 ^a	0.4 ^a	0.5 ^a	0.3 ^a	0.4 ^a	0.3 ^a	0.2 ^a	0.4 ^a	0.9 ^a
	174-1	0.062	0.8 ^a	0.5 ^a	0.5 ^a	0.6 ^a	0.6 ^a	0.2 ^a	0.6 ^a	0.3 ^a	0.1 ^a	0.7 ^a
	175-1	0.093	0.7 ^a	0.2 ^a	1.1 ^a	0.7 ^a	1.0 ^a	0.7 ^a	0.6 ^a	0.5 ^a	0.5 ^a	0.4 ^a
Co	172-1	0.055	0.7 ^a	0.4 ^a	0.5 ^a	0.8 ^a	1.1 ^b	0.8 ^a	0.5 ^a	0.6 ^a	0.4 ^a	0.8 ^a
	173-1	0.030	0.5 ^a	0.6 ^a	0.4 ^a	0.7 ^a	0.5 ^a	0.7 ^a	0.5 ^a	0.5 ^a	0.8 ^b	1.0 ^b
	174-1	0.020	0.8 ^b	0.7 ^a	0.6 ^a	0.4 ^a	0.5 ^a	0.5 ^a	0.7 ^a	0.6 ^a	0.5 ^a	0.5 ^a
	175-1	0.010	0.1 ^a	0.4 ^a	0.9 ^c	0.4 ^a	0.5 ^a	0.5 ^a	0.4 ^a	0.4 ^a	0.4 ^a	0.4 ^a
Ti	168-1	0.065	0.7 ^a	0.4 ^a	0.6 ^a	0.8 ^a	1.3 ^a	1.3 ^a	0.6 ^a	0.8 ^a	1.4 ^a	1.0 ^a
	169-1	0.013	0.2 ^a	0.3 ^a	0.4 ^a	0.3 ^a	0.3 ^a	0.1 ^a	0.3 ^a	0.2 ^a	0.1 ^a	0.4 ^a
	170-1	0.097	0.9	1.8	1.1	0.6	1.2	0.8	0.8	0.7	0.9	0.7
	171-1	0.038	0.5 ^a	0.2 ^a	0.4 ^a	0.2 ^a	0.6 ^a	0.2 ^a	0.4 ^a	0.4 ^a	0.2 ^a	0.3 ^a

Table 5. Calculating formulas of the measurement repeatability in a sample derived from the results of the comparative sample

Element	Concentration range (%)	Formula	Root-dispersion ($\sqrt{V_{yx}}$)
C	0.065 ~0.19	$\sigma_{wN} = 0.00149 + 0.0265\%C$	0.00104
Ni	0.022 ~0.135	$\sigma_{wN} = 0.00049 + 0.0118\%Ni$	0.00065
Cr	0.036 ~0.131	$\sigma_{wN} = 0.00054 + 0.0035\%Cr$	0.00028
Mo	0.011 ~0.120	$\sigma_{wN} = 0.00021 + 0.0193\%Mo$	0.00031
V	0.007 ~0.10	$\sigma_{wN} = 0.00013 + 0.0144\%V$	0.00035
Co	0.013 ~0.074	$\sigma_{wN} = 0.00015 + 0.0126\%Co$	0.00030
Ti	0.004 ~0.057	$\sigma_{wN} = -0.00003 + 0.0357\%Ti$	0.00040
Al	0.005 ~0.058	$\sigma_{wN} = 0.00056 + 0.0058\%Al$	0.00030
As	0.008 ~0.046	$\sigma_{wN} = 0.00160 + 0.0145\%As$	0.00053
Sn	0.005 ~0.085	$\sigma_{wN} = 0.00039 + 0.0101\%Sn$	0.00031
B	0.0002~0.005	$\sigma_{wN} = 0.000032 + 0.0466\%B$	0.00028
Nb	0.005 ~0.096	$\sigma_{wN} = -0.00028 + 0.0608\%Nb$	0.00051
Zr	0.005 ~0.094	$\sigma_{wN} = 0.00128 + 0.0255\%Zr$	0.00084

sample by emission spectroscopic analysis

Element	JSS No.	Standard value (%)	Repeatability [σ_{wJ}] ($10^{-3}\%$)									
			I	II	III	IV	V	VI	VII	VIII	IX	X
Al	168-1	0.047	0.3 ^a	1.2 ^b	0.2 ^a	1.4 ^b	0.4 ^a	1.2 ^b	0.8 ^a	0.2 ^a	0.4 ^a	0.3 ^a
	169-1	0.046	1.4 ^b	1.1 ^a	0.6 ^a	0.5 ^a	1.1 ^a	0.2 ^a	0.6 ^a	0.3 ^a	0.6 ^a	0.4 ^a
	170-1	0.049	0.9 ^a	1.1 ^a	0.3 ^a	0.1 ^a	0.9 ^a	0.5 ^a	1.4 ^b	1.2 ^b	0.8 ^a	0.2 ^a
	171-1	0.052	1.0 ^a	0.9 ^a	0.7 ^a	0.2 ^a	0.2 ^a	1.4 ^b	0.3 ^a	0.4 ^a	0.4 ^a	0.2 ^a
	172-1	0.015	0.2 ^a	0.4 ^a	0.7 ^a	0.1 ^a	0.3 ^a	0.1 ^a	1.2 ^b	0.6 ^a	0.3 ^a	0.1 ^a
	173-1	0.024	0.6 ^a	0.1 ^a	0.3 ^a	0.5 ^a	0.1 ^a	0.1 ^a	0.3 ^a	0.2 ^a	0.1 ^a	0.1 ^a
	174-1	0.032	0.1 ^a	0.1 ^a	0.4 ^a	0.1 ^a	0.4 ^a	0.2 ^a	0.5 ^a	0.5 ^a	0.4 ^a	0.4 ^a
	175-1	0.054	0.3 ^a	0.5 ^a	0.2 ^a	0.5 ^a	0.8 ^a	0.1 ^a	0.2 ^a	0.5 ^a	0.8 ^a	0.4 ^a
As	168-1	0.010	2.0 ^a	0.7 ^a	2.2 ^a	2.1 ^a	1.7 ^a	1.3 ^a	1.1 ^a	1.0 ^a	1.2 ^a	1.6 ^a
	169-1	0.005	0.6	0.4	0.3	0.9	0.3	0.4	1.4	1.7	0.2	0.3
	170-1	0.028	1.2 ^a	1.3 ^a	1.5 ^a	0.7 ^a	2.2 ^a	2.9 ^b	1.4 ^a	2.0 ^a	2.7 ^b	2.7 ^b
	171-1	0.046	2.8 ^a	2.7 ^a	3.3 ^b	1.4 ^a	2.5 ^a	1.8	1.9 ^a	1.6 ^a	3.3 ^b	2.4 ^a
Sn	168-1	0.005	0.2 ^a	0.1 ^a	0.3 ^a	0.3 ^a	0.3 ^a	0.3 ^a	0.2 ^a	0.2 ^a	0.4 ^a	0.3 ^a
	169-1	0.011	0.5 ^a	0.3 ^a	0.4 ^a	0.2 ^a	0.1 ^a	0.2 ^a	0.3 ^a	0.4 ^a	0.1 ^a	0.1 ^a
	170-1	0.053	0.6 ^a	1.5 ^b	0.9 ^a	0.8 ^a	0.9 ^a	1.3 ^b	1.0 ^a	1.4 ^b	1.2 ^a	1.2 ^a
	171-1	0.032	0.9 ^a	0.6 ^a	0.7 ^a	0.3 ^a	0.7 ^a	0.4 ^a	0.6 ^a	0.5 ^a	1.0 ^a	0.5 ^a
B	172-1	0.0021	0.08 ^a	0.07 ^a	0.04 ^a	0.04 ^a	0.05 ^a	0.04 ^a	0.05 ^a	0.05 ^a	0.05 ^a	0.04 ^a
	173-1	0.0031	0	0.13 ^a	0.07 ^a	0.04 ^a	0.05 ^a	0.10 ^a	0.07 ^a	0.10 ^a	0.08 ^a	0.13 ^a
	174-1	0.0052	0.10 ^a	0.07 ^a	0.09 ^a	0.13 ^a	0.14 ^a	0.04 ^a	0.12 ^a	0.11 ^a	0.17 ^a	0.12 ^a
	175-1	0.0085	0.15	0.11	0.17	0.04	0.26	0.16	0.08	0.21	0.12	0.15
Nb	172-1	0.053	1.6 ^a	1.3 ^a	0.4 ^a	1.0 ^a	1.2 ^a	0.9 ^a	1.2 ^a	0.5 ^a	1.0 ^a	1.7 ^a
	173-1	0.032	0.6 ^a	0.6 ^a	0.6 ^a	0.6 ^a	0.5 ^a	0.7 ^a	0.6 ^a	0.3 ^a	0.7 ^a	1.5 ^a
	174-1	0.021	0.9 ^a	0.6 ^a	0.6 ^a	0.6 ^a	0.6 ^a	0.3 ^a	0.6 ^a	0.3 ^a	0.3 ^a	0.6 ^a
	175-1	0.011	0.4 ^a	0.1 ^a	0.8 ^a	0.5 ^a	0.7 ^a	0.5 ^a	0.5 ^a	0.3 ^a	0.5 ^a	0.3 ^a
Zr	172-1	0.009	0.5 ^a	0.2 ^a	0.4 ^a	0.3 ^a	0.2 ^a	0.5 ^a	0.6 ^a	0.5 ^a	0.8 ^a	0.4 ^a
	173-1	0.019	0.8 ^a	0.8 ^a	0.9 ^a	0.8 ^a	0.6 ^a	0.2 ^a	0.8 ^a	0.2 ^a	1.0 ^a	1.5 ^a
	174-1	0.028	1.7 ^a	0.7 ^a	1.7 ^a	1.2 ^a	0.7 ^a	0.9 ^a	0.4 ^a	1.6 ^a	0.4 ^a	2.0 ^a
	175-1	0.048	0.9 ^a	0.6 ^a	0.4 ^a	1.7 ^a	2.4 ^a	1.0 ^a	1.4 ^a	1.4 ^a	0.9 ^a	0.8 ^a
Ca	168-1	0.0007	0.12	0.03	0.12	0.03	0.05	0.03	0.03	0.03	0.03	0.03
	169-1	0.0013	0.04	0.05	0.08	0.04	0.08	0.05	0.10	0.04	0.10	0.05
	170-1	0.0017	0.25	0.12	0.09	0.24	0.05	0.07	0.08	0.02	0.10	0.07
	171-1	0.0027	0.20	0.15	0.09	0.08	0.04	0.22	0.13	0.08	0.04	0.18

2. Segregation between Sample

The fluctuation of the content between samples was investigated according to Section IV. 1. Each element concentration was determined by emission from four points on one analyzing surface and the average (A_{N1}) of the results was obtained, and then the analyzed surface was polished. The determination was repeated ten times by the same procedure and averages ($A_{N1} \sim A_{N10}$) and their standard deviations (σ_{bN}) were calculated.

Then the simple regression equation for the relation between σ_{bN} and the corresponding analytical value was obtained, and the standard deviations ($\sqrt{V_{yx}}$) were obtained according to Section IV. 1, shown in Table 7.

σ_{bJ} was calculated from ten pieces of A_J for the sample randomly obtained at Section IV. 1, and σ_{bcJ} was calculated by substituting a standard value into the equation in Table 7. Results of the comparison between σ_{bJ} and σ_{bcJ} were represented by the shoulder mark of *a*, *b* and *c* (Table 8).

Though σ_{bcJ} for the comparative sample was obtained from the results of repeated determinations on the same sample and σ_{bJ} for the prepared sample was obtained from the results of determinations on ten samples, most of σ_{bJ} were marked “*a*” and it was confirmed that this series had a small segregation and good suitability as standard samples.

V. Calibration Curve

Figure 2 shows some calibration curves for the determinations of Minor Element Series B and Standardization Series A by emission spectroscopic method under the conditions represented in Table 3.

It is known that metallurgical history or inclusions and precipitates present in steel affect the emission spectroscopic analysis. So, in addition to this series other standard series is desired to be used for drawing a calibration curve corresponding to property, content and metallurgical history of objective steel at each laboratory.

The calibration curve for boron of this series was

Table 7. Calculating formulas of the measurement repeatability between samples derived from the results of the comparative sample

Element	Concentration range (%)	Formula	Root-dispersion ($\sqrt{V_{yx}}$)
C	0.065 ~0.19	$\sigma_{bN}=0.00079 + 0.0138\%C$	0.00074
Ni	0.022 ~0.135	$\sigma_{bN}=0.00080 + 0.0085\%Ni$	0.00043
Cr	0.036 ~0.131	$\sigma_{bN}=0.00028 + 0.0046\%Cr$	0.00016
Mo	0.011 ~0.120	$\sigma_{bN}=0.00016 + 0.0122\%Mo$	0.00020
V	0.007 ~0.100	$\sigma_{bN}=0.00001 + 0.0093\%V$	0.00032
Co	0.013 ~0.074	$\sigma_{bN}=0.00042 + 0.0041\%Co$	0.00033
Ti	0.004 ~0.057	$\sigma_{bN}=0.00012 + 0.0189\%Ti$	0.00028
Al	0.005 ~0.058	$\sigma_{bN}=0.00035 - 0.0018\%Al$	0.00014
As	0.008 ~0.046	$\sigma_{bN}=0.00093 + 0.0179\%As$	0.00036
Sn	0.005 ~0.085	$\sigma_{bN}=0.00022 + 0.0085\%Sn$	0.00017
B	0.0002~0.005	$\sigma_{bN}=0.000051 + 0.0109\%B$	0.000044
Nb	0.005 ~0.096	$\sigma_{bN}=0.00032 + 0.0119\%Nb$	0.00026
Zr	0.005 ~0.094	$\sigma_{bN}=0.00057 + 0.0198\%Zr$	0.00154

Table 8. Test results on segregation between samples by emission spectroscopic analysis

Element	Repeatability [σ_{wJ}] ($10^{-3}\%$)							
	168-1	169-1	170-1	171-1	172-1	173-1	174-1	175-1
C	2.9	2.2	1.8	3.2 ^b	3.3 ^b	3.2 ^b	2.3 ^a	3.3 ^b
Ni	0.8	1.1 ^a	0.9 ^a	2.4 ^b				
Cr	0.5	1.0 ^b	0.4 ^a	0.3 ^a				
Mo	1.2 ^a	0.9 ^a	0.3	0.5 ^a				
V					0.1 ^a	0.4 ^a	0.6 ^a	0.5 ^a
Co					0.4 ^a	0.5 ^a	0.4 ^a	0.3 ^a
Ti	0.9 ^a	0.2 ^a	0.8	0.5 ^a				
Al	0.4 ^a	0.2 ^a	0.2 ^a	0.3 ^a	0.4 ^b	0.3 ^a	0.3 ^a	0.3 ^a
As	1.8 ^b	1.1 ^a	1.3 ^a	2.2 ^a				
Sn	0.4 ^a	0.4 ^a	0.5 ^a	0.5 ^a				
B					0.07 ^a	0.05 ^a	0.06 ^a	0.12 ^a
Nb					0.7 ^a	0.5 ^a	0.6 ^a	1.8 ^a
Zr					0.4 ^a	0.9 ^a	0.8 ^a	0.4 ^a
Ca	0.04	0.08	0.05	0.12

Fig. 2. Calibration curve for each element in the sample of Minor Element Series B and Standardization Series A by emission spectroscopic method

Fig. 2. Continued

The averages shown in Certificate are the arithmetic mean calculated from the remain not rejected by each verification.
(Since 1975, the standard deviations of the data adopted have been added.)

Fig. 3. Procedure for the decision of standard value

different from that of Standardization Series, and it seemed that the metallurgical history or the state of precipitates and inclusions present in steel had effects on the determinations (the studies about this has been going on). For all the elements except boron, however, each analytical value of an element was plotted on one calibration curve.

VI. Decision of Standard Value

The method for the decision of standard values of Japanese Standard Sample for Iron and Steel is described in the rules of the Committee on Iron and Steel Standard Samples for Analysis. Figure 3 shows the procedure.

JIS (Japanese Industrial Standard) method or equivalent ones should be applied as analytical method because it is defined by JIS K0501 (general rules for chemical standards material) that a standard sample belongs to ‘Component Standard Material’ and the content should be determined by the method prescribed in JIS.

Recently, however, some other methods have been adopted in consideration of kinds of steel and involved elements, after suitability for analytical method had been studied at each laboratory. The use of various analytical methods for the decision may give accurate values without the specific tendency by a particular

one method.

Moreover, the analytical methods adopted most frequently coincide with the method which had been studied thoroughly by Iron and Steel Analysis Committee, Joint Research Society, ISIJ, ISO/TC 17/SC.1 (Iron and Steel Analysis) Committee in Japan.

The analytical methods adopted for the decision of standard values are shown in Table 9, and the simple regression equations of standard deviation ($\sigma_{\bar{x}}$) in the measurement for the decision of standard value in Table 10.

VII. Conclusion

The production and quality of Minor Element Series B of Japanese Standard Samples for Iron and Steel Analysis are described.

The standard samples are confirmed to be not inferior to comparative samples of NBS No. 1160 series and BAS SS samples for spectrometric analysis.

The problem to be solved further is that the calibration curve for boron of this series is different from that of the Standardization Series. This is now being studied and it will result in a satisfactory settlement by the Subcommittee of the Committee on Iron and Steel Standard Samples for Analysis.

The method of decision of the standard value and the precision for analysis of trace amounts of elements

Table 9. Analytical methods used for the determination of standard values

Element	Method	Element	Method
C	JIS G 1211-1969 Combustion-Coulometric Method	Al	JIS G 1224-1969 Chromazurol S Spectrophotometric Method
	JIS G 1211-1969 Combustion-Electro Conductometric Method		JIS G 1257-1975 Atomic Absorption Method
Ni	JIS G 1216-1969 Dimethylglyoxime Spectrophotometric Method after Separating Ferric Hydroxide	As	JIS G 1225-1969 Arsenic Iodide Extraction Molybdenum Blue Spectrophotometric Method
	JIS G 1257-1975 Atomic Absorption Method	Sn	JIS G 1226-1969 Tin Iodide Extraction Phenylfluorone Spectrophotometric Method
Cr	JIS G 1217-1969 Diphenylcarbazide Spectrophotometric Method		JIS G 1257-1975 Atomic Absorption Method
	JIS G 1257-1975 Atomic Absorption Method	B	JIS G 1227-1969 Methylene Blue Extraction Spectrophotometric Method
Mo	JIS G 1218-1969 Thiocyanate Spectrophotometric Method		JIS G 1227-1969 Curcumin Spectrophotometric Method after Distillation
	JIS G 1218-1969 Thiocyanate Extraction Spectrophotometric Method		Quinalizalin Spectrophotometric Method after Distillation
	JIS G 1257-1975 Atomic Absorption Method		Emission Spectrographic Method-Solution Technique
V	JIS G 1221-1969 N-BPHA Extraction Spectrophotometric Method	Nb	Sulphochlorophenol S Spectrophotometric Method
	JIS G 1257-1975 Atomic Absorption Method		JIS G 1231-1969 Thiocyanate Spectrophotometric Method
Co	JIS G 1222-1969 β -nitroso- α -naphthol Extraction Spectrophotometric Method		JIS G 1231-1969 Pyrogallol Spectrophotometric Method
	JIS G 1222-1969 Nitroso R Salt Spectrophotometric Method	Zr	JIS G 1232-1969 Xylenol Orange Spectrophotometric Method
	Nitroso R Salt-TOA Chloroform Extraction Spectrophotometric Method		Arsenazo-III Spectrophotometric Method
	JIS G 1257-1975 Atomic Absorption Method	Ca	JIS G 1257-1975 Aromic Absorption Method
Ti	JIS G 1223-1969 TOPO Extraction Thiocyanate Spectrophotometric Method	Sb	Brilliant Green Spectrophotometric Method
	JIS G 1223-1969 Hydrogen peroxide Spectrophotometric Method		Rhodamine B Spectrophotometric Method
	Diantipyrylmethane Spectrophotometric Method		JIS G 1257-1975 Atomic Absorption Method
	JIS G 1257-1975 Atomic Absorption Method		

Table 10. Calculating formulas of reproducibility on the measurement for the determination of standard values

Element	Concentration range (%)	Formula (%)
Ni	0.01 ~0.10	$0.00121 + 0.0088 \times \{\text{Ni}(\%)\}$
Cr	0.01 ~0.10	$0.00045 + 0.0253 \times \{\text{Cr}(\%)\}$
Mo	0.01 ~0.10	$0.00069 + 0.0168 \times \{\text{Mo}(\%)\}$
V	0.01 ~0.10	$0.00039 + 0.0236 \times \{\text{V}(\%)\}$
Co	0.01 ~0.05	$0.00030 + 0.0303 \times \{\text{Co}(\%)\}$
Ti	0.01 ~0.10	$0.00072 + 0.0203 \times \{\text{Ti}(\%)\}$
Al	0.01 ~0.05	$0.00104 + 0.0116 \times \{\text{Al}(\%)\}$
As	0.01 ~0.05	$0.00023 + 0.0390 \times \{\text{As}(\%)\}$
Sn	0.01 ~0.05	$0.00051 + 0.0333 \times \{\text{Sn}(\%)\}$
B	0.002 ~0.01	$0.00019 + 0.0137 \times \{\text{B}(\%)\}$
Nb	0.01 ~0.05	$0.00023 + 0.0401 \times \{\text{Nb}(\%)\}$
Zr	0.01 ~0.05	$0.00109 + 0.0185 \times \{\text{Zr}(\%)\}$
Ca	0.0005~0.003	$0.00007 + 0.0443 \times \{\text{Ca}(\%)\}$
Sb	0.002 ~0.02	$0.00014 + 0.0301 \times \{\text{Sb}(\%)\}$

are mentioned.

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