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Effect of the Counter-Electrode Material on the Emission Spectrochemical Determination of Silicon and Manganese in Steel

Takanori SUZUKI*[1] and Tomihito KAMBARA

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo

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The line intensities of Si and Mn appear much more strongly in the spectrochemical analysis of high-carbon low-alloy steels when a low-voltage spark is employed. Considering the change in the line intensity with the time under various excitation conditions with graphite and zinc counter-electrodes, the present authors have established an improved method for the spectrochemical determination of Si and Mn. The effect of the heat-treatment on the metallurgical structure has been investigated by means of an electron-probe microanalyzer, and the results compared with the spectrochemical data.

The accuracy of an emission spectrochemical determination is influenced by many factors, such as the fractional distillation, the excitation conditions, self-absorption, and third-element effects. These complicated factors are generally called the matrix effect, which has been discussed in many articles.[1-5] In the analysis of iron and steel, one must also take metallurgical hysteresis and the structure of the specimen into consideration. Several investigations dealing with the matrix effects in special steels[6-11] have been reported, and solution methods[12-13] and powder

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[*1] Present address: Muroran Plant, Japan Steel Works (Nihon Seikosho, Ltd.), Muroran.

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Table 1. Low and high voltage spark (LVS and HVS) excitation conditions

No.	Spectrograph	Primary voltage Volt	Secondary voltage Volt	Capacity μF	Inductance μH	Resistance Ω	Counter-electrode	Estimated temp. K°
LVS	GQ-220		870	10	50	1.25	Graphite	—
HVS 1	GQ-220	150	16500	0.007,0	0	0	Zinc	—
HVS 2	GQ-220	150	16500	0.007,0	100	0	Graphite and zinc	—
HVS 3	GE-340	70	10500	0.006,6	800	0	Graphite	5170—5430
HVS 4	GE-340	70	10500	0.006,6	80	0	Graphite	5540—5730
HVS 5	GE-340	70	10500	0.006,6	80	0	Zinc	6380—6610

methods[14-16] have both been proposed in order to overcome the above-mentioned difficulties.

The results of the spectrochemical determination of silicon and manganese in high-carbon low-alloy steel have now been found to depend remarkably on the metallurgical structure. In the present study the excitation conditions for a more accurate determination will be examined.

Experimental

Apparatus. A direct-reading Quantorecorder (GQ-220) and an Ebert-mounting grating spectrograph (GE-340), both made by Shimadzu, were employed. The spark was generated by means of a multisource Feussner equipment. In the photographic measurement of line intensities, a microphotometer was used. The electron-probe microanalyzer was a product of the Japan Electron Optics Laboratory (Nihon Denshi), type JXA-304.

Electrodes. The steel specimens were used as the plane self-electrodes. As the counter-electrodes we employed graphite rods, 6 mm in diameter and 120° in cone angle, and zinc rods, 5 mm in diameter and 80° in cone angle, prepared by casting metal 99.9% pure.

Excitation Conditions. Six conditions were chosen for the determination of silicon and manganese; they are listed in Table 1.

Analytical Lines. The characteristics of the spectral lines utilized for the quantitative analysis are listed in Table 2. All the manipulations were done according to the Japanese Industrial Standards.[17]

Table 2. Analytical lines

Wavelength of analytical line Å	Excitation voltage, eV	Spectrograph used
Fe II 2714.41	7.90	GQ-220
Si I 2516.12	8.12	GQ-220
Mn II 2933.06	12.83	GQ-220, GE-340
Fe II 2926.59	13.12	GE-340
Si I 2881.58	5.08	GE-340
Fe I 2874.17	4.31	GE-340
Fe 2880.76	13.19	GE-340

Results and Discussion

Results Obtained with the Direct-reading Quantorecorder. Quenched and annealed specimens of five steel samples were analyzed spectrochemically for several elements by means of the working curves prepared for routine analysis with a series of BCS standard steels. The results are tabulated in Table 3. The results of the standard chemical analysis are given in Table 4 for comparison.

It can be seen that the spectrochemical results for nickel, chromium, copper, and molybdenum agree well with the values obtained by the standard chemical analysis. However, remarkable positive deviations were found for silicon and manganese, especially with the quenched specimens. In the LVS excitation with a graphite counter-electrode it was found that the spark did not focus well. The change in the line intensities with the time was measured by changing the presparking time, as is shown in Fig. 1. Both silicon and manganese always showed stronger intensities than the theoretical values throughout the 360-sec presparking time. When a zinc rod was used as the counter-electrode, the intensities of not only silicon and

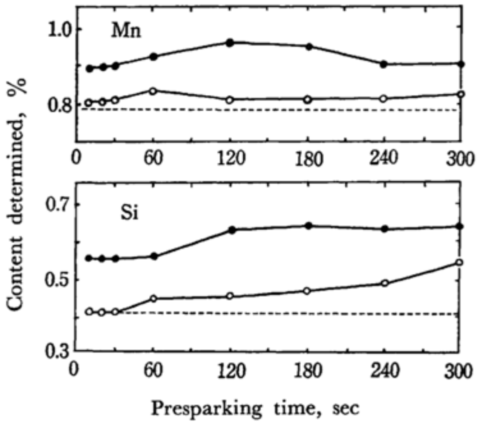

Fig. 1. Change of line intensity. Excitation condition LVS. Sample No. 2. ○ Annealed and ● quenched specimen. The horizontal dashed lines show the contents determined by the standard chemical analysis. Analytical lines: Fe 2714, Si 2516, Mn 2933 Å.

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15) J. Y. Ellenburg, *ibid.*, **34**, 230 (1962).
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Table 3. Analytical results obtained with LVS excitation

Sample No.[a]	Si, % Found	Si, % d[b]	Mn, % Found	Mn, % d	Ni, % Found	Ni, % d	Cr, % Found	Cr, % d	Cu, % Found	Cu, % d	Mo, % Found	Mo, % d
1Q	0.55	+0.15	1.30	+0.35	0.15	0	1.06	+0.01	0.18	−0.01	0.39	+0.01
1A	0.43	+0.03	1.10	+0.15	0.14	−0.01	1.04	−0.01	0.17	−0.02	0.37	−0.01
2Q	0.55	+0.14	0.90	+0.14	0.28	−0.01	1.08	−0.02	0.12	0	0.31	−0.01
2A	0.40	−0.01	0.85	+0.09	0.28	−0.01	1.07	−0.03	0.11	−0.01	0.30	−0.02
3Q	0.64	+0.09	1.10	+0.11	0.15	0	1.04	−0.01	0.13	−0.01	0.38	0
3A	0.53	−0.02	1.06	+0.07	0.15	0	1.03	−0.02	0.13	−0.01	0.36	−0.02
4Q	0.46	+0.10	0.95	+0.07	0.11	+0.01	1.00	0	0.13	−0.01	0.33	−0.01
4A	0.37	+0.01	0.89	+0.01	0.11	+0.01	0.98	−0.02	0.13	−0.01	0.33	−0.01
5Q	0.67	+0.13	1.16	+0.20	0.14	+0.01	0.98	+0.01	0.11	−0.01	0.34	+0.01
5A	0.52	−0.02	1.05	+0.09	0.12	−0.01	0.99	+0.02	0.12	0	0.32	−0.01

a) Q=quenched, A=annealed specimen.
b) d=difference of spectrochemical data from those obtained by standard chemical analysis.

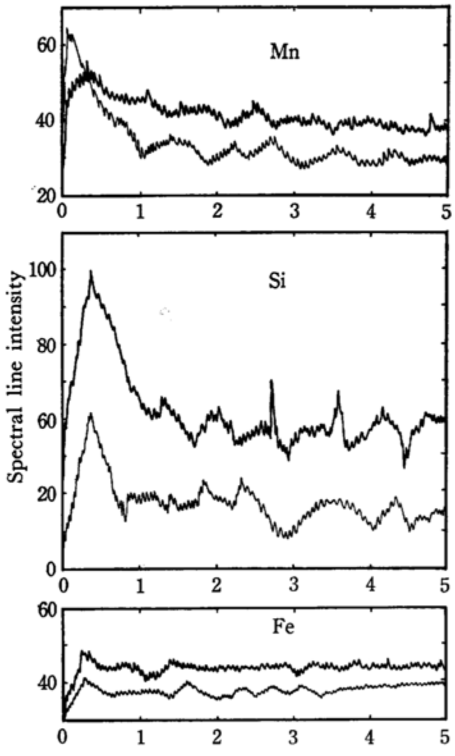

Fig. 2. Change of line intensity. Excitation condition HVS 1. Sample No. 2. Fine line indicates the annealed specimen and bold line the quenched. Analytical lines are the same as in Fig. 1.

manganese but also of iron decreased considerably.

Since the annealed specimen behaves differently from the quenched specimen, it may be supposed that the change in metallurgical structure has caused a matrix effect.

Figures 2, 3, and 4 show the changes in the spectral line intensities with the time under the excitation conditions of HVS 1 and 2, listed in Table 1. With HVS 1 the Fe 2714 Å line intensity is stable, but the lines of silicon and manganese fluctuate, as Fig. 2 shows. Figures 3 and 4 obviously show that the spectral lines of the three elements show stable intensities after 3 min. Thus, it may be safe to say that the interference by the metallurgical structure can well be eliminated under the HVS 2 excitation condition.

Results Obtained with the Ebert-mounting Spectrograph. The intensity ratios for iron-silicon and iron-manganese couples were measured, with varying presparking times, under the excitation conditions of HVS 3, 4, and 5. The results are illustrated in Figs. 5, 6, and 7 respectively. With a graphite counter-electrode, the stabilization of the line intensity ratio takes about 3 min, while with a zinc electrode the persistent and stable intensity ratio can be attained within 2 min.

Measurement of the Spark Temperature. Let us now discuss the ionization equilibrium in the gas phase on the basis of the famous Saha equation.[18] Provided that the light source is thermally equilibrated, one has for the radiation intensity, I, of a spectral line the following expression:[1−5]

$$I = Ah\nu N_0 \cdot \frac{g}{g_0} \cdot \exp\left(\frac{-E}{kT}\right) \qquad (1)$$

Here, A is the transition probability; ν, the frequency of the spectral line; N_0, the number of atoms or ions in the ground state; g and g_0, the statistical weights for the activated and ground states respectively and E, the excitation potential, while $\boldsymbol{h}$, $\boldsymbol{k}$, and T have their usual significances. In the Gerlach internal standard method, therefore, the two line intensities, I_1 and I_2, of two elements are related by:

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[18] M. N. Saha, *Phil. Mag.*, (6) **40**, 472 (1920).

TABLE 4. RESULTS OBTAINED BY THE STANDARD CHEMICAL ANALYSES

Sample No.	Si, %	Mn, %	Ni, %	Cr, %	Cu, %	Mo, %	C, %
1	0.40	0.95	0.15	1.05	0.19	0.38	1.20
2	0.41	0.76	0.29	1.10	0.12	0.32	1.21
3	0.55	0.99	0.15	1.05	0.14	0.38	1.42
4	0.36	0.88	0.10	1.00	0.14	0.34	1.17
5	0.54	0.96	0.13	0.97	0.12	0.33	1.37

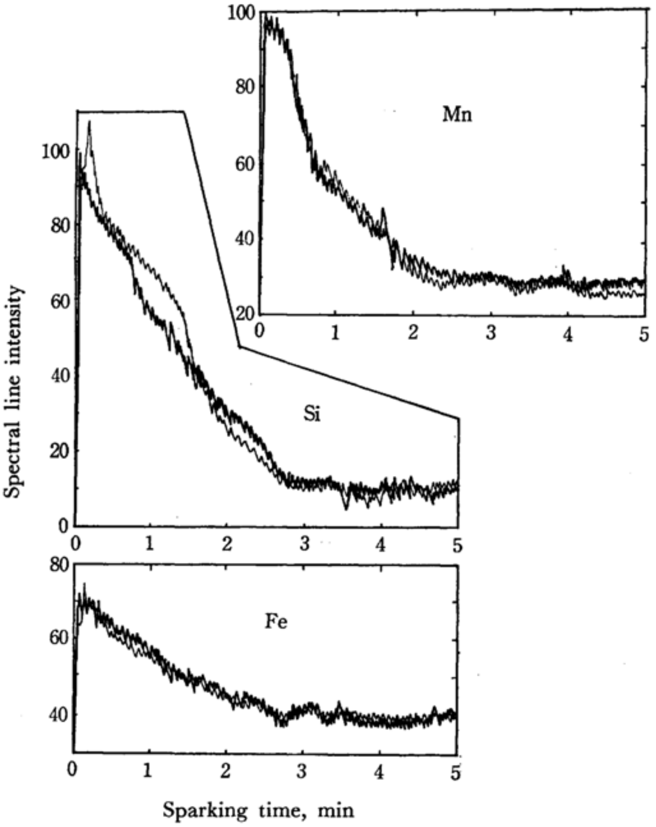

Fig. 3. Change of line intensity. Excitation condition HVS 2 with a graphite counter-electrode. Others are the same as in Fig. 2.

$$\frac{I_1}{I_2} = \text{const}\cdot\frac{N_1}{N_2}\cdot\exp\left\{\frac{-(E_1-E_2)}{\boldsymbol{kT}}\right\} \qquad (2)$$

If the two excitation potentials, E_1 and E_2, differ a little, the ratio of line intensities should be proportional to the ratio of the amounts of the two elements.

Several authors[19-21] have reported on the spark temperature as measured by the intensity ratio method. As Ornstein[21] has shown, by taking the logarithm of Eq. (1), one derives:

TABLE 5. SPECTRAL LINES OF IRON EMPLOYED FOR THE TEMPERATURE MEASUREMENT

Wave-length Å	Excitation energy cm^{-1}	νgA[a]	log I		
			HVS 3	HVS 4	HVS 5
2999.52	40527	309	0.6335	0.7076	0.3979
3024.03	33947	14.1	1.0828	1.1523	0.7993
3030.15	52613	3230	1.4014	1.3324	0.8325
3031.21	52769	2820	1.4914	1.3711	0.8808

a) From Shimazu.[19] See also "American Institute of Physics Handbook," 7-87, McGraw-Hill, New York (1957).

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19) M. Shimazu, *Bunko Kenkyu (J. Spectr. Soc. Japan)*, **9**, 81 (1961).

20) Research Group Concerning Spectroscopic Light Sources, H. Kawaguchi *et al.*, *ibid.*, **13**, 1 (1964).

21) L. S. Ornstein, *Physik. Z.*, **32**, 517 (1931).

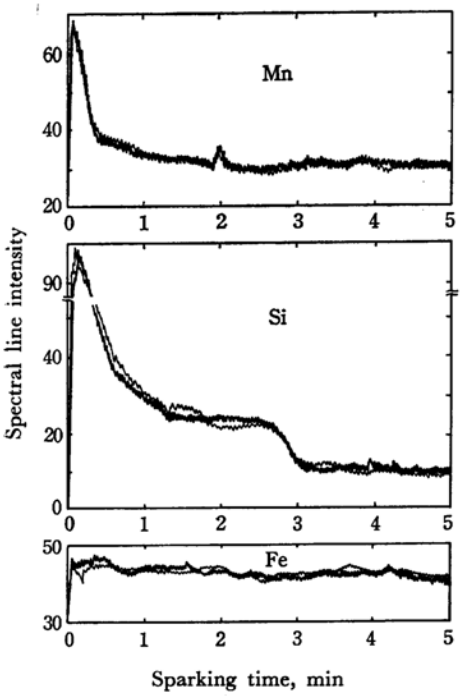

Fig. 4. Change of line intensity. Excitation condition HVS 2 with zinc counter-electrode. Others are the same as in Fig. 2.

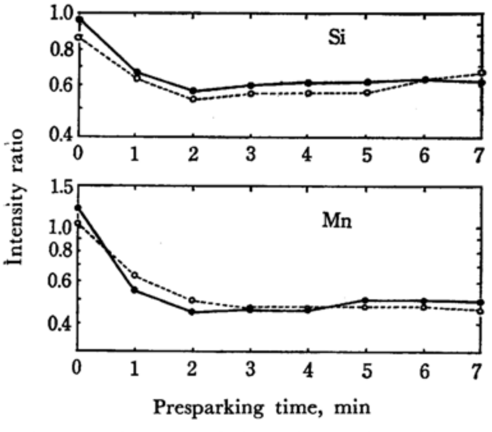

Fig. 5. Change of intensity ratio with time. ○ Annealed and ● quenched specimen. Excitation condition HVS 3. Line pairs are Fe 2880/Si 2881 and Fe 2926/Mn 2933.

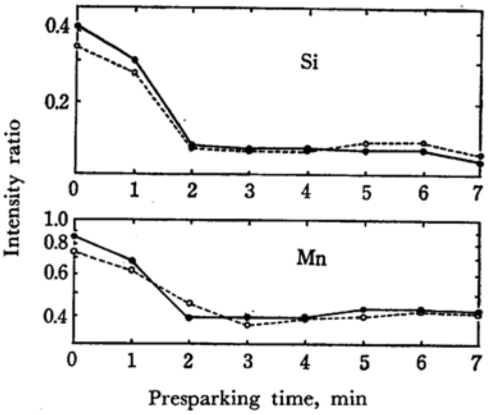

Fig. 6. Change of intensity ratio with time. Excitation condition HVS 4. Others are the same as in Fig. 5.

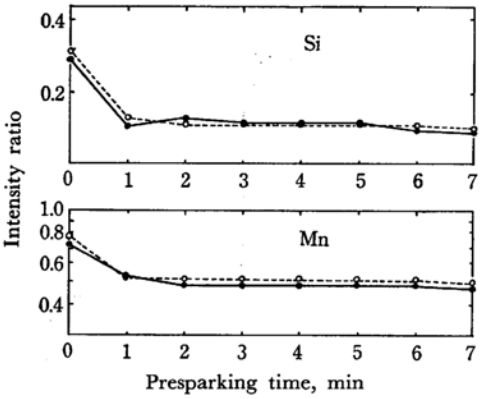

Fig. 7. Change of intensity ratio with time. Excitation condition HVS 5. Others are the same as in Fig. 5.

$$\log\frac{I}{\nu g A} = \log\frac{N_0\boldsymbol{h}}{g_0} - \frac{0.625}{T}E' \tag{3}$$

Here E' is the excitation energy expressed in cm^{-1}. From the slope of the plot of $\log(I/\nu gA)$ against E', we can estimate the light source temperature, as is shown in Fig. 8. The numerical values utilized are listed in Table 5.

A small deviation from linearity is seen in Fig. 8, but such a tendency has already been reported by Shimazu.[19] The estimated temperatures are listed in Table 1.

Metallurgical Structure. The structure of high-carbon low-alloy steel varies with different heat treatments. Figure 9 shows microscopic pictures of this. In many cases cementite appears in a net-structure at the boundaries of the austenite and surrounds the pearlite. Whether silicon and manganese are distributed uniformly or locally was investigated with the aid of an X-ray microanalyzer. As Fig. 10 shows, it can be concluded that manganese is enriched a little in the cementite phase (from 0.95 to 1.06%) but is depleted in pearlite (from 0.95 to 0.71%). As to the other elements, such as silicon, nickel, chromium, and molybdenum, no appreciable segregation is observed.

Discharge Crater. The property of a spark may be judged by the discharge crater remaining on the iron plane electrode surface. The craters observed on the various counter-electrode materials are shown in Fig. 11. It was found that, with the

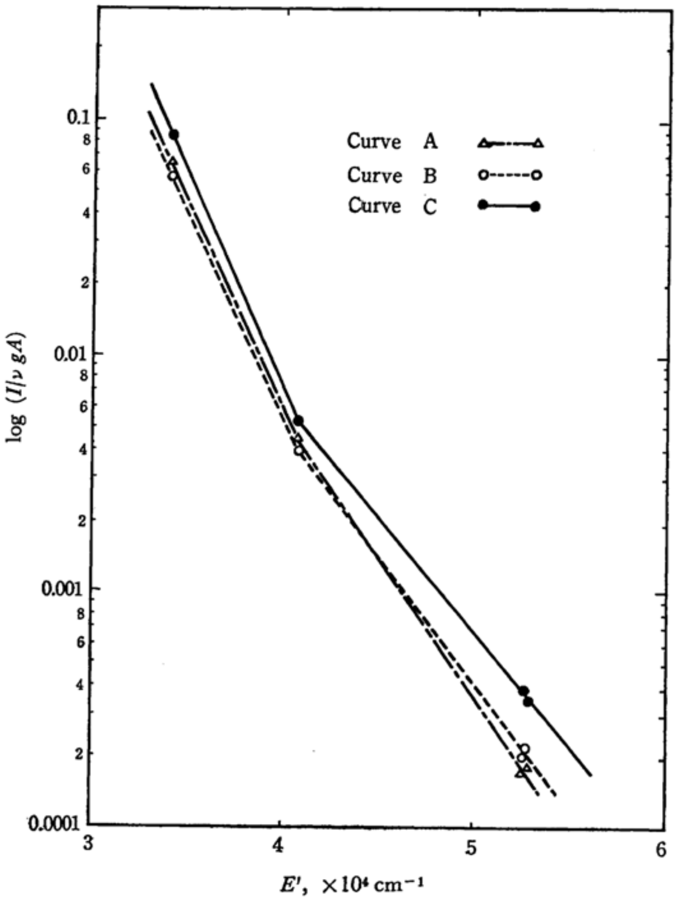

Fig. 8. log $(I/\nu gA)$ plotted against E'. Curve A HVS 3, B HVS 4 and C HVS 5.

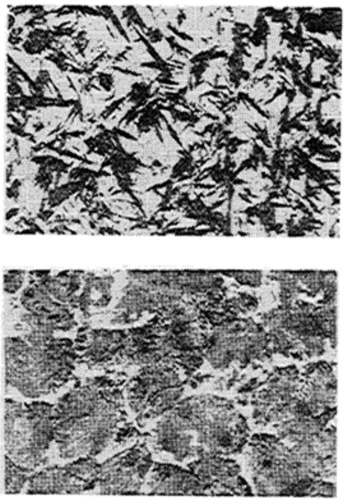

Fig. 9. Microscopic pictures. The sample steel was taken in a steel mould (30 mm diameter 50 mm length). Etched with 1% nitric acid in alcoholic picric acid solution. ×400. The specimens are sample No. 1, water-quenched (upper) and sample No. 2, air-quenched (lower).

zinc electrode, the spark plasma was stable and well-focused. With the graphite electrode, however, the spark tended to dance and to be diffuse. As Table 1 shows, with the zinc electrode the temperature became about 800°K higher than with graphite (HVS 4 and 5).

As for the other electrode materials, with silver the spark does not focus well in the atmospheric environment, while with magnesium, as Fig. 11 shows, although a well-focused and stable spark is attained, the strong lines of Mg 2802, 2928, 2936, and 3092 Å strongly interfere with the determination.

Improved Method of Determination. From the above experimental results, it can be expected that, under the excitation conditions of HVS 2 and 5, one may obtain better determination data than under the conditions of LVS, HVS 1, 3, and 4. Utilizing the series of BCS standard steels, the calibration curves for HVS 2 and 5 were prepared, with which the determination of silicon and manganese was then carried out. The results are tabulated in Tables 6 and 7.

The deviation of the results of the analysis by

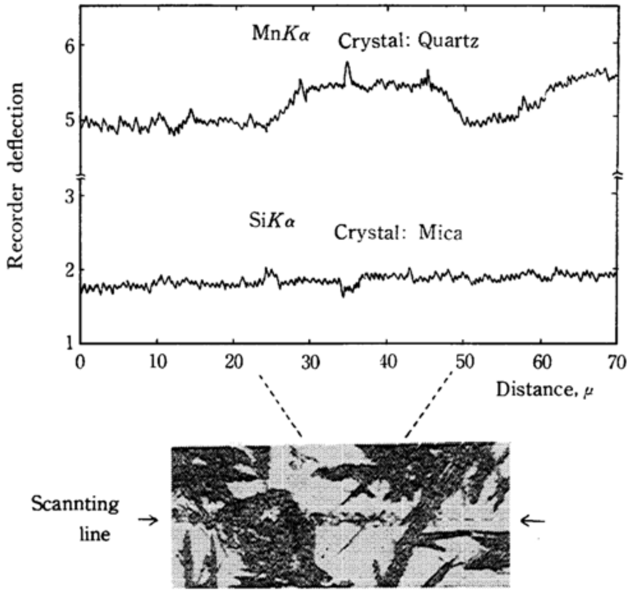

Fig. 10. Analysis by electron probe microanalyzer. The upper curves show the variations of characteristic X-ray intensities and the lower picture the corresponding electron microscopic photograph. The dashed line indicates the scanning line. Acceleration voltage 20 kV. Electron probe diameter 2 μ. Current absorbed by specimen 0.20 μA. Detector : Proportional gas flow counter.

TABLE 6. ANALYTICAL RESULTS OBTAINED BY HVS 2 EXCITATION WITH ZINC COUNTER-ELECTRODE

Sample[1]	Si, %		Mn, %	
	Found	d[2]	Found	d[2]
1Q	0.39	−0.01	0.90	−0.05
	0.39	−0.01	0.92	−0.03
1A	0.42	+0.02	0.85	−0.10
	0.41	+0.01	0.89	−0.06
2Q	0.38	−0.03	0.69	−0.07
	0.37	−0.04	0.70	−0.06
2A	0.39	−0.02	0.74	−0.02
	0.39	−0.02	0.72	−0.04
3Q	0.60	+0.05	0.93	−0.06
	0.58	+0.03	0.96	−0.03
3A	0.55	0	0.94	−0.05
	0.55	0	0.95	−0.04
4Q	0.35	−0.01	0.91	+0.03
	0.35	−0.01	0.90	+0.02
4A	0.34	−0.02	0.88	0
	0.35	0	0.89	+0.01
5Q	0.59	+0.05	0.98	+0.02
	0.60	+0.06	0.97	+0.01
5A	0.52	−0.02	0.99	+0.03
	0.51	−0.03	0.97	+0.01

1) Q=quenched, A=annealed specimen
2) d=difference of spectrochemical data from those obtained by standard chemical analysis.

TABLE 7. ANALYTICAL RESULTS OBTAINED BY HVS 5 EXCITATION

Sample[1]	Si, %		Mn, %	
	Found	d[2]	Found	d[2]
1Q	0.38	−0.02	0.94	−0.01
1A	0.39	−0.01	0.92	−0.03
2Q	0.40	−0.01	0.77	+0.01
2A	0.41	0	0.78	+0.02
3Q	0.53	−0.02	0.97	−0.02
3A	0.54	−0.01	0.97	−0.02
4Q	0.35	−0.01	0.89	+0.01
4A	0.34	−0.02	0.90	+0.02
5Q	0.52	−0.02	0.93	−0.03
5A	0.53	−0.01	0.92	−0.04

1) and 2) same as in Table 6.

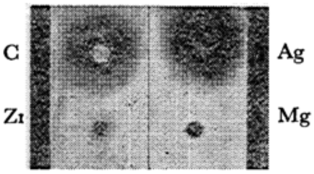

Fig. 11. Variation of the spark discharge craters produced on the iron plane electrode with varying counter-electrode materials. Excitation condition HVS 5.

the spectrochemical method from the results obtained by the standard chemical analysis is treated statistically. The familiar Student t test has already been applied to test the difference between the means obtained by the two methods in a number of analyses of specimens differing in their composition.[22]

The results of the t tests are tabulated in Table 8. The distinct deviations of the silicon and manganese determinations by LVS from the data obtained by the standard chemical analyses are obviously much improved by applying HVS 5, only the silicon determination still showing a significant difference. Under the strong excitation conditions with HVS 2, the observed t_0-value being less than the t-value in the table, no difference between the means can be seen at the significant level of 5%.

TABLE 8. THE t TESTS

Excitation condition	t from table ($\alpha=0.05$)	Degree of freedom	Heat treatment	t_0 for Si	t_0 for Mn
LVS	2.776	4	Q	*10.517*	*4.000*
			A	0.208	*3.644*
HVS 2 (Zn)	2.262	9	Q	0.701	1.964
			A	1.489	2.080
HVS 5	2.776	4	Q	*6.530*	1.025
			A	2.577	0.793

Note. Italic figures indicate $t_0>t$, *i. e.* there is a significant difference between two means.

Conclusion

The remarkable positive deviation in the determination data of silicon and manganese in high-carbon low-alloy steel when analyses are carried out under low-voltage excitation conditions is due to the matrix effect caused by the differences in the volatilization rate and the degree of ionization or excitation in the spark plasma, *etc.* The metallurgical structure of the sample steel clearly affects the analytical results. The application of the high-voltage spark with a zinc counter-electrode results in a much stronger excitation and permits an accurate determination to be made, that is not interferred with by the metallurgical structure.

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[22] V. V. Nalimov, "The Application of Mathematical Statistics to Chemical Analysis," translated from Russian by P. Basu and edited by M. Williams, Pergamon, Oxford (1963), p. 103.