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著者	YOKOYAMA Yu
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Spectrographic Determination of Ferroalloys. I

Spectrographic Determination of Microamounts of Arsenic and Antimony in Ferromanganese*

Yû YOKOYAMA

The Research Institute for Iron, Steel and Other Metals

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Synopsis

A rapid and accurate method was examined with a quartz spectrograph of medium type to determine arsenic and antimony contained in ferromanganese as impurities. Stable excitation conditions were studied for both block sample and powdered sample, and it was found optimal to excite a mixture of powdered sample and graphite powder by direct current intermittent arc. Silver was introduced into the mixture as the internal standard, and Ag 2309.64Å/AsI 2288.12Å and Ag 2309.64Å/SbI 2311.47Å were used as analytical line pairs. By this method arsenic and antimony in ferromanganese were determined with variation coefficients of 5 to 11 per cent and about 6 per cent, respectively.

I. Introduction

Recently, it becomes necessary to determine various impurities in ferroalloys. However, because of the presence of a second main component besides iron, chemical analyses of these impurities are troublesome and frequently require plenty of time. Therefore, an attempt was made to determine the different impurities simultaneously by spectrographic analysis. Of ferroalloys ferromanganese was first chosen, and the spectrographic determination of arsenic and antimony in it was investigated.

II. Experiments and results

1. Apparatus

The excitation sources used were a selenium rectifier, a direct current intermittent arc generator, and a Feussner spark generator. Photographs were taken with Carl Zeiss Qu 24 spectrograph, and photometry was carried out with Carl Zeiss spectral-line photometer. Electrode used was the graphite rod (5.5 mm in diameter) for spectral analysis supplied from the Nippon Carbon Co., Ltd.

2. Preliminary experiments

(i) Excitation conditions

In spectrographic analysis of iron and steel, the sample itself is usually used as self-electrode and excited by spark or intermittent arc method. For ferroalloys

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it was expected that a second main component constituting the alloy has influence on excitation conditions. Therefore, an attempt was made to obtain stable excitation conditions for ferromanganese by using it as self-electrode.

(a) Block sample: As ferromanganese is supplied generally in the form of block, a pin-type electrode holder could not be used, and therefore, it was replaced by a Petry stand of my own making. Block sample was set on the upper holder (+) and a graphite rod on the lower holder (-). When direct current arc giving 8 amp. at 200 volts was discharged between the block sample and the graphite rod, fiery particles spattered from the arc point and stained the condensing lense. Continuing further the discharge, the block sample cracked at the arc point, which made it difficult to maintain the discharge. Diminishing of the voltage and the amperage of the discharge had no effect on the suppression of the fiery particles. When electrolytic iron rod was used as the counter-electrode in place of graphite rod, fiery particles spattered more violently.

When direct current intermittent arc was used to prevent the elevation of the temperature of block sample, it did not crack, and yet fiery particles spattered. When block sample was excited by spark discharge, these unfavorable phenomena did not appear, but the spectral lines of arsenic and antimony were too weak to be measured. Thus, in case of block sample the spectral lines could not be enhanced without spattering of fiery particles.

(b) Powdered sample: From observing the surface of block sample during excitation, it was found that red-hot particles spattered from the locally heated parts on its surface. Therefore, block sample was crushed down into powder smaller than 100 meshes, and it was put in the crater of graphite rod. A direct current arc giving 8 to 9 amp. at 200 volts was discharged between the powdered sample and a tapered graphite rod which was used as cathode; nevertheless, fiery particles spattered out of the crater, and sometimes violent combustion took place. It was all the same for powdered sample smaller than 170 meshes, too. Observing the sample remaining in the crater after arcing, it was ascertained that the original powdered sample had been changed into a fused globule. It seemed that the heat of arc melted the powdered sample into a globule, from which fiery particles spattered. Diminishing of the voltage and the amperage down to about 185 volts and 6.5 amp. was effective in suppressing the spattering, but the spectral lines of arsenic and antimony weakened.

By exciting the powdered sample by direct current intermittent arc, fiery particles could be fairly suppressed without weakening the intensity of the spectral lines. Then, it was observed that the intensity of pale green radiation from manganese vapor repeated alternately the increase and the decrease during arcing, that is, the evaporation of sample was not uniform. In order to clarify this phenomenon further, the following studies were carried out: (1) the change in the *Mn/As line pair ratio** during discharge, and (2) the reproducibility of

* It means the ratio of the transmittancy of the spectral line of manganese to that of arsenic on a photographic plate.

the Mn/As line pair ratios in repetitional photographs of the same sample. The excitation conditions were as follows:

Electrode— Lower electrode (+): crater, 2.5 mm in diameter, 3 mm in depth.
Upper electrode (-): sharpened to a truncated cone. Sample is loaded eight-tenth full into the crater.

Current— Direct current 220 volts, 10 amp., interrupted at a rate of 6 cycles per second, with an on-off ratio of 1 : 2.

The spectra were photographed for 60 seconds at 20-seconds intervals. The line pair ratios of Mn 2352.93Å/AsI 2349.84Å, Mn 2384.05Å/AsI 2349.84Å, and Mn 2387.02Å/AsI 2349.84Å were measured. The results were as follows: (1) in any line pair the Mn/As line pair ratio fluctuated considerably during the discharge of arc. (2) The reproducibility of the values of these Mn/As line pair ratios was not good at any of three 20-sec. intervals. Even for the line pair Mn 2384.05Å/AsI 2349.84Å, for which the reproducibility was the best of three, the variation coefficient was 16.4 per cent in 8-replicate photographs of the spectra.

(c) Mixture of sample powder and graphite powder: It has been known that in arcing a powdered sample, stable arc discharge is generally obtained by exciting a mixture of the sample and graphite powder. Accordingly, it was expected that, by exciting a mixture of powdered ferromanganese and graphite powder, the fluctuation of the Mn/As line pair ratios could be suppressed and moreover the powdered ferromanganese would be hindered from making a globule during arc discharge. A test in which a sample-graphite mixture of the ratio of 1 to 1/3 in weight was arced under the same conditions as in case of the powdered ferromanganese alone showed that neither fiery particles nor globules were produced, where the variation coefficient, in 8-replicate photographs of the spectra, of Mn 2384.05Å/AsI 2349.84Å line pair ratio was 10.3 per cent. Thus, it was found that graphite powder stabilized the arc discharge of ferromanganese, too.

Silver⁽¹⁾ was selected as a possible internal standard from the point of view that silver belongs to the volatile group together with arsenic and antimony, and has its spectral lines in the neighborhood of the analytical lines of arsenic and antimony. And silver and manganese were tested for their suitability as internal standard. Silver was added in the form of silver oxide, which had been prepared by precipitating from the solution of silver nitrate (G.R.), washing and then drying up. By taking into consideration the intensity of the internal standard line of silver, silver oxide added was 1/3 of the amount of ferromanganese. When the amount of graphite powder was less than 1/3 of that of ferromanganese, the stabilization was imperfect, and, when it lay between 1/3 and 1/2, the effect was complete. Consequently, the mixing ratio of ferromanganese, graphite and silver oxide was determined to be 1 : 1/2 : 1/3.

(ii) Selection of line pairs

Strong spectral lines of arsenic are AsI 2349.84Å, AsI 2288.12Å and AsI

(1) Y. Yokoyama, J. Chem. Soc. Japan, 77 (1956), 1668; Sci. Rep. RITU, A9 (1957), 419.

2780.20Å, but the last line is so closely overlapped by Mn 2780.00Å, that it could not be utilized. And as SbI 2598.06Å is subject to hindrance of FeII 2598.37Å, the next strong line, SbI 2311.47Å⁽¹⁾ was used. Thus, as the available lines of arsenic and antimony lie in the neighborhood of 2300Å, three internal standard lines, Mn 2352.93Å, Mn 2384.05Å and Ag 2309.64Å, were selected. The spectra was excited under the conditions stated in the "Analytical procedure" 3 and photographed for 25 seconds after pre-arcng of 5 seconds. The line pair ratios of Mn 2352.93Å/AsI 2288.12Å, Mn 2384.05Å/AsI 2288.12Å, Ag 2309.64Å/AsI 2349.84Å, and Ag 2309.64Å/AsI 2288.12Å were measured. The variation coefficients of them, in 8-replicate photographs of the spectra, are shown in Table 1. It is obvious that (a) in using

Table 1. Comparison of several spectral line pairs.

Line pair	Mn 2352.93Å	Mn 2384.05Å	Ag 2309.64Å	Ag 2309.64Å	Ag 2309.64Å*
	AsI 2349.84Å	AsI 2349.84Å	AsI 2349.84Å	AsI 2288.12Å	AsI 2288.12Å
Line pair	0.75	0.55	0.60	0.62	0.61
ratio	0.91	0.65	0.60	0.62	0.60
	0.88	0.65	0.65	0.64	0.58
	0.78	0.60	0.57	0.59	0.57
	0.83	0.65	0.62	0.64	0.65
	0.88	0.62	0.62	0.65	0.55
	0.88	0.64	0.61	0.63	0.61
	0.73	0.55	0.54	0.58	0.55
Average	0.83	0.61	0.60	0.62	0.59
Variation coefficient	±8.3%	±7.1%	±5.6%	±4.0%	±5.8%

* This was photographed for 30 seconds without pre-arcng.

the same arsenic line, the variation coefficient of the Ag/As line pair ratio was smaller than those of Mn/As line pair ratio; (b) in using the same silver line, the variation coefficient for AsI 2288.12Å was smaller than that for AsI 2349.84Å; (c) in using the same line pair, the variation coefficient for the spectra photographed after pre-arcng of 5 seconds was much smaller. From the results of (a) and (b), Ag 2309.64Å was selected as the internal standard line, and also AsI 2288.12Å as the analytical line of arsenic.

(iii) Exposure time

Experiments were carried out in order to clarify the cause of the above-mentioned (c). The spectra were excited under the excitation conditions stated in the "Analytical procedure" and photographed for 28 seconds at 7-seconds intervals. And the intensities of Ag 2309.64Å,

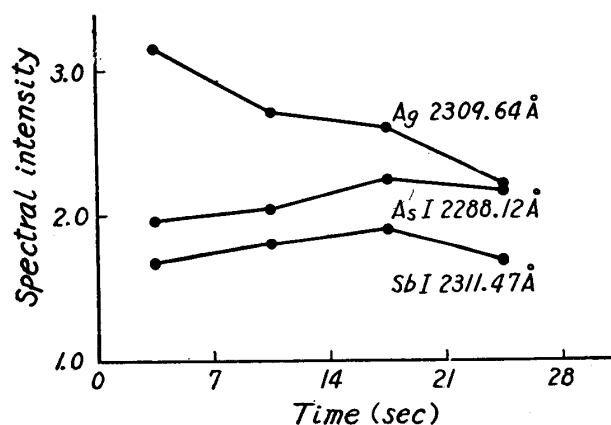


Fig. 1. Evaporation curves of As, Sb and Ag.

AsI 2288.12Å and Sb 2311.47Å were measured. As shown in Fig. 1, at the first 7-sec. exposure the intensity of the silver line gave the maximum, which was unlike that of arsenic and antimony. It seemed that this might derive from the difference of evaporation rate between silver and the others at the earlier period. Therefore, in the final procedure the spectra were photographed for 20 sec. after 7-sec. pre-arcng period.

3. Analytical procedure

(i) Preparation of sample

Block of ferromanganese is ground in a diamond mortar until the grain size smaller than 100 meshes. This is intimately mixed with graphite powder and silver oxide in an agate mortar. The ratio is as follows: sample: graphite: silver oxide=1:1/2:1/3 in weight. The standard samples with known contents for arsenic and antimony are prepared in this manner, too.

(ii) Determination conditions

Unknown samples and standard samples are photographed on a photographic plate, and working curves are constructed on the basis of the standard samples. Excitation conditions and photographic conditions are as follows:

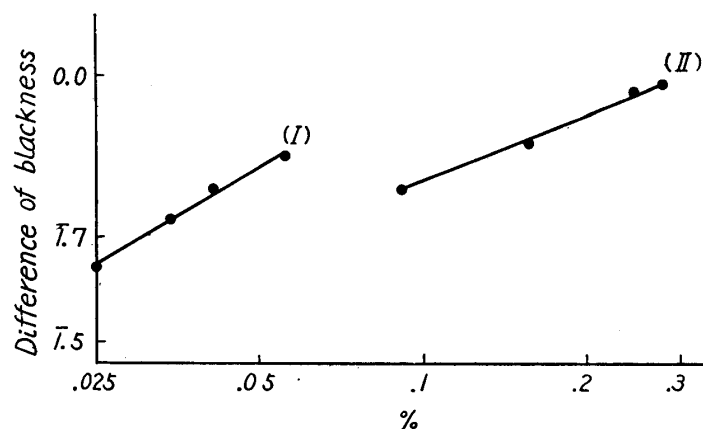
Spectrograph—	Carl Zeiss Qu 24 medium-type spectrograph
Optical system—	Intermediate screen irradiation
Analytical gap—	2.5 mm
Intermediate screen—	5 mm
Slit width—	10 μ
Electrode—	Nippon carbon Co. Ltd., graphite rod for spectral analysis, 5.5 mm in diameter. Crater, 2.5 mm in diameter, 3 mm in depth with a wall of about 0.5 mm in width. Counter-electrode, sharpened to a cone with a flat of 1 to 2 mm. Powdered mixture is loaded eight-tenth full into the crater.
Current—	Direct current 220 volts, 10 amp. The polarity of the sample-holding electrode is positive.
Interrupter—	6 cycles per second, with the on-off ratio of 1:2.
Exposure—	20 seconds after 7-sec. pre-arcng
Photographic plate—	Fuji, spectroscopic, process type
Development—	FD-31, at 18°C for 4 minutes
Line pairs—	Ag 2309.64Å/AsI 2288.12Å, Ag 2309.64Å/SbI 2311.47Å.

Working curves constructed on the basis of 4 standard samples analyzed chemically* are shown in Fig. 2. They are found to give a good linearity.

4. Analytical results

The averages and the reproducibilities of the values determined from the working curves, in replicate photographs of the spectra of two samples, are shown in

* Arsenic and antimony were determined by stannous chloride reduction method, and by methyl violet absorption photometry, respectively.



(I) Ag 2309.64 Å / Sb I 2311.47 Å
 (II) Ag 2309.64 Å / As I 2288.12 Å

Fig. 2. Working curves.

Table 2. It is seen that this method is applicable to routine analysis with satisfactory accuracy and precision.

Table 2. Analytical results.

Sample number	1		2	
	As	Sb	As	Sb
Result of chemical analysis (%)	0.19	0.042	0.26	0.054
Results of spectrographic analysis (%)	0.15	0.040	0.23	0.048
	0.18	0.042	0.24	0.052
	0.20	0.044	0.24	0.055
	0.18	0.045	0.25	0.055
	0.17	0.044	0.26	0.055
	0.21	0.049	0.24	0.052
	0.16	0.043		
	0.17	0.043		
	0.20	0.048		
Average (%)	0.18	0.044	0.24	0.053
Variation coefficient	±11%	±6.4%	±4.6%	±5.3%

Summary

- (1) A spectrographic method was developed to determine simultaneously micro-amounts of arsenic and antimony in ferromanganese.
- (2) Discharge was stabilized by exciting a mixture of powdered sample with graphite powder by direct current intermittent arc.
- (3) Silver was added to the mixture as internal standard, and Ag 2309.64 Å/As I 2288.12 Å and Ag 2309.64 Å/Sb I 2311.47 Å were used as analytical line pairs.
- (4) The variation coefficients for arsenic and antimony were 5 to 11 per cent and about 6 per cent, respectively.

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