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Influence of Arsenic on the Analysis of Iron and Steel. I
The Determination of Sulfur and Phosphorus in Iron and Steel*

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Synopsis

The effects of arsenic on the determinations of sulfur and phosphorus in iron and steel were studied, and a method for avoiding the interference of arsenic was established. It was found that the determination of sulfur was not affected by arsenic for any of the combustion, evolution, and gravimetric methods, but that arsenurretted hydrogen evolved during the evolution method so that it seemed advisable to have this gas absorbed in a solution of potassium permanganate in a bottle connected to the end of the apparatus. Determination of phophorus by the usual molybdate method was found to give higher value in proportion to the content of arsenic in the sample, but this error could be lessened to the range of analytical error by the precipitation of phosphomolybdate at low temperatures.

I. Introduction

In our country, the contents of arsenic found in iron and steel have become higher since the last World War. There is no likelihood of the presence of arsenic in the iron and steel in foreign countries, and so the effects of arsenic on the determinations of other elements have not greatly been studied, and such an example is found only in the removal of arsenic during the determination of phosphorus. Therefore, the present authors carried out studies on the effects of arsenic in the determination of sulfur and phosphorus and on the method of avoiding such effects.

II. Determination of sulfur

The following are the usual methods used for the determination of sulfur in iron and steel; (1) the combustion method,(1) in which the sample is ignited in oxygen atmosphere to change the sulfur into sulfur dioxide and sulfur trioxide and the gas is volumetrically determined; (2) the evolution method,(2) in which the sample is dissolved in non-oxidative strong acids to change the sulfur into hydrogen sulfide which is volumetrically estimated with iodine; (3) the gravimetric method,(3) in which the sulfur in sample is converted with a strongly oxidative

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(1) *Rapid Analytical Method*, Japanese Council for the Promotion of Science: *Handbook of Chemical Analysis of Iron and Steel* (in Japanese), Vol. 2, 174.

(2) *Japan Engineering Standards Method*: *Industrial Analysis* (in Japanese), 202.

(3) *Japan Engineering Standards Method*: *Handbook of Chemical Analysis of Iron and Steel*, (in Japanese), Vol. 2, 151.

acid to sulfuric acid and then precipitated as barium sulfate. Experiments were, therefore, carried out to see the effects of arsenic in these three methods.

1. Determination of sulfur by the combustion method

A sample of steel containing arsenic was burned in an oxygen stream at combustion temperatures of 1350–1400°, sulfur dioxide and trioxide formed by the oxidation of sulfur was absorbed in a solution of hydrogen peroxide, and this solution was titrated with standard sodium hydroxide solution. After the completion of this experiment, arsenic both in the cap and the absorption solution was determined by the colorimetric method,(4) but none was found and the presence of arsenic did not affect the determination of sulfur by this method.

2. Determination of sulfur by the evolution method

The sample was dissolved in hydrochloric acid in a carbon dioxide atmosphere, the hydrogen sulfide thereby evolved was absorbed in a mixed solution of zinc and cadmium acetate, a slight excess of standard iodine solution was added, and the excess of iodine was back-titrated with the standard sodium thiosulfate solution, from which the amount of sulfur was calculated.

In this experiment, arsenuretted hydrogen evolving together with hydrogen sulfide was collected in a bottle containing 2 per cent potassium permanganate solution, after passing through the solution of zinc and cadmium acetate. The amount of arsenic in the mixed solution of zinc and cadmium acetate and in the mother liquor left after decomposition of the sample was determined by the usual stannous chloride reduction method.(5) Transition of arsenic was also followed by attaching two bottles, each containing 2 per cent potassium permanganate solution after the hydrogen sulfide absorption bottle, and the amount of arsenuretted hydrogen in these solutions was determined in the following manner: 10 ml of perchloric acid and a small amount of 30 per cent hydrogen peroxide solution was added to decompose the permanganate to the solution in which arsenuretted hydrogen had been absorbed, and the mixture was heated until white fumes began to evolve, and arsenic was determined by the stannous chloride reduction method.(5) The results obtained are shown in Table 1, which indicates that only a minute amount (0.05 mg or 0.001 per cent) of arsenic is present in the hydrogen sulfide absorption bottle while about 1/3 of the original amount of arsenic remains in the mother liquor in which the sample had been decomposed. The remainder of arsenic was detected in the absorption bottle for arsenuretted hydrogen. It follows, therefore, that the majority of arsenic escapes as arsenuretted hydrogen in an ordinary apparatus, and it would be advisable, from the standpoint of public health, that a bottle for the absorption of this gas should be attached to the end of the ordinary apparatus. However, only a trace is absorbed together with hydrogen sulfide, and so the gas does not seem to affect the determination of sulfur.

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(4) Rapid Analytical Method, Japanese Council for the Promotion of Science: Handbook of Chemical Analysis of Iron Steel (in Japanese), Vol. 2, 300.

(5) Japanese Engineering Standards Method: Ibid., Vol. 2, 298.

Table 1.

Arsenic in sample (%)	Arsenic in residual solution (%)	Arsenic in absorption solution of H_2S (%)	Arsenic in absorption solution of H_3As (%)	Total arsenic (%)
0.087	0.034 0.035	0.0012 0.0005	0.057 0.060	0.092 0.096
0.094	0.031 0.030	0.0011 0.0013	0.064 0.061	0.096 0.092
0.110	0.045 0.035	0.0013 0.0012	0.072 0.071	0.118 0.107
0.155	0.055 0.056	0.0012 0.0012	0.105 0.107	0.161 0.164

Results of the comparative experiments on the combustion and evolution methods are listed in Table 2, from which it will be seen that there is no effect of arsenic on the determination of sulfur even in steel samples containing a large amount of arsenic.

Table 2.

Arsenic in sample (%)	Sulfur obtained (%)			Difference of each method (%)
	Combustion method	Evolution method		
0.055	0.033	0.034 0.034 0.034	0.034	0.001
0.087	0.024	0.021 0.020 0.022	0.021	0.003
0.094	0.043	0.043 0.043 0.043	0.043	0.000
0.110	0.043	0.044 0.044 0.044	0.044	0.001
0.129	0.055	0.055 0.056 0.056	0.056	0.001
0.155	0.043	0.044 0.044 0.043	0.044	0.001
0.364	0.026	0.027 0.026 0.027	0.027	0.001
1.07	0.033	0.034 0.034 0.033	0.034	0.001
1.50	0.027	0.027 0.026 0.027	0.027	0.000

3. Determination of sulfur by the gravimetric method

The usual Japanese Engineering Standards Method was used. 5 grams of electrolytic iron was decomposed by heating in a mixture of nitric acid and potassium chlorate, 10 ml of potassium sulfate solution (sulfur, 0.294 mg/ml) and various amounts of arsenic trioxide solution (arsenic, 1.25 mg/ml) were added, the mixture was evaporated to about 10 ml, hydrochloric acid was added, and again evaporated to dryness. The residual salts were dissolved by addition of hydrochloric acid, zinc pellets were added to reduce ferric iron to ferrous state and after dilution of this solution, barium chloride was added. This mixture was stirred and allowed to stand over-night. The precipitated barium sulfate was collected by filtration, ignited, and weighed as barium sulfate. In this procedure, arsenic was reduced to arsenuretted hydrogen by zinc simultaneously with the reduction of iron, and escaped from the solution. Experiments were carried out to find the amount, if any, of arsenic that remained in the solution. In this case, sulfuric acid was added to the solution after the reduction, heated until evolution of white fumes, and arsenic was determined by the usual colorimetry.(4) This result, as shown in Table 3, indicated that even with a large amount of about 25 mg (0.5 per cent) of arsenic, the amount remaining in the solution after the reduction was about 0.8 mg (0.016 per cent) and that the majority was found to have escaped as arsenuretted hydrogen.

Table 3. Sulfur added : 2.94 mg (0.059 %)

Arsenic added	Amounts of arsenic found after the reduction of ferric iron	
(mg)	(mg)	(%)
6.25 (0.12%)	0.250 0.214	0.005 0.004
12.49 (0.24%)	0.525 0.515	0.011 0.010
24.98 (0.50%)	0.810 0.840	0.016 0.017

Sample taken 5 g

The effect of arsenic on the precipitation of barium sulfate was then examined on the basis of about 0.8 mg (0.016 per cent) of arsenic remaining at the time of the formation of barium sulfate from about 25 mg (0.5 per cent) in the original solution before reduction. Sulfur was determined by the same procedures as the above in 10 ml of potassium sulfate solution (sulfur, 2.94 mg or 0.059 per cent) added with various amounts of arsenic trioxide solution so as to contain 6–25 mg (0.1–0.5 per cent) of arsenic in the solution. As shown in Table 4, the results indicated that there was no effect of arsenic even in the presence of about 25 mg (0.5 per cent) of arsenic.

Table 4. Sulfur added : 2.94 mg (0.059 %)

As added (mg)	Sulfur obtained (mg)	Difference (mg)	Sulfur obtained (%)	Difference (%)
6.25 (0.12%)	2.98 2.93 2.95	0.04 0.01 0.01	0.060 0.059 0.059	0.001 0.000 0.000
12.49 (0.24%)	2.91 2.94 2.99	0.03 0.00 0.05	0.058 0.059 0.060	0.001 0.000 0.001
24.98 (0.50%)	2.94 2.99 2.91	0.00 0.05 0.03	0.059 0.060 0.058	0.000 0.001 0.001

Sample taken 5 g

III. Determination of phosphorus

Though there are various methods for the determination of phosphorus in iron and steel, the standard method(6) is carried out by alkalimetric titration after ammonium molybdate precipitation. When the sample contains arsenic, a yellow precipitate of ammonium arseno-molybdate is formed with the composition similar to that of phosphorus, and so arsenic has to be removed as a sulfide or bromide. This makes the determination procedures rather complicated, and so the experiments were carried out to find the effect of arsenic and to avoid such an interference of arsenic without its prelimiary separation.

1. Analytical procedure

The experiments were carried out in the same way as in the standard method. After treatment of 3 g of electrolytic iron with nitric acid, 10 ml of the standard diammonium phosphate solution (P, 0.168 mg/ml) and various amounts of the standard arsenic trioxide solution (As, 0.616 mg/ml) were added, arsenic was oxidized with potassium permanganate solution, and the excess of nitric acid was neutralized with ammonium hydroxide, thereby allowing the presence of a suitable amount of free nitric acid and ammonium nitrate in the solution. A solution of ammonium molybdate was added to this solution, the precipitate of ammonium phosphomolybdate thereby formed was collected by suctional filtration through a Gooch crucible with two pieces of filter paper (No. 5c), and the precipitate was washed, first with nitric acid solution (2 : 100) and then about five times with nitric acid solution (2 : 1000). The precipitate was dissolved by adding a slight excess excess of standard sodium hydroxide solution, and the excess sodium hydroxide was back-titrated with standard nitric acid solution to determine the amount of phosphorus. Examinations were made regarding the temperature at which the precipitate was formed and the time for standing before filtration in the foregoing procedure.

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(6) Japanese Engineering Standards Method : Handbook of Chemical Analysis of Iron and Steel (in Japanese), Vol. 2, 108.

2. Effect of temperature in formation of the precipitate

In the foregoing procedure, the temperature of the precipitate formation was varied, and the precipitate in the solution was allowed to stand at these temperatures for 1 hour, and then at room temperature over-night. Then, the amount of phosphorus was determined, the positive errors of phosphorus values which were derived from co-precipitation of ammonium arsenomolybdate were calculated. As shown in Fig. 1, it will be seen that the higher the temperature of the pre-

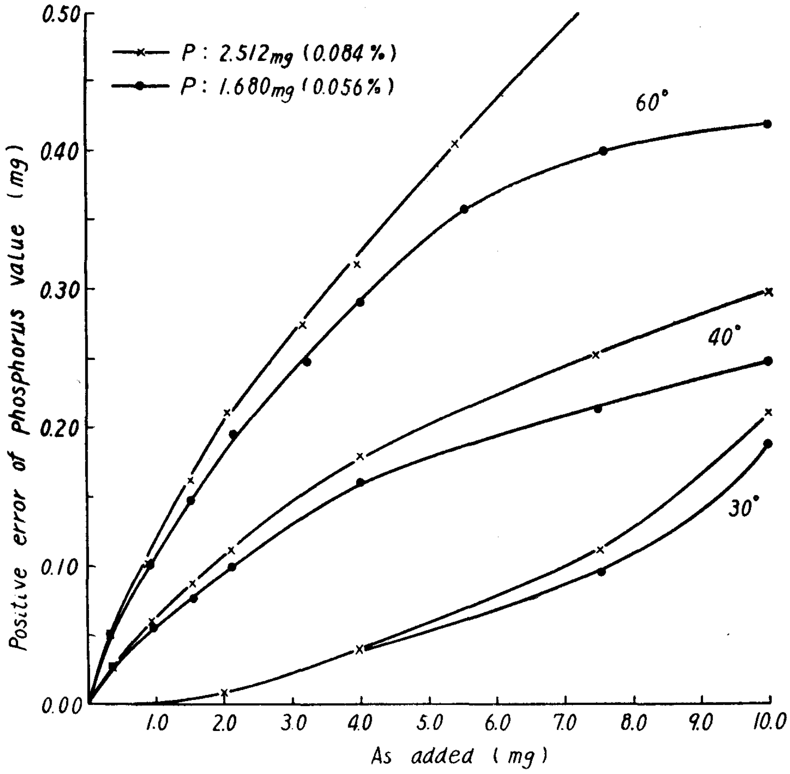

Fig. 1.

Table 5.

Arsenic added		Phosphorus obtained		Positive errors of phosphorus value		Temp. of precipitate formation (°C)
(mg)	(%)	(mg)	(%)	(mg)	(%)	
0.377	0.012	1.733	0.0578	0.053	0.0018	60
0.748	0.024	1.792	0.0597	0.112	0.0037	
1.496	0.049	1.831	0.0610	0.151	0.0050	
0.748	0.025	1.704	0.0568	0.024	0.0008	40
1.496	0.049	1.710	0.0570	0.030	0.0010	
2.244	0.075	1.782	0.0594	0.102	0.0034	
3.740	0.124	1.849	0.0613	0.169	0.0056	
2.241	0.075	1.688	0.0563	0.008	0.0003	30
3.740	0.124	1.740	0.0580	0.060	0.0020	
7.480	0.249	1.778	0.0593	0.098	0.0033	
11.220	0.374	1.876	0.0625	0.196	0.0065	

Stamdard value of P : 1.68 mg (0.056%), sample taken 3 g.

Values are the means of three measurements. The amounts increased by co-precipitation of ammonium arsenomolybdate are calculated as phosphorus contents.

cipitate formation, the higher the amount of accompanying arsenic. Also it will be seen from a part of the results listed in Table 5, that the occlusion of arsenic in the precipitate is within the analytical errors, if the amount of arsenic present is up to about 0.4 mg (0.013 per cent), at the temperature of precipitate formation of 60°, or about 1.5 mg (0.05 per cent) at the temperature of 40°, or about 4 mg (0.13 per cent) at the temperature of 30°, so that a good result can be obtained with steels containing this range of arsenic if the precipitation is formed at the above temperatures.

Results of experiments carried out with samples of phosphorus content of 2.51 mg (0.084 per cent) showed that the values tended to become higher as the phosphorus content increased, and that when the amount of arsenic present was small, the results were similar to those listed in Table 5.

3. Duration of warming

The results described above were seemed to be dependent on the duration of warming, and the minimum duration of time required at each temperature for phosphorus determination was examined. It was found, as indicated in Fig. 2, that phosphorus was quantitatively precipitated by warming for over 30 minutes at 40° or for over 3 hours at 30°. The effect of arsenic was also examined at the minimum duration of time found in the foregoing experiments. The results are listed in Table 6. The occlusion of arsenic was found to be within the analytical errors when about 2 mg (0.07 per cent) was present, with standing for 20 minutes at 60°, and when about 5 mg (0.16 per cent), with standing for 30 minutes at 40°, and when about 7 mg (0.23 per cent), with standing for 3 hours at 30°. Since the ordinary steel samples contain less than 0.2 per cent of arsenic, phosphorus can be determined without the effect of arsenic by the formation of a precipitate by maintaining the precipitate at 30° for 30 minutes.

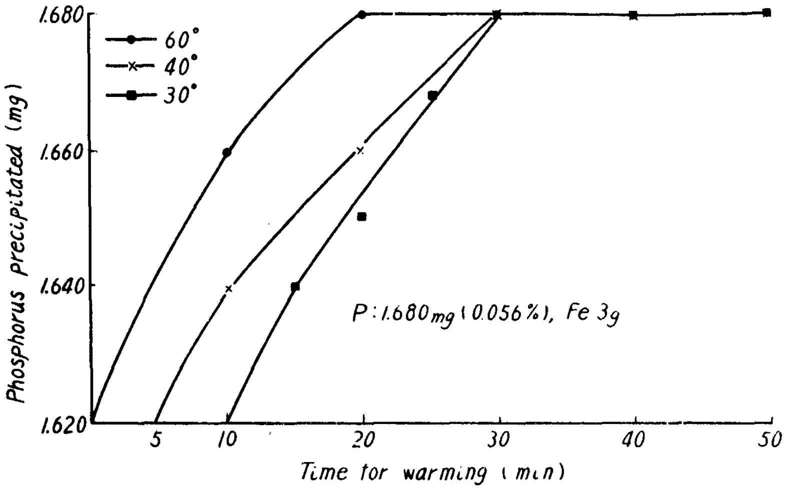

Fig. 2.

Experiments were then made with pig iron containing a large amount of phosphorus, with various duration of warming to form the precipitate. Some

Table 6.

Arsenic added		Phosphorus obtained		Positive errors of phosphorus value		Time for warming	Temp. of precipitate formation
(mg)	(%)	(mg)	(%)	(mg)	(%)	(min)	(℃)
1.12	0.037	1.696	0.0565	0.016	0.0005	20	60
1.87	0.062	1.717	0.0572	0.037	0.0012		
3.74	0.124	1.760	0.0587	0.080	0.0026		
5.61	0.187	1.844	0.0615	0.164	0.0054		
3.74	0.124	1.694	0.0565	0.014	0.0004	30	40
4.47	0.149	1.717	0.0572	0.037	0.0012		
5.61	0.186	1.736	0.0579	0.056	0.0018		
8.94	0.298	1.813	0.0604	0.133	0.0044		
6.00	0.200	1.701	0.0567	0.021	0.0007	180	30
7.50	0.250	1.724	0.0575	0.044	0.0014		
10.00	0.333	1.780	0.0593	0.100	0.0033		
12.00	0.400	1.863	0.0621	0.183	0.0061		

Standard value of P : 1.68 mg (0.058%), sample taken 3 g.

Values are the means of three measurements.

The amounts increased by co-precipitation of ammonium arseno-molybdate are calculated as phosphorous contents.

Table 7.

Arsenic added		Phosphorus obtained		Positive errors of phosphorus value		Time for warming	Temp. of precipitate formation
(mg)	(%)	(mg)	(%)	(mg)	(%)	(min)	(℃)
2.00	0.20	1.699	0.1699	0.019	0.0019	20	60
2.50	0.25	1.719	0.1719	0.039	0.0039		
3.00	0.30	1.732	0.1732	0.052	0.0052		
4.00	0.40	1.771	0.1771	0.091	0.0091		
2.50	0.25	1.690	0.1690	0.010	0.0010	30	40
3.00	0.30	1.710	0.1710	0.030	0.0030		
3.50	0.35	1.736	0.1736	0.056	0.0056		
4.50	0.45	1.768	0.1768	0.088	0.0088		
5.00	0.50	1.691	0.1691	0.011	0.0011	180	30
5.50	0.55	1.707	0.1707	0.027	0.0027		
6.00	0.60	1.726	0.1726	0.046	0.0046		
6.50	0.65	1.753	0.1753	0.073	0.0073		

Standard value of P : 1.68 mg (0.168%), sample taken 1 g.

Values are the means of three measuements.

The amounts increased by co-precipitation of ammonium arseno-molybdate are calculated as phosphorous contents.

results obtained are listed in Table 7. No great effect of arsenic was found by the presence of up to about 25 mg (0.25 per cent) of arsenic, with standing for 20 minutes at 60°, up to about 3 mg (0.3 per cent), with standing for 30 minutes at 40°, and up to about 5 mg (0.5 per cent), with standing for 3 hours at 30°.

4. Results of analysis

From the foregoing experiments, comparative examinations were made with the results obtained by the standard method involving the removal of arsenic as its bromide and the results using the present method of treatment at lower temperatures, since the formation of a precipitate at 30° for 3 hours gave a simple procedure. As shown in Table 8, satisfactory results were obtained.

Table 8.

Kind of sample (As %)	Phosphorus* (%)	Phosphoruos (Obtained by this method) (%)		Difference (%)
Steel (0.055)	0.066	0.066 0.063 0.064	0.064	0.002
Steel (0.087)	0.074	0.075 0.076 0.076	0.076	0.002
Steel (0.094)	0.081	0.079 0.083 0.082	0.081	0.000
Steel (0.110)	0.074	0.074 0.078 0.076	0.076	0.002
Pig iron (0.750)	0.233	0.237 0.239 0.236	0.237	0.004

* The values obtained by standard method involving the removal of arsenic as its bromide.

Summary

(1) Various effects of arsenic on the determination of sulfur and phosphorus in iron and steel were examined.

(2) Determinations of sulfur by the combusion, evolution, and gravimetric methods were found to be unaffected by the presence of arsenic; but in the case of the evolution method, it was found to be better, from the stand-point of public health, to attach a gas absorption bottle with potassium permanganate solution at the end of the evolution apparatus to absorb the arsenuretted hydrogen evolved.

(3) In the determination of phosphorus, the increasing amount of arsenic affected the determination by the usual molybdate method. It was found that the effect of arsenic could be removed by precipitation at lower temperatures, with the usual amount of arsenic contained in ordinary iron and steel samples.

(4) From the results of the foregoing experiments, it became possible to remove the effect of arsenic during the determination of sulfur and phosphorus in iron and steel.

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