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Influences of Arsenic on the Analysis of Iron and Steel. III Determination of Titanium and Molybdenum in Iron and Steel*

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Synopsis

When titanium was reduced directly by liquid zinc amalgam and titrated with standard ferric solution immediately after the dissolution of steel sample, the presence of 0.15 per cent of arsenic caused about 0.03 per cent high result for titanium. So the removal of arsenic as arsenic tribromide with bromine in hydrochloric acid solution was recommended. In the gravimetric or volumetric determination after the separation of titanium with sodium thio-sulfate or ammonium phosphate, there was no interference by arsenic. For the determination of molybdenum in the volumetric method, it was necessary to remove arsenic as tribromide. In the gravimetric method with α -benzoin oxime, however, arsenic had no influence.

I. Introduction

In continuation of the preceding two papers^(1,2), effects of arsenic on the determinations of titanium and molybdenum were studied and the results obtained to date are herein described.

II. Determination of titanium

There are many methods for the determination of titanium in iron and steel. In the present series of experiments, the effect of arsenic on the titanium determination was examined in the direct volumetric method using liquid amalgam without isolation, the gravimetric method with thiosulfate separation, and the volumetric method with ammonium phosphate separation.

1. Volumetric method with amalgam reduction

The reduction of titanium with liquid zinc amalgam and the titration of the trivalent iron solution using potassium thiocyanate as an indicator enable us to carry out a simple determination of titanium without separating it from iron. First, the solutions containing known amounts of arsenic alone in 1.5 N sulfuric acid, were reduced with zinc amalgam and titrated with 0.1N ferric sulfate standard solution, using potassium thiocyanate solution as an indicator. Next, the reduction was carried out similarly, then arsenuretted hydrogen in the reductor was removed

* The 846th report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Japan Institute of Metals, **19** (1955), 12. Read at the Tôkyô Meeting of the Japan Institute of Metals, April, 1954.

(1) H. Gotô and S. Watanabe, J. Japan Inst. Metals, **18** (1954), 470; Sci. Rep. RITU, **A8** (1956), 157.

(2) H. Gotô and S. Watanabe, *Ibid.*, **18** (1954), 474; Sci. Rep. RITU, **A8** (1956), 223.

by passing carbon dioxide, absorbed in a solution of 2 per cent potassium permanganate solution, and the amounts of arsenic in this solution was determined by colorimetry⁽³⁾ or by reduction method with stannous chloride⁽⁴⁾. At the same time the amount of arsenic remaining in the original solution from which arsenuretted hydrogen had been removed was also determined by the same method. As the results in Table 1 show, the larger the amount of arsenic, the greater became the

Table 1. (Factor of N/10 ferric solution : 1.1021.)

As added (mg)	Titers of N/10 ferric solution (ml)	Amount of As removed by CO ₂ gas (mg)	Amount of As remained in solution (mg)
0.63 —	0.18 0.13	* 0.21 * 0.26	* 0.43 * 0.36
2.50 —	0.30 0.48	** 2.04 ** 2.19	* 0.56 * 0.46
6.25 —	1.20 1.40	** 5.50 ** 5.42	* 0.90 * 0.99

* Colorimetric method ; ** Volumetric method with SnCl₂ separation.

titers of 0.1N ferric sulfate solution. The amount of arsenic removed with carbon dioxide and that remaining in the solution after passing of carbon dioxide were also found to increase. The determination of titanium by titration was then carried out by using the solution containing known amount of titanium and arsenic without iron. The results are shown in Table 2, from which it may be seen that when the amount of arsenic is about 6 mg, the titers are higher by about 6.5 mg as converted to the amount of titanium.

Table 2. (Ti taken : 3.74 mg)

As added (mg)	Ti found (mg)	Difference (mg)
0.62	4.18 4.12	+ 0.44 + 0.38
1.25	4.58 4.65	+ 0.84 + 0.91
2.50	5.68 5.64	+ 1.94 + 1.90
6.25	10.12 10.60	+ 6.38 + 6.86

2 grams of steel containing arsenic was decomposed by heating with sulfuric acid, oxidized with hydrogen peroxide, 10 ml of standard titanium solution (Ti 0.374 mg) was added, the acidity of the solution was adjusted to about 1.5N, and reduced with zinc amalgam. This was titrated with 0.1N ferric sulfate solution, using ammonium thiocyanate solution as an indicator to find the effect of arsenic

(3) Y. Kakita, Sci. Rep. RITU, A1 (1949), 399.

(4) Ibid., 2 (1950), 477.

on the determination values of titanium and the results are shown in Table 3. The value was approximately 0.03 per cent higher in the case of the sample containing about 0.15 per cent of arsenic, and it was shown that arsenic must be removed with bromine from the hydrochloric acid solution.

Table 3. (Ti taken 3.74 mg(0.187%). Steel taken : 2.000(g).)

As percent in steel	Ti found		Difference	
	(mg)	Percentage for sample	(mg)	(%)
0.055	3.89	0.194	+ 0.15	+ 0.007
	3.96	0.198	+ 0.22	+ 0.011
	3.86	0.193	+ 0.12	+ 0.006
0.155	4.43	0.221	+ 0.69	+ 0.034
	4.35	0.217	+ 0.61	+ 0.030
	4.33	0.216	+ 0.59	+ 0.029

2. Gravimetric method by separation with sodium thiosulfate

5 grams of steel containing arsenic was treated with hydrochloric acid, standard titanium solution (Ti 1.122 mg/ml) was added, and titanium was precipitated with sodium thiosulfate solution. The precipitate was treated with hydrofluoric acid to remove silicon, fused with sodium carbonate, and dissolved in hydrochloric acid. The acid solution was neutralized with ammonium hydroxide, acidified with acetic acid, and titanium precipitated again with sodium thiosulfate. The precipitate was ignited and titanium was determined as titanium dioxide. The results are shown in Table 4. When the sample was decomposed with hydrochloric acid, most of

Table 4. (Ti taken : 11.22 mg(0.224%). Steel taken : 5.000(g).)

As percent in steel	Ti found		Difference	
	(mg)	Percentage for sample	(mg)	(%)
0.055	11.16	0.221	- 0.06	- 0.003
	11.28	0.225	+ 0.06	+ 0.001
	11.18	0.223	+ 0.04	- 0.001
0.155	11.25	0.225	+ 0.03	+ 0.001
	11.20	0.224	- 0.02	+ 0.000
	11.17	0.223	- 0.05	- 0.001

Table 5. (Ti taken : 11.22 mg(0.224%). Steel taken : 5.000(g).)

As percent in steel	Ti found		Difference	
	(mg)	percentage for sample	(mg)	(%)
0.055	11.20	0.224	- 0.02	0.000
	11.15	0.223	- 0.07	- 0.001
	11.18	0.223	- 0.04	- 0.001
0.155	11.26	0.225	+ 0.04	+ 0.001
	11.24	0.225	+ 0.02	+ 0.001
	11.18	0.223	- 0.04	- 0.001

arsenic evaporated as hydrogen arsenuretted so that the sample was decomposed with a mixed acids (hydrochloric acid + sulfuric acid + nitric acid) and the amount of titanium was determined to see the effect of such a treatment. As shown in Table 5, no adverse effect was caused by such a treatment in iron containing around 0.15 per cent of arsenic.

3. Volumetric method by separation with diammonium hydrogen phosphate

5 grams of steel sample containing arsenic was treated with a mixture of hydrochloric acid and sulfuric acid, standard titanium solution added, neutralized with ammonium hydroxide (1:1), and titanium precipitated with diammonium hydrogen phosphate in the presence of acetic acid. Titanium precipitate was collected by filtration, dissolved and heated in an acid mixture (nitric acid + sulfuric acid + perchloric acid) until white fumes began to evolve, and after the dilution with water this was reduced with zinc amalgam. Titanium was determined by titration with 0.1N ferric sulfate solution using ammonium thiocyanate solution as an indicator. The effect of arsenic in this case was also examined and the results are shown in Table 6. It will be seen from these values that no effect is observed in iron containing approximately 0.15 per cent of arsenic.

Table 6. (Ti taken : 11.22 mg(0.224%). Steel taken : 5.000(g).)

As percent in steel	Ti found		Difference	
	(mg)	Percentage for sample	(mg)	(%)
0.055	11.26	0.225	+ 0.04	+ 0.001
	11.20	0.224	- 0.02	0.000
	11.30	0.226	+ 0.08	+ 0.002
0.155	11.33	0.227	+ 0.11	+ 0.003
	11.22	0.224	0.00	0.000
	11.28	0.226	+ 0.06	+ 0.002

III. Determination of molybdenum

In numerous methods of the determination of molybdenum in iron and steel, the most widely used is the volumetric method using sodium hydroxide for separation and the gravimetric method using α -benzoin oxime for the separation. The effect of arsenic in the determination of molybdenum was examined by these methods.

1. Volumetric method using sodium hydroxide for separation

First, standard solutions containing various amounts of arsenic, in 1.5N sulfuric acid solution, was reduced with liquid zinc amalgam, and titrated with 0.1N potassium permanganate solution. With arsenic content of about 0.5 mg, 0.5 ml of standard 0.1N potassium permanganate solution was consumed and it was seen that the titers increased with the increase of arsenic. Next, various amounts of standard arsenic solution and 10 ml of the standard molybdenum solution (Mo 1.454 mg/ml) were added to 1.5 N sulfuric acid solution, reduced with zinc amalgam,

and titrated with 0.1N potassium permanganate solution to find the effect of arsenic on the determined values of molybdenum. The results obtained are shown in Table 7. With about 1 mg of arsenic, the titer became higher by about 3 mg of

Table 7. (Fe : None, Mo taken : 14.54 mg.)

As added (mg)	Mo found (mg)	Difference (mg)
1.00	17.67	+ 3.15
	17.88	+ 3.37
	17.79	+ 3.27
2.00	20.68	+ 6.16
	20.54	+ 6.02
	21.09	+ 6.57
4.00	23.33	+ 8.81
	22.88	+ 8.36
	23.51	+ 8.99

molybdenum and with about 4 mg of arsenic, the end-point of titration become obscure. Actual samples were analysed by the following procedures. 2 grams of steel containing arsenic was heated and decomposed with hydrochloric acid, carbides decomposed by the addition of nitric acid, the solution neutralized with sodium hydroxide solution, and poured into warm 6 N sodium hydroxide solution (added with disodium hydrogen phosphate solution). After the solution was cooled, it was transferred to a measuring flask, filtered through a dry filter, and a definite aliquot was neutralized with sulfuric acid. To this was added sulfuric acid and heated until white fume began to evolve. This was diluted, adjusted to about 1.5N sulfuric acid, reduced with zinc amalgam, and molybdenum was determined by titration with 0.1N potassium permanganate solution. The effect of arsenic on the determination of molybdenum was examined by adding the standard molybdenum solution (Mo 1.45 mg/ml) to the decomposed solution of 2 g of arsenic-containing steel, followed by above procedure. The amount of arsenic in the solution was also determined by the reduction method with stannous chloride⁽⁴⁾. The results obtained are shown in Table 8. In this case, the decomposition of the sample with hydro-

Table 8. (Steel taken : 2.000(g). Mo taken : 14.5 mg(0.73%).)

As percent in steel	Mo found		Difference (mg)		Amount of As in solution	
	(mg)	Percentage for sample	(mg)	(%)	(mg)	(%)
0.056	14.49	0.72	-0.03	-0.01	0.21	0.009
	14.49	0.72	-0.03	-0.01	—	—
	14.60	0.73	+0.80	0.00	0.18	0.010
0.124	14.67	0.73	+0.15	0.00	0.38	0.019
	14.95	0.75	+0.43	+0.02	—	—
	14.67	0.73	+0.15	0.00	0.43	0.021
0.155	15.02	0.75	+0.50	+0.02	0.45	0.023
	14.74	0.74	+0.22	+0.01	—	—
	14.85	0.74	+0.33	+0.01	0.52	0.026

chloric acid resulted in the volatilization of the most of arsenic as arsenuretted hydrogen and there was no large effect of arsenic on the results. When the amount of arsenic became approximately 0.16 per cent, the determined values became somewhat higher, being about 0.5 mg (0.025 per cent) as converted to the amount of molybdenum. These results indicate that, when the sample contains high arsenic, in this volumetric method using sodium hydroxide most arsenic must be removed with bromine in hydrochloric acid acidity before neutralization with sodium hydroxide.

2. Gravimetric method with α -benzoin oxime

In accordance with the usual method, 1 g of arsenic-containing steel was decomposed with sulfuric acid, standard molybdenum solution (Mo 1.452 mg/ml) was added, oxidized with nitric acid, and heated with the addition of sulfuric acid until the evolution of white fumes began. After dissolving the salts with addition of water, ferric ammonium sulfate was added to reduce vanadium and chromium in the sample, the mixture cooled to below 10°C, and α -benzoin oxime solution was added to the mixture. Bromine water was added together with filter paper pulp, filtered, and ignited. Impure molybdenum trioxide thereby obtained was weighed, ammonia water added to this to dissolve molybdenum oxide, the solution filtered, the filter paper was ignited, and the amount weighed was subtracted from the amount of impure molybdenum trioxide to obtain the amount of molybdenum trioxide, from which the amount of molybdenum was calculated. The effect of arsenic on the determination of molybdenum was examined by such experimental procedures, and the results obtained are shown in Table 9. It was thereby shown that there was no effect of arsenic in samples containing around 0.4 per cent of arsenic.

Table 9. (Mo taken : 7.30 mg(0.73%). Steel taken : 1.000(g).)

As percent in steel	Mo found		Difference	
	(mg)	Percentage for sample	(mg)	(%)
0.056	7.41	0.74	+ 0.11	+ 0.01
	7.19	0.72	- 0.11	- 0.01
	7.34	0.73	+ 0.04	0.00
0.155	7.33	0.73	+ 0.03	0.00
	7.41	0.74	+ 0.11	+ 0.01
	7.34	0.73	+ 0.04	0.00
0.38	7.46	0.75	+ 0.16	+ 0.02
	7.38	0.74	+ 0.08	+ 0.01
	7.38	0.73	+ 0.03	0.00

Summary

- (1) The effect of arsenic on the determination of titanium and molybdenum in iron and steel was examined.
- (2) Such effect in the determination of titanium was examined by the volumetric

method using direct zinc amalgam reduction, the gravimetric method using sodium thiosulfate for separation, and the volumetric method using diammonium hydrogen phosphate for separation. It was shown that in the analytical procedure using direct reduction with zinc amalgam and titration with standard ferric sulfate solution, the presence of about 0.15 per cent of arsenic in sample gave about 0.03 per cent higher value than the theoretical one, and that arsenic should be removed with bromine in hydrochloric acid solution prior to determination. In the case of the gravimetric method with sodium thiosulfate and the volumetric method after the disodium hydrogen phosphate separation, no such effect was observed.

(3) In the determination of molybdenum by the volumetric method using sodium hydroxide, the presence of a large amount of arsenic in the sample was found to give higher values so that arsenic must be removed with bromine in the hydrochloric acid solution prior to the determination. In the case of the gravimetric method using α -benzoin oxime, no such effect was found to exist.

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