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# Influence of Arsenic on the Analysis of Iron and Steel. II The Determination of Copper and Manganese in Iron and Steel\*

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## Synopsis

The influence of arsenic on the determination of copper and manganese in iron and steel was studied. On the determination of copper, there was no direct influence of arsenic in the sodium thiosulfate separation method and hydrogen sulfide separation method. But in the separating procedure of copper from iron with hydrogen sulfide, the amount of iron coprecipitated with sulfides became larger by the presence of arsenic, and so the reprecipitation of ferric hydroxide was necessary for the perfect separation of copper. It was found also that arsenic had no effect on the determination of manganese by any of the usual methods.

## I. Introduction

In succession to the first report of this series<sup>(1)</sup>, the effect of arsenic on the determination of copper and manganese in iron and steel, and the counter-plot were studied.

## II. Determination of copper

There are various methods for the determination of copper in iron and steel. The standard method<sup>(2)</sup> generally used is as follows: copper is precipitated as its sulfide by sodium thiosulfate or hydrogen sulfide, and then the precipitate is collected, washed, and ignited to cupric oxide. The oxide is dissolved in the mixture of nitric and sulfuric acids and submitted to iodometry. The present experiments were carried out to find the effect, if any, of arsenic during this procedure.

### 1. Determination of copper by the sodium thiosulfate separation

#### (i) Procedure

To a solution of 5 g of electrolytic iron dissolved in aqua regia, standard copper sulfate solution (Cu, 0.80 mg/ml) and standard disodium arsenate solution (As, 1.249 mg/ml) were added, and it was cooled, and further, a solution of sulfuric acid (1:1) was added. This was heated until white fume was evolved, and boiled after addition of water to dissolve the salts. This solution was diluted, to which 50 per cent sodium thiosulfate solution was then added, and boiled to form cupric sulfide.

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

(2) Japan Engineering Standard Method: *Handbook of Chemical Analysis of Iron and Steel* (in Japanese), **2**, 190.

The precipitate of the sulfide was collected by filtration, washed, and ignited to cupric oxide. The oxide was dissolved in nitric acid, the residue was filtered off, and to the combined filtrate and washings sulfuric acid was added. This solution was evaporated to white fume, diluted, neutralized with ammonium hydroxide, and acidified with acetic acid. To this acid solution was added 3~5 g of potassium iodide and the liberated iodine was titrated with 0.02N sodium thiosulfate to determine the amount of copper. The amount of arsenic in cupric oxide during the foregoing procedure and the effect of arsenic on the determined amount of copper were examined.

(ii) Amount of arsenic in cupric oxide

The foregoing procedure was carried out without the addition of the standard copper sulfate solution but there was no precipitation of arsenic. The experiment was then carried out with the addition of 10 ml (Cu, 8.00 mg) of the standard copper sulfate solution and the amount of arsenic in cupric oxide was determined by colorimetry. The results in Table 1 show that about 1 mg of arsenic is present in cupric oxide when about 25 mg of arsenic is originally present. This will be due to the coprecipitation of a part of arsenic with cupric sulfide and the arsenic remaining without sublimation even by ignition. When the ignition temperature was raised to about 800°, the amount of arsenic in cupric oxide decreased to less than about 0.6 mg when about 25 mg of arsenic had been added.

Table 1.

Cu added (mg)	As added (mg)	As found	Temp. of ignition(°C)
8.00	12.50	1.01	700
		1.09	
8.00	25.00	1.05	700
		1.61	
8.00	25.00	0.61	800
		0.25	

Table 2.

Cu added (mg)	As added (mg)	Cu found (mg)	Difference (mg)
8.00	6.25	7.93	-0.07
		8.06	+0.06
		7.97	-0.03
8.00	12.50	7.99	-0.01
		8.00	0.00
		7.93	-0.07
8.00	25.00	8.00	0.00
		7.92	-0.08
		7.94	-0.06

(iii) Determination value of copper

According to the foregoing experiments, about 1 mg of arsenic was present in cupric oxide, and so the experiments were carried out with samples of various amounts of arsenic added. The results in Table 2 show that there is no effect of arsenic on the determination of copper even in samples containing about 25 mg of arsenic.

(iv) Experimental results with steel samples

Based on the foregoing experiments, a comparison was made between the results by the standard method, after removal of arsenic as a bromide, and those by the direct sodium thiosulfate precipitation method. The results are shown in

Table 3, from which it will be seen that there is no effect of arsenic on the determination of copper by the direct sodium thiosulfate precipitation method.

Table 3.

Sample		Direct sodium thiosulfate precipitation method Cu (%)	Difference (%)
As (%)	Cu (%)		
0.088	0.231	0.230 } 0.231 0.231 }	0.000
0.087	0.176	0.172 } 0.175 0.178 }	-0.001
0.095	0.191	0.189 } 0.189 0.189 }	-0.002
0.094	0.202	0.201 } 0.200 0.199 }	-0.002

Temperature of ignition 700°C.

## 2. Determination of copper by the hydrogen sulfide separation

### (i) Procedure

Under the same condition as in the foregoing sodium thiosulfate method, copper was precipitated as cupric sulfide by the passage of hydrogen sulfide, and then copper was determined by the same procedure. The amount of arsenic oxide, the determination of copper in a synthetic sample, and the adsorption of copper by ferric hydroxide were examined by this procedure.

### (ii) Amount of arsenic in cupric oxide

The foregoing analytical procedure was carried out with the addition of 10 ml (8.00 mg) of standard copper sulfate solution and various amounts of standard

Table 4.

Cu added (mg)	As added (mg)	As found (mg)	Temp. of ignition (°C)
0	12.49	0.178 0.235 0.330	700
0	24.98	0.195 0.245 0.235	700
8.01	12.49	1.310 1.400 1.225	700
8.01	24.98	1.575 1.615 1.825	700
8.01	12.49	1.025 1.200	800
8.01	24.98	1.150 1.075	800

disodium arsenate solution. The amount of arsenic in cupric oxide was determined by colorimetry. The results are shown in Table 4. Although arsenic precipitates with copper, the most of arsenic vaporizes during ignition (vaporizes above 570°). In the absence of copper, about 0.2 mg of arsenic still remains, and the amount of remaining arsenic increases with the increasing amount of arsenic present. The amount of arsenic decreases somewhat when the ignition temperature is raised.

(iii) Determination value of copper

From the foregoing experimental results, it was found that about 1.5 mg of arsenic and a small amount of iron remained in cupric oxide. Hence, their effects on the determination were examined by adding various amounts of arsenic. The results obtained are shown in Table 5. It will be seen that a synthetic sample containing about 25 mg of arsenic has no effect on the determination of copper, but due to the large amount of residual iron, copper salts was adsorbed in ferric hydroxide which is to be removed in ammonical solution and, therefore, it was necessary to carry out reprecipitation of ferric hydroxide. In this case, cupric oxide was dissolved in a mixture of a few drops of sulfuric acid (1:1) and about 2 ml of nitric acid (1:1) and evaporated until white fume evolved.

Table 5.

Cu taken (%)	As added (mg)	Cu found (%)	Amount of Cu adsorbed with Fe(OH) <sub>3</sub> (%)	Total Cu (%)	Difference (%)	Fe in CuO (mg)
0.16	0	0.157	0.005	0.162	+0.002	2.87
		0.156	0.004	0.160	0.000	—
0.16	6.247	0.154	0.005	0.159	-0.001	—
		0.148	0.013	0.161	+0.001	6.09
		0.156	0.004	0.160	0.000	—
0.16	12.493	0.148	0.014	0.162	+0.002	7.49
		0.153	0.007	0.160	0.000	—
		0.156	0.006	0.162	+0.002	4.27
0.16	24.987	0.154	0.007	0.161	+0.001	5.18
		0.157	0.005	0.162	+0.002	—
		0.157	0.005	0.162	+0.002	—

(iv) Amount of copper adsorbed by ferric hydroxide

As can be seen from Table 5, about 5 mg of iron is occluded in the precipitated sulfides of arsenic and copper. Therefore, experiments were carried out with cupric oxide obtained, in this case, by decomposition with a few drops of sulfuric acid solution (1:1) and about 5 ml of nitric acid solution (1:1), and by decomposition with the same acid and then evaporated until white vapor evolved. As shown in Fig. 1, about 0.4 mg of copper was adsorbed by ferric hydroxide even in the presence of about 2 mg of iron when it was treated by the latter method. When treated only with the above acid without fuming, the amount of copper adsorbed was found to be small and the solution of cupric oxide was complete, and therefore, in later experiments, the cupric oxide was dissolved in a few drops of sulfuric

acid solution (1:1) and 5 ml of nitric acid solution (1:1) with warming, and the subsequent procedures followed the usual method. The foregoing results showed that it was necessary to carry out reprecipitation when arsenic was present.

Table 6.

Sample		Hydrogen sulfide method Cu (%)	Difference (%)
As (%)	Cu (%)		
0.088	0.231	0.230 0.228 } 0.229	-0.002
0.087	0.176	0.176 0.178 } 0.177	+0.001
0.095	0.191	0.191 0.192 } 0.192	+0.001
0.094	0.202	0.204 0.203 } 0.204	+0.002

Temperature for ignition 700°

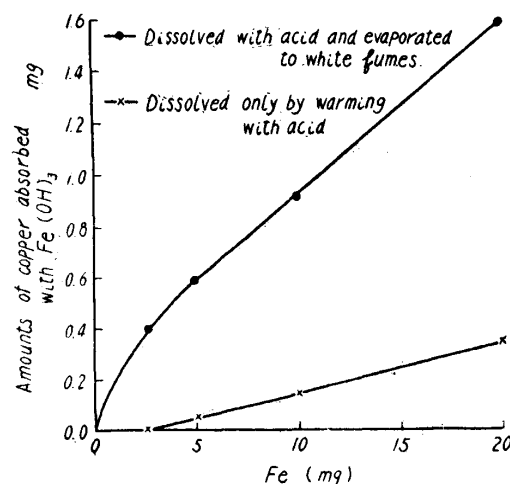


Fig. 1.

#### (v) Analytical results with steel samples

Based on the foregoing experiments, a comparison was made between the results obtained by the standard method, after removal of arsenic as its bromide, on several arsenic-containing steel samples and those by the direct hydrogen sulfide precipitation method. As shown in Table 6, the determination of copper by the direct hydrogen sulfide separation method requires reprecipitation of ferric hydroxide after the treatment of cupric oxide with a few drops of sulfuric acid solution (1:1) and about 5 ml of nitric acid solution (1:1).

### III. Determination of manganese

There are numerous methods for the determination of manganese in iron and steel but the most widely used are the volumetric method with ammonium ferrous sulfate following back titration with potassium permanganate after oxidation with ammonium persulfate, the direct titration with ammonium ferrous sulfate with diphenylamine as the indicator, and the direct titration with arsenic trioxide. The effect of arsenic on the determination of manganese by these methods was examined.

#### 1. Volumetric method with ammonium ferrous sulfate following back titration with potassium permanganate

According to the usual method, 1 g of electrolytic iron was decomposed by treating with the mixture of sulfuric and nitric acids, and then the standard manganese solution (Mn, 1.023 mg/ml) and the standard disodium arsenate solution (As, 1.25 mg/ml) were added, and the whole volume was brought to about 200 ml after the addition of silver nitrate, phosphoric acid and ammonium persulfate. This mixture was boiled to oxidize the manganese perfectly, and to decompose the excess of ammonium persulfate, it was cooled in cold water, and an excess of about 10 ml

of 0.1N ammonium ferrous sulfate solution was accurately added, and titrated back with 0.1N potassium permanganate, and thus the amount of manganese was determined.

In the foregoing experimental procedure, examinations were made on whether a redox reaction would occur between  $\text{AsO}_4^{3-}$  and  $\text{Fe}^{2+}$  and on its effect from the observed values of manganese. The results are shown in Table 7. It was thereby seen that even about 6 mg of arsenic had no effect on the determination of manganese.

Table 7. Mn Added: 10.23 (mg)  
(1.02% for iron), Fe  
Added: 1 (g).

As Added (mg)	Mn found (mg)	Difference (mg)
1.50	10.22	-0.01
	10.26	+0.03
	10.26	+0.03
3.00	10.32	+0.09
	10.32	+0.09
	10.25	+0.02
6.00	10.26	+0.03
	10.32	+0.09
	10.22	-0.01

Table 8. Mn Added: 10.23 (mg)  
(1.02% for iron), Fe  
Added: 1 (g).

As Added (mg)	Mn found (mg)	Difference (mg)
1.50	10.22	-0.01
	10.14	-0.09
	10.25	+0.02
3.00	10.19	-0.04
	10.23	0.00
	10.18	-0.05
6.00	10.23	0.00
	10.18	-0.05
	10.19	-0.04

## 2. Direct titration method with ammonium ferrous sulfate

After oxidation of manganese by the same procedure as the above, the solution was directly titrated with 0.1N ammonium ferrous sulfate solution, with diphenylamine-phosphoric acid solution as the indicator to determine manganese. The effect of arsenic was sought in this experimental procedure and the results are shown in Table 8. About 6 mg of arsenic was found to have no effect.

## 3. Direct titration method with arsenic trioxide

According to the usual method, 0.25 g of electrolytic iron was decomposed by heating with a mixed acid of sulfuric and nitric acids, and then the standard manganese solution and the standard arsenic trioxide solution were added, and the whole volume was brought to about 150 ml with warm water. After the addition of silver nitrate solution, the mixture was heated while adding ammonium persulfate, and the solution was boiled for further 1 min. to oxidize manganese perfectly. After cooling the mixture in cold water, sodium chloride solution was added, stirred well, and titrated immediately with the standard arsenic trioxide solution to determine the amount of manganese. Effect of arsenic on the determination of manganese was examined by this procedure, first without the addition of iron. As shown in Table 9, about 6 mg of arsenic was found to have no effect on the determination. The same experimental procedure was carried out on synthetic samples to find the effect of arsenic on the determination of manganese. As shown in Table 10, about 0.6 per cent of arsenic was found to have no effect.

Table 9. Mn Added: 2.56 (mg),  
Fe None.

As Added (mg)	Mn obtained (mg)	Difference (mg)
0.39	2.55	-0.01
	2.54	-0.02
	2.56	0.00
	2.57	+0.01
0.78	2.53	-0.03
	2.58	+0.02
	2.55	-0.01
	2.56	0.00
1.56	2.57	+0.01
	2.58	+0.02
	2.54	-0.02
	2.55	-0.01

Table 10. Mn Added: 2.56 (mg)  
(1.02% for iron), Fe:  
0.25 (g),

As Added (mg) (to for iron)	Mn obtained (mg)	Difference (mg)
0.39 (0.15%)	2.55	-0.01
	2.54	-0.02
	2.56	0.00
	2.54	-0.02
0.78 (0.31%)	2.55	-0.01
	2.56	0.00
	2.53	-0.03
	2.55	-0.01
1.56 (0.62%)	2.55	-0.01
	2.53	-0.03
	2.56	0.00
	2.55	-0.01

### Summary

- (1) The effect of arsenic on the determination of copper and manganese in iron and steel was examined.
- (2) In the determination of copper, arsenic had no direct effect on the sodium thiosulfate method and the hydrogen sulfide method. However, it was found that the presence of arsenic caused the amount of residual iron with copper and arsenic sulfides to become larger, and consequently, affected the adsorption of copper by ferric hydroxide, so that the reprecipitation was necessary.
- (3) In the determination of manganese, arsenic was found to have no effect by any of the methods of determination, that is, either by the volumetric method with ammonium ferrous sulfate following back titration of potassium permanganate after oxidation with ammonium persulfate, or by the direct titration with ammonium ferrous sulfate with diphenylamine-phosphoric acid solution as the indicator, or by the titration with arsenic trioxide.

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