

Determination of copper trace in steel by direct method using atomic absorption spectrophotometry

N. GHARIB NASERI

Ahwaz Faculty of Petroleum Engineering, Petroleum University of Technology (Iran)

(Received: May 20, 2007; Accepted: June 28, 2007)

ABSTRACT

The trace concentrations of copper in several British steel samples and standards have been investigated in this research by direct method using hydrochloric and nitric acid mixture, and sulphuric acid, Phosphoric acid and water mixture. Three standard steels containing copper in the range of 0.13% - 0.39% were used. These were low alloy steel B.C.S. No. 257/1 (0.13% Cu), carbon steel B.C.S. No. 239/2 (0.18% Cu) and alloy steel B.C.S. No. 253/1 (0.39% Cu). The dissolution procedure of steels, led to a solution which was analysed directly by atomic absorption spectrophotometry. Absorption due to copper was measured at 324.8 nm by atomizing the solution in a 10 cm slot burner using an air-acetylene flame with air flow rate 5.2 L/min and acetylene flow rate 1.2 L/min and operating the hollow cathode lamp at 5 mA. Burner height was set at point 6. The appropriate calibration solutions were aspirated, followed by the sample solutions. Water was aspirated between each test when the zero was checked. The copper content of the sample solutions were read from the calibration graphs. The absorption of each solution measured at least three times. The results obtained in this research for copper content of steel samples indicate that a mixture of hydrochloric and nitric acids is to be preferred as the solvent medium, especially when iron is added to the standard solutions, when the copper contents found are near to the certificate values.

Keywords: Copper, copper trace, steel, direct method, atomic absorption spectrophotometry.

INTRODUCTION

The influence of trace concentrations of copper in steel has been investigated by Kramer, Siegel and Brooks.¹ They found that copper in small amounts has a considerable influence on the hardenability of steel. They stated that as little as 0.1% copper increases the hardenability by 17%. It has been shown quite conclusively that small additions of copper to unalloyed wrought steels, considerably improves their resistance to atmospheric corrosion.^{2,3,4} The presence of copper in steel does not retard the initial rate of atmospheric corrosion, in fact, the corrosion rate is not appreciably retarded until a copper or copper oxide film is formed on the surface by preferential dissolution of iron. It is interesting to know that only relatively small amount of copper is necessary to enhance the resistance to atmospheric corrosion. It has also been claimed that paint adheres better

and that zinc coatings last longer on copper-bearing steels than on copper-free steels.⁵ Copper additions increase the fluidity of cast steel. Copper is added to a number of stainless steel and heat resisting steels to improve mechanical properties. This improvement is most marked in low-carbon steel. Copper is very effective when used in conjunction with the other alloying elements, such as Mn, Cr, Silicon. Despite the advantages mentioned above of the presence of copper in steel, it has some disadvantages as well; the most important is an embrittling effect on steel. It has been reported that in copper-bearing steels, cracking increased with increasing copper content (up to 0.6%) after soaking in all atmospheres except the neutral atmosphere containing SO₂, whereupon cracking is negligible.⁶ Copper decreases the rate of solution of steel in sulphuric or hydrochloric acid and increases the rate of attack in nitric acid but these effects are generally too small to be of any practical importance. Copper

has no appreciable influence on the rate of solution of steel in various salt solutions (Tables 1 and 2).

Copper is an important element in ferrous metallurgy and many methods of quantitative analysis have been developed. Classical schemes use gravimetric,⁸ volumetric,^{8,9} and electrometric methods which in comparison with other analytical methods are tedious and less accurate. Instrumental techniques including colorimetry,¹⁰ photometry,¹¹ and spectrophotometry¹² have been widely used and are more sensitive for the determination of copper in

steel. Of these, colorimetric methods suffer from the general disadvantage that it is often difficult to isolate absorption due to copper from absorption due to the matrix. Walsh¹³ indicated that atomic absorption spectroscopy is practically free from interferences and this technique has been applied to the determination of copper in agricultural^{14,15} and metallurgical^{16,17} materials. Wallace¹⁸ in 1961 obtained high results for copper in steel using an air-acetylene flame and dissolving the sample in hydrochloric acid. Since then Beyer¹⁹, Knight²⁰, Nall et al²¹, and Gidley et al²² have determined copper

Table -1. Effect of Copper on the resistance of Chromium Steel to acid corrosion.⁷

Acid	Concentration %	Duration of attack (hour)	Loss (g.m ² .hr ⁻¹)	
			Steel A ^a	Steel B ^b
Sulphuric	5	7	22.1	10.5
Sulphuric	35	6	265.0	45.0
Sulphuric	50	6	8.8	6.4
Hydrochloric	Normal	7	5.8	1.8
Nitric	Normal	6	7.1	7.6
Acetic	5	24	0.32	0.16

in steel and have shown that the analysis was simple and free from interferences. Although in 1964 Kinson and Belcher¹² and Sprague et al.²³ in their determination of small amounts of copper in steel by atomic absorption spectrophotometry found a small depressive effect of iron on copper absorption, they indicated that the interference could be overcome by using either standard steel or pure iron added to aqueous copper solutions for the calibration. Thomeson and Price²⁴ discovered that the presence of 1% of iron depressed the copper absorption in perchloric acid by about 10%, but satisfactory results were obtained when iron was incorporated in the calibration standards.

EXPERIMENTAL

The work reported here has been carried out using an E.E.L. 240 Mark I atomic absorption spectrophotometer manufactured by Evan Electro-Selenium Ltd., of Halstead, Essex, England. Two separate burners are provided; one for the air/

Table -2: %Weight composition of elements found in the steels used in the work

Steel type	%C	%Si	%Mn	%Cr	%Ni	%Cu
Steel A	0.16	0.28	0.17	12.1	0.44	0.08
Steel B	0.22	0.28	0.17	12.1	0.47	1.20

acetylene flame and one for the nitrous oxide/acetylene flame. Three standard steel were selected containing a range of copper content. These were low alloy steel B.C.S. No. 257/1 (0.13% Cu), carbon steel B.C.S. No. 239/2 (0.18% Cu) and alloy steel B.C.S. No. 253/1 (0.39% Cu). All the chemicals used in this work were AnalaR grade supplied by BDH and Merck. Standard copper with high purity (Hilger) and standard iron with high purity (iron sponge from Johnson Matthey Chemical Ltd.) were used.

Effect of fuel/oxidant ratio on copper absorption

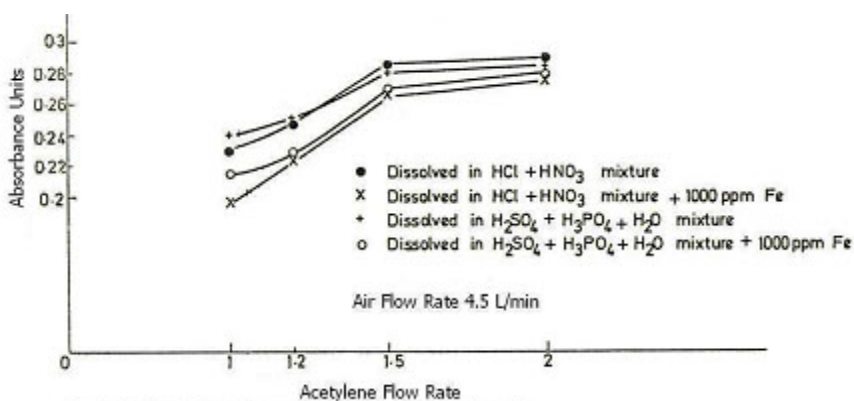
The flowmeter incorporated in the E.E.L. 240 instrument is small and relatively insensitive to changes in the flow rate of air. In order to measure this effect more accurately, a more sensitive rotometer was introduced into the air supply line. This meter, however, was sensitive to the pulsation from the compressor and no steady reading could be obtained. A series of results were obtained by using compressed air from a cylinder. Tables 3 and 4 summarize the absorbance values obtained when solutions prepared from the stock solutions containing 7 ppm copper were aspirated into the flame and the flow rate of fuel and oxidant was varied. From the graphs 1 and 2 the optimum sensitivity was obtained at air flow rate 4.5 L/min and fuel flow rate 1.2 L/min. It is apparent that the presence of iron affects the absorbance.

Effect of burner height on copper absorbance

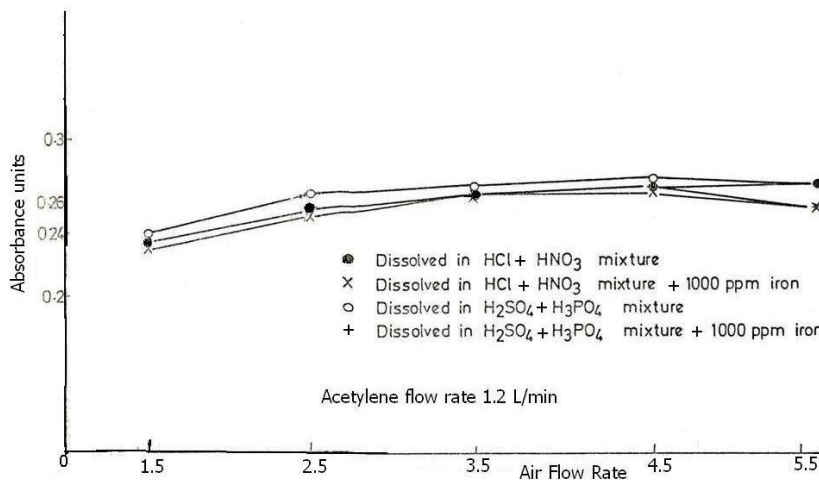
To investigate the effect of burner height on the copper signal, the solutions of pure copper dissolved in each acid mixture were aspirated into the flame and the burner height was varied as given in Table 5. Graph number 4.3 shows the effect of burner height on Cu absorbance and it is clear that the maximum sensitivity for all solutions was obtained at point 6.

Effect of iron on copper absorbance

The effect of different iron concentrations on the absorbance of copper was investigated by addition of a constant concentration of copper to a series of iron (as pure iron) solutions of increasing concentration as shown in Table 5. The absorption by copper was measured for these solutions using different flame conditions, the results are given in



Graph -1: Effect of acetylene flow rate on copper absorption



Graph -2: Effect of air flow rate on copper absorption

Table 5. The conclusion from this experiment is that the presence of iron can apparently suppress or enhance the copper absorbance depending upon the air/fuel ratio. This effect is virtually eliminated with an air flow rate of 4.5 L/min and an acetylene flow rate of 1.2 L/min and these conditions were used in the subsequent experiments with the standard steels.

Preparation of the steel sample solutions; dissolution using hydrochloric and nitric acids

The weight of samples selected for the three standard steels was that which gave a final solution containing approximately 6 ppm copper. These were 0.5 g of steel B.C.S. No. 257/1 (0.13% Cu), 0.3 g carbon steel B.C.S. No. 239/2 (0.18% Cu) and 0.15 g alloy steel B.C.S. No. 253/1 (0.39% Cu). Appropriate samples of the steels were accurately weighed and transferred to 100 mL

beakers and dissolved in 15 mL of HCl and HNO_3 acid mixture (HCl, sp. gr. 1.18, HNO_3 , sp. gr. 1.42 in the ratio of 4:1 v/v, respectively). The solutions were heated on a hot plate until all reactions had ceased and a clear solution was obtained. It was necessary to filter the solutions of steel B.C.S. No. 253/1 in order to remove precipitated silica. The solutions were quantitatively transferred into 100 mL volumetric flasks. After cooling, the samples were diluted to volume with distilled water. These solutions were then aspirated directly into the flame and the absorption due to copper measured. The results are given in Table 3.

Preparation of the steel sample solutions; dissolution using phosphoric and sulphuric acids

A similar procedure to that above was carried out to dissolve the steel samples in 18 mL

Table -3: Variation of air flowmeter at acetylene flow rate 1.2 L/min.

External Rotameter (L/min)	Instrumental flowmeter air flow (L/min)	7 ppm Cu dissolved in $\text{HCl} + \text{HNO}_3$		7ppm Cu dissolved in $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$	
		No Fe	1000 ppm Fe	No Fe	1000ppm Fe
		Absorbance*		Absorbance*	
5.5	5.5	0.27	0.255	0.27	0.255
4.5	5.2	0.27	0.265	0.275	0.27
3.5	5.0	0.265	0.265	0.27	0.265
2.5	4.7	0.255	0.25	0.265	0.255
1.5	4.4	0.235	0.23	0.24	0.235

* Absorbances are average of three readings.

Table - 4: Variation of acetylene flowmeter at air flow rate 4.5 L/min

Instrumental flowmeter air flow (L/min)	7 ppm Cu dissolved in $\text{HCl} + \text{HNO}_3$		7ppm Cu dissolved in $\text{H}_2\text{SO}_4 + \text{H}_3\text{PO}_4$	
	No Fe	1000 ppm Fe	No Fe	1000 ppm Fe
	Absorbance		Absorbance	
1.0	0.230	0.195	0.24	0.215
1.2	0.248	0.223	0.25	0.23
1.5	0.285	0.265	0.28	0.27 ^a
2.0	0.290	0.275	0.285	0.28 ^a

* Absorbances are average of three readings.

a = Luminous flame

of the sulphuric acid, phosphoric acid and water mixture (sulphuric acid, sp. gr. 1.84, phosphoric acid, sp. gr. 1.75 and water in the ratio of 1:1:4, respectively). When the reaction had ceased, nitric acid was added dropwise to oxidize carbides and to clarify the solution. After filtration of silica when necessary the solutions were transferred to 100 mL graduated flasks and diluted to volume with distilled water. These solutions were then aspirated directly into the flame and the absorption due to copper measured. The results are given in Table 4.

Preparation of stock solutions

Stock solutions containing 500 ppm copper and 10,000 ppm iron were prepared for each of the acid mixtures in exactly the same way as those of the preparation of the steel sample solutions described above (in 4 and 5). These stock solutions

were further diluted in order to make the range of stock solutions needed for calibration.

Preparation of working standard solutions

Separate working standards were made for each of the two acid mixtures used above, and for each acid mixture, two sets of standards were prepared. One set consisted of mixed acid solutions containing copper from 2-10 ppm. The other set of working standards, at the same levels as the first set, contained in addition 1000 ppm iron.

Analysis of the sample solutions by atomic absorption spectrophotometry

Each of the prepared solutions was analysed by comparing the absorption for each sample against that obtained by the calibration solutions. Graphs were prepared of absorbance

Table - 5: Effect of Iron on copper absorbance at various air flow rate.

Air flow (external rotometer) L/minute Solutions	5.5	4.5	3.5	2.5	1.5
	Absorption				
5 ppm Cu + 0 ppm Fe	0.178	0.178	0.178	0.170	0.155
5 ppm Cu + 1000 ppm Fe	0.178	0.178	0.185	0.175	0.157
5 ppm Cu + 2000 ppm Fe	0.175	0.180	0.188	0.178	0.160
5 ppm Cu + 3000 ppm Fe	0.173	0.180	0.190	0.185	0.161
5 ppm Cu + 5000 ppm Fe	0.170	0.178	0.192	0.186	0.165

Acetylene flow constant at 1.2 L/min.

Table - 6: Effect of burner height on copper absorbance

Burner height	5 ppm Cu dissolved in HCL + NH_4OH		5 ppm Cu dissolved in H_2SO_4 + H_3PO_4	
	No Fe Absorbance	1000 ppm Fe Absorbance	No Fe Absorbance	1000 ppm Fe Absorbance
1	0.155	0.135	0.165	0.140
2	0.165	0.145	0.172	0.150
3	0.170	0.155	0.180	0.160
4	0.175	0.165	0.182	0.170
5	0.180	0.165	0.185	0.172
6	0.180	0.170	0.185	0.175
7	0.175	0.170	0.180	0.175
8	0.170	0.165	0.175	0.172
9	0.160	0.160	0.170	0.168
10	0.155	0.155	0.160	0.160
11	0.150	0.150	0.155	0.153

Table - 7: Absorption values for copper content of steels samples and standards*

Cu standards Concentration in (ppm)	Acid solvents $H_2SO_4+H_3PO_4+H_2O$		Acid Solvents $HCL+HNO_3$	
	No Fe	1000 ppm Fe	No Fe	1000 ppm Fe
	Absorbance		Absorbance	
2	0.075	0.082	0.080	0.076
5	0.192	0.185	0.195	0.182
7	0.255	0.255	0.270	0.248
10	0.370	0.355	0.370	0.344
Steel sample solutions		Absorbance	Absorbance	
Steel B.C.S. No. 257/1		0.200	0.225	
		0.200	0.222	
		0.200	0.210	
		0.198	0.230	
Steel B.C.S. No. 239/2		0.170	0.187	
		0.170	0.192	
		0.172	0.190	
		0.171	0.185	
Steel B.C.S. No. 253/1		0.188	0.211	
		0.185	0.213	
		0.185	0.210	
		0.185	0.214	

Each reading of absorption is the average of at least three determinations.

versus concentration and from these, the concentration of the copper in the sample solutions was determined and subsequently the percentage by weight of the copper in the original sample.

Calibration Graphs

To provide the calibration graphs, first the approximate concentration of copper in each steel sample was calculated, second the concentration range of the copper standards were prepared. The appropriate calculations were made, for example for a steel containing 0.13% of copper, the concentration in ppm of copper, C_s , in 0.5 g portion of steel in 100 mL was obtained by the relation:

$$C_s = \frac{0.13}{100} \times \frac{0.5}{100} \times 1,000,000 = 6.5 \text{ ppm}$$

Thus, the range of concentration of the copper standard series was prepared to be: 2, 5, 7 and 10 ppm. The aim was to have the concentration

in the sample in the mid-range of the calibration. Similar calculations were made for each sample.

Instrumental settings

The instrument was set up according to the optimum conditions obtained in the preliminary experiments for maximum sensitivity and reproducibility. Absorption due to copper was measured at 324.8 nm by atomizing the solution in a 10 cm slot burner using an air-acetylene flame with air flow rate 5.2 L/min and acetylene flow rate 1.2 L/min and operating the hollow cathode lamp at 5 mA. Burner height was set at point 6. The appropriate calibration solutions were aspirated, followed by the sample solutions. Water was aspirated between each test when the zero was checked. The copper content of the sample solutions were read from the calibration graphs. The absorption of each solution measured at least three times.

Table - 8: Calculated values of the copper content in steels samples by weight in HCl + HNO₃ mixture.

Steel Samples	Certificate Value	Standard without Fe Found Value	% difference	Standard With Fe Found Value	% difference
B.C.S. No. 257/1	0.13	0.015	-0.015	0.125	-0.005
	0.13	0.113	-0.017	0.123	-0.007
	0.13	0.107	-0.023	0.114	-0.016
	0.13	0.118	-0.012	0.128	-0.002
B.C.S. No. 239/2	0.18	0.158	-0.022	0.172	-0.008
	0.18	0.163	-0.017	0.176	-0.004
	0.18	0.160	-0.020	0.175	-0.005
	0.18	0.156	-0.024	0.170	-0.010
B.C.S. No. 253/1	0.39	0.356	-0.034	0.390	-0.000
	0.39	0.360	-0.030	0.393	+0.003
	0.39	0.356	-0.034	0.386	-0.004
	0.39	0.363	-0.027	0.396	+0.006

Table - 9: Calculated values of the copper content in steels samples by weight in H₂SO₄ + H₃PO₄

Steel Samples	Certificate Value	Standard without Fe Found Value	% difference	Standard With Fe Found Value	% difference
B.C.S. No. 257/1	0.13	0.107	- 0.023	0.107	- 0.023
	0.13	0.107	- 0.023	0.108	- 0.022
	0.13	0.107	- 0.023	0.108	- 0.022
	0.13	0.106	- 0.024	0.108	- 0.022
B.C.S. No. 239/2	0.18	0.150	- 0.030	0.152	- 0.028
	0.18	0.150	- 0.030	0.152	- 0.028
	0.18	0.152	- 0.028	0.154	- 0.026
	0.18	0.152	- 0.028	0.153	- 0.027
B.C.S. No. 253/1	0.39	0.333	- 0.057	0.336	- 0.054
	0.39	0.330	- 0.060	0.333	- 0.057
	0.39	0.330	- 0.060	0.333	- 0.057
	0.39	0.330	- 0.060	0.333	- 0.057

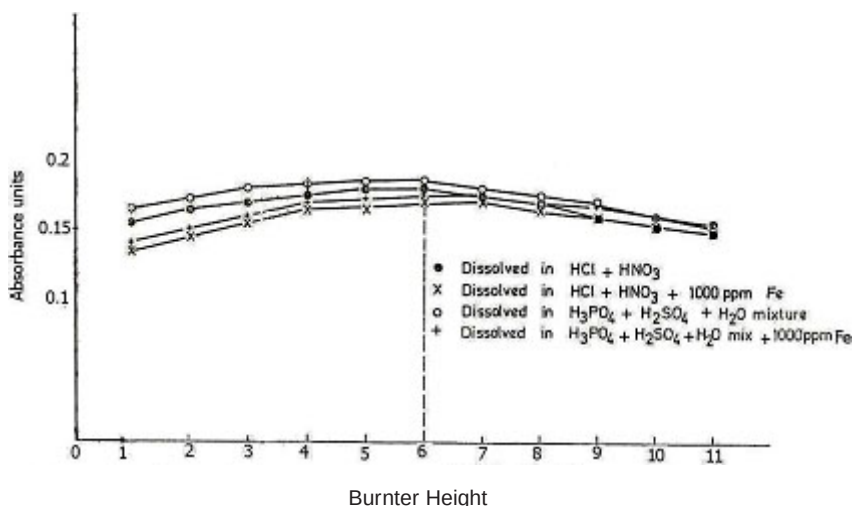
Table - 10: Values for %error in H₂SO₄ + H₃PO₄ mixture in the presence of iron

Steel Sample	Certificate Value%	Average value Found%	Average %error
B.C.S. No. 257/1	0.13	0.108	16.92
B.C.S. No. 239/2	0.18	0.152	15.55
B.C.S. No. 253/1	0.39	0.333	14.60

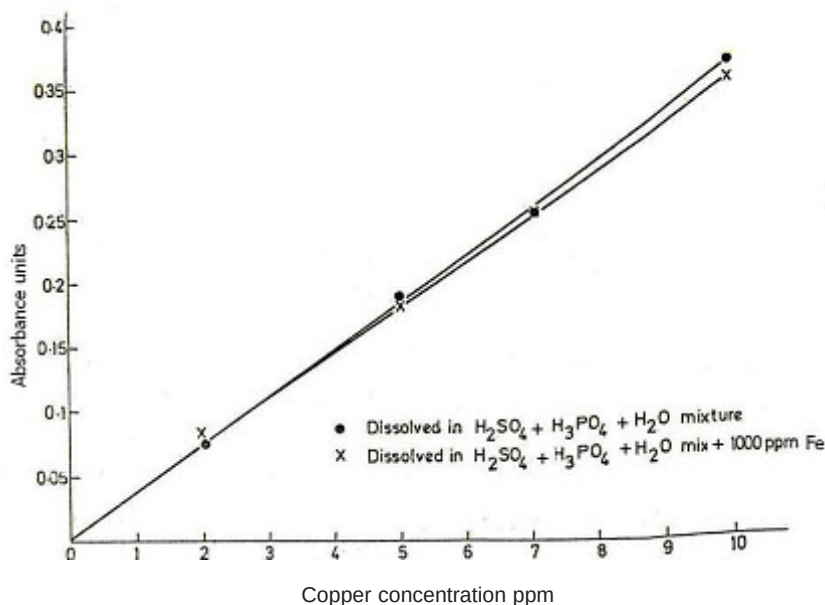
RESULTS AND DISCUSSION

Before any attempt was made to determine copper in steel, a series of preliminary experiments were carried out to find out how the different variables discussed by other workers affected the absorption of copper. These indicated that the air/fuel ratio, the concentration of iron and the acidity of the test solution could affect the absorption due to copper. The ratio of fuel to oxidant gas is one of the parameters which have important effects on the copper absorbance as used in atomic

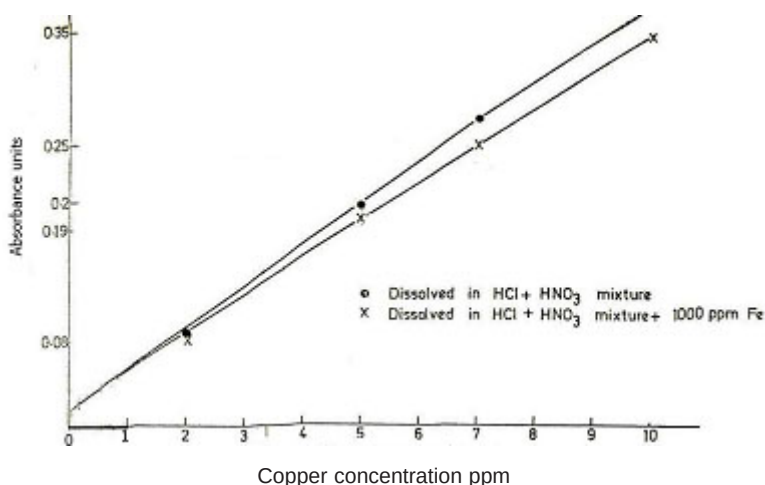
absorption determination and this investigation was carried out to determine the best ratio of acetylene/air flow rate to use for further work. The results are given in Tables 3 and 4. From the graphs 1 and 2 the optimum sensitivity was obtained at air flow rate 4.5 L/min and fuel flow rate 1.2 L/min. It is apparent that the presence of iron affects the absorbance. Effect of burner height on copper absorbance was investigated in the acid solutions used in this research. The results are given in Table 6. From the graph 3, it was found that the maximum sensitivity for all solutions used in the measurement of copper,



Graph - 3: Effect of burner height on copper absorption



Graph - 4: Calibration graphs using copper standard with and without iron



Graph - 5: Calibration graphs using copper standard with and without iron

was obtained at point 6. The effect of different iron concentrations on the absorbance of copper was also investigated by addition of a constant concentration of copper to a series of iron (as pure iron) solutions of increasing concentration as shown in Table 5. The conclusion from this experiment is that the presence of iron can apparently suppress or enhance the copper absorbance depending upon the air/fuel ratio. This effect is virtually eliminated with an air flow rate of 4.5 L/min and an acetylene flow rate of 1.2 L/min and these conditions were used in the subsequent experiments with the standard steels. Preliminary work in this project showed that atomization of an aqueous solution of the sample prepared by dissolution in an acid mixture was simple and rapid but was not as accurate as expected.

Kinson and his co-workers¹² dissolved their steel samples in a mixture of H_3PO_4 , H_2SO_4 and H_2O (4.5:4.5:91 v/v/v, respectively). The samples were then oxidized by dropwise addition of nitric acid. However, it was found in this work that this mixture did not dissolve all of the copper in the samples, but by increasing the acid content to a (1:1:4 v/v/v, respectively) mixture of phosphoric acid, sulphuric acid and water, complete solution was obtained. The method proposed by Beyer¹⁹ in which steel was dissolved in hydrochloric acid (1:1 v/v) followed by oxidation with nitric acid, also did not completely dissolve the steels in this work.

However, a mixed acid solution containing 20% nitric acid and 80% hydrochloric acid by volume as proposed by Sabina Sprague and Slavin²³ was successfully used to dissolve the samples.

Four separate samples of each of the standards were dissolved in each of the acid mixtures according to the procedure given in experiment 9. The copper absorption of each of these standard steel samples was compared with those obtained for standard copper solutions in the presence or absence of iron. Table 7 gives the absorption value for the calibration solutions and the four determinations for each steel sample solution. A typical calibration graph is also shown in Graph 4 and in Graph 5. From the results shown in table 7, four calibration graphs were drawn and the experimental values of the copper content of the steels were calculated for each solvent medium. These results are shown in tables 8 and 9. From table 9 it is apparent that with a mixture of sulphuric and phosphoric acids, the addition of iron to standards makes little difference to the results obtained for the copper absorbance. The percentage error for each sample has been calculated and is shown in Table 10. From Table 10, it can be seen that the percentage error is almost the same over the range of copper content of the steel samples used. On the other hand with a mixture of hydrochloric and nitric acids, the addition of iron to the standards gives more accurate results

for copper absorbance (Table 8), but even with no iron present in the standards, the results are better than with a mixture of sulphuric and phosphoric acids. Also in hydrochloric and nitric acids, the percentage error varies with the copper content of steel samples (as shown in Table 11) and is less for higher concentrations.

The results obtained in this research for copper content of steel samples indicate that a mixture of hydrochloric and nitric acids is to be preferred as the solvent medium, especially when iron is added to the standard solutions, when the copper contents found are near to the certificate values.

Table - 11: Values for %error in HCl + HNO₃

Steel Sample	Certificate Value%	Standard without		Standard with Fe	
		Fe Average value found%	Fe Average %error	Average value found%	Average %error
B.C.S. No. 257/1	0.13	0.113	-13.1	0.123	-5.38
B.C.S. No. 239/2	0.18	0.159	-11.67	0.173	-3.75
B.C.S. No. 253/1	0.39	0.359	-7.9	0.393	+0.769

An alternative approach was therefore to use a solvent extraction technique to separate the copper in the solution from iron before determination

by atomic absorption spectrophotometry (The results will be published in the second part of this work in another article).

REFERENCES

- Kramer IR, Siegel S and Brooks JG, A.I.M.E., Tech. Pub. 2029. *Metals Tech.*, June (1946.).
- Daeves K, Gas- U. Wasserfach, 1941, **84**, 718; *Chemical Abstracts*, **37**, Part II, 2496 (1943).
- Reprot of committee A-5 on Corrosion of Iron and Steel, Proc. Am. Soc. *Testing Materials*, **41**, 96 (1941).
- Taylorson ES, *J. Iron Steel Inst.*, **143**, 287 (1941).
- Gregg JL and Danlloff BN, "Alloys of Iron and Copper", McGraw Hill Book Company, Inc., New York, (1934).
- Rolls R and Preece A, "Metal Treatment and Drop Forging", 139 (1960).
- Monypenny JHG, "Stainless Iron and Steel", John Wiley and Sons Inc., New York, (1931).
- A.S.T.M., "Methods of Chemical Analysis of Metals", E30 (1960).
- British Standard, 1121, part 14, (1956).
- Sandel EB, "Colorimetric Determination of Traces of Metals", 2nd edition, Interscience Publishers, Inc., New York, (1950).
- Dean JA and Lady JH, *Anal. Chem.*, **27**, 1533 (1955).
- Kinson K and Belcher CB, *Anal. Chim. Acta*, **31**, 180 (1964).
- Walsh A, *Spectrochim. Acta*, **7**, 108 (1955).
- David DJ, *Analyst*, **83**, 655 (1958).
- Allan JE, *Spectrochim. Acta*, **17**, 459 (1961).
- Stumpe KE and Gonsior T, Colloquium Spectroscopium. Internationale IX, Lyons, (1961).
- Wallace FJ, *Hilger J.*, **7**, 65 (1963).
- Wallace FJ, *Foseco Dev.*, **7**, 54 (1961).
- Beyer M, *Atomic Absorption Newsletter*, **4**, 212 (1965).
- Knight DM and Pyzyna MK, *Atomic Absorption Newsletter*, **8**, 129 (1968).
- Nall WR, Brumhead D and Whitham R, *Analyst*, **100**, 555 (1974).
- Elwell WT and Gidley JAF, *Atomic Absorption Spectrophotometry*, 2nd edition, Pergamon Press, Oxford, London, p. 68 (1966).
- Slavin W and Sprague S, *Atomic Absorption Newsletter*, **3**, 72 (1964).
- Thomerson DR and Price WJ, *Analyst*, **96**, 825 (1971).