Materials Science Research india Vol. **4**(1), 115-126 (2007)

The effect of two comlexing agents (NaDDC and ZnDBC) on the determination of copper trace in steel using atomic absorption spectrophotometry

N. GHARIB NASERI

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

(Received: May 11, 2007; Accepted: June 20, 2007)

ABSTRACT

A method of solvent extraction is described for concentrating and separating the copper from an aqueous solution of steel into an organic solvent prior to analysis by flame atomic absorption spectroscopy. The choice of possible chelating agents and solvent was made after a series of preliminary experiments. More detailed experiments were then carried out with those solvent extraction systems which appeared to be most promising. This research was carried out by using NaDDC and ZnDBC as chelating agents for carrying out solvent extraction, separation of copper from steel and subsequent determination of the copper directly in the organic solvent. The copper content of steel sample solutions were determined by extraction as either a copper diethyldithiocarbamate (CuDDC) complex from aqueous alkaline solution into methyl isobutyl ketone (MIBK) or copper dibenzyldithiocarbamate (CuDBC) complex from the acidic solution into MIBK, and then by spraying the MIBK extract into an air-acetylene flame. The conclusion is that for a rapid determination of copper in the steel samples, direct atomization of aqueous solution when dissolved in hydrochloric acid and nitric acid mixture is to be preferred if high accuracy is not required (~ 4% error). More accurate results can be obtained using a longer extraction procedure using ZnDBC (~ 1% error).

Key words: Copper, copper trace, steel, solvent extraction method, NaDDC, ZnDBC, atomic absorption spectrophotometry.

INTRODUCTION

Solvent extraction of trace metals is probably the most widely used separation technique, as it can be reduced to a very simple procedure. The choice of chelating or complexing reagent is not limited as in colorimetry to one which makes a strong colour for the metal being determined, and complicated methods involving extraction and back extraction in order to improve specificity are avoided. The extraction of an element from an aqueous solution into an organic solvent which was then sprayed into the flame was first described by Dean and Lady[1] and since then, a number of papers have reported the application of this technique to the determination of various elements by atomic absorption spectrophotometry. Allan[2] has studied the use of a number of organic solvents for the determination of copper. He reported that a useful gain in sensitivity could be obtained in the determination of copper by the atomic absorption method, when the element was extracted into an organic solvent prior to nebulization. A number of chelating agents have been used to form extractable compounds with copper ions. Typical of these chelates are diphenylthiocarbazone (dithizone),[3-6] cupferron,[7-9] sodium diethyldithiocarbamate (NaDDC),[10-15] zinc dibenzyldithiocarbamate (ZnDBC),[16-19] ammonium pyrrolidinedithiocarbamate (APDC) and 1-(2-pyridylazo)-2-naphthol (PAN). Of these, Cupferron, dithizone and PAN did not give satisfactory results. These reagents were developed for colorimetry where the presence of some other elements (e.g. Fe) could be tolerated. Also the extraction procedures were sometimes very tedious and did not contribute to an acceptable alternative to direct atomization. PAN is a sensitive reagent and its solutions and also solutions of its complexes

are stable, but the stability of its complexes is greatly affected by acidity. PAN forms complexes with most metals (Mn, Cu, Fe (III), Co, Ni, Sn,…) therefore, selectivity of PAN in the determination of copper in steel requires close control of pH and the use of a suitable masking agent. These restrictions make the use of PAN, very complex in that the slight alteration of conditions when modifying a colorimetric procedure ends in nonreproducible results or even no results being obtained. Methods using dithizone and cupferron for colorimetric determination were not suitable and had to be modified for atomic absorption spectrophotometry procedures. The results were still far from acceptable for copper in steel, because with dithizone, copper was extracted in carbon tetrachloride or chloroform and the extracted solution was evaporated to dryness. The complex was destroyed by heating with a mixture of concentrated nitric acid and sulphuric acid before determination by atomic absorption spectrophotometry. This procedure was not satisfactory and it was also rather tedious. The amount of copper determined in the steel samples was always lower than the certificate value. Cupferron is a specific reagent for iron (III) as well as for copper and therefore extraction of copper from steel was difficult with iron present in large quantities. The use of a masking agent for iron did not improve the extraction and even prevented the copper from being extracted with cupferron.

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/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.

Fuel:oxidant ratio

Experiments to find the flow rates for air and acetylene when using a solution in methylisobutyl ketone (MIBK) were performed in the following way: 150 µg of copper (15 mL of 10 ppm standard solution) was extracted as CuDDC complex into 20 mL of MIBK. This solution was aspirated into the flame and the absorption measured for different flow rates of air and acetylene. The results are given in Tables 1 and 2. Similar results were obtained using ZnDBC, giving the optimum condition of acetylene flow rate 1 L/min and air flow rate 5.2 L/min (instrument flowmeter).

Part A:Using sodium diethyldithiocarbamate (NaDDC) as the chelating agent:

Preparation of Stock Solutions for the measurement of CuDDC

Stock solutions containing 500 ppm copper and 10,000 ppm iron were prepared for each of the acid mixtures (HCl, sp. gr. 1.18, HNO_3, sp. gr. 1.42 in the ratio of 4:1 v/v, respectively) and (sulphuric acid, phosphoric acid and water (1:1:4 v/v/v, respectively) as described in earlier work.[20] These stock solutions were further diluted in order to make the range of working standard solutions needed for calibration.

Table - 1: Effect of air flow rate on copper absorption

Air flow (external rotometer, arbitrary units)*	Absorption
5.5	0.247
4.5	0.250
3.5	0.255 luminous
2.5	0.500 luminous
1.5	Flame lifts off

Acetylene flow constant at 1 L/min. (the minimum that could safely be attained).

*4.5 of the external rotometer=5.2 L/min. of flowmeter of the instrument

Table - 2: Effect of fuel flow rate on copper absorption

Acetylene flow (L/min.)	Absorption
1.0	0.250
1.2	0.235 luminous
1.5	Flame lifts off

Air flow constant at 4.5 (arbitrary units)*
*4.5 of the external rotometer=5.2 L/min. of flowmeter of the instrument

Preparation of working standard solutions for the measurement of CuDDC

Two sets of working standard solutions were prepared from the stock solution of copper, one set contained copper from 50-200 µg and the other set at the same level as the first one, contained in addition 20,000 µg iron. Then working standards were treated with the extraction procedure detailed in (8) and the copper absorption measured.

Preparation of the steel sample solutions

Dissolution using hydrochloric and nitric acids for the measurement of CuDDC: 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.

Preparation of the Steel Sample Solutions

Dissolution using Phosphoric and Sulphuric acids for the measurement of CuDDC: A similar procedure to that above (4) was carried out to dissolve the steel samples in 18 mL 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.

Stability of copper diethyldithiocarbamate complex (CuDDC)

To check the stability, several solutions of pure copper (50, 100, 150, 200 µg) and 20,000 µg iron were extracted with NaDDC into 20 mL MIBK at pH 9-10. The absorbance of the organic phase was measured by atomic absorption spectrophotometry at different times after extraction. The results are given in Table 3.

Effect of NaDDC concentration on the extraction of copper

Tests of the variation of copper absorbance with increasing concentration of NaDDC in MIBK were carried out (Table 4). The results showed that

Table - 3: Stability of CuDDC complex

Copper solutionµg	Iron solutionµg	Time after extraction (hours) 0.0	0.5	4	24
		Absorption			
50	20,000	0.092	0.093	0.095	0.105
100	20,000	0.170	0.175	0.180	0.195
150	20,000	0.247	0.253	0.255	0.270
200	20,000	0.335	0.342	0.350	0.370

optimum concentration of the reagent (NaDDC) was in the range of 0.1% - 0.15% in which the copper absorbance remained constant for an extract concentration 100 µg copper and 20,000 µg iron.

Extraction of copper with NaDDC through solvent extraction method

To a 20 mL aliquot of the solution prepared in (4) of each steel, was added 10 mL tartaric acid (15% aq.) solution. This was then neutralized with an excess of concentrated NH_4OH to get pH 9-10 and 10 mL of EDTA (4% solution) was added. The solution was cooled to room temperature and transferred to a separatory funnel, followed by the addition of 10 mL NaDDC (0.1% aq.). 20 mL of MIBK was pippeted into the funnel and shaken vigorously for 5 minutes. After cooling in running water, the layers were allowed to separate. The aqueous layer was drawn off and the absorption of copper in the organic solvent layer was then measured by atomic absorption spectroscopy.

Measurement of copper content of steel samples with NaDDC

The copper content of two separate samples of each of the standard steel which were dissolved in each of the acid mixtures, was extracted with NaDDC into MIBK according to the procedures given above (8). The absorption of copper in the organic solvent layer of these standard steel samples was compared with those obtained for standard copper solutions in the presence or absence of iron. Table 5 shows the absorption values for the calibration solutions and the two determinations for each sample solution. From these data the experimental values of the copper content of steels were calculated for each acid mixture. These results are listed in Tables 6 and 7 and plotted graphically in graph 1.

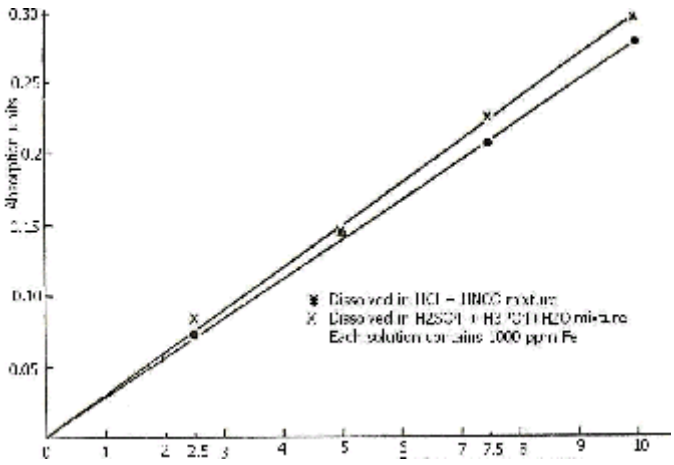
Part B:Using zinc dibenzyldithiocarbamate (ZnDBC) as the chelating agent:

Preparation of stock solutions for the measurement of CuDBC

Stock solutions containing 500 ppm copper and 10,000 ppm iron were prepared for each of the acid mixtures (HCl, sp. gr. 1.18, HNO_3, sp. gr. 1.42 in the ratio of 4:1 v/v, respectively) and (sulphuric acid, hydrochloric acid and water (3:3:5 v/v/v, respectively) as described in earlier work.[20]These stock solutions were further diluted in order to make the range of working standard solutions needed for calibration.

Preparation of working standard solutions for the measurement of CuDBC

Two sets of working standard solutions were prepared from the stock solution of copper, one set contained copper from 15-50 µg and the



Copper concentration ppm

Graph - 1: Absorption of copper extracted wiht NaDDC into MIBK for different acid solvent

Table - 4: Effect of NaDDC concentration on the extraction of copper in steel

Copper Solution	Iron solution µg	Concentration NaDDC solution	Absorption
100	20,000	0.05%	0.262
100	20,000	0.10%	0.270
100	20,000	0.15%	0.270
100	20,000	0.20%	0.280

other set at the same level as the first one, contained in addition 10,000 µg iron. Then working standards were treated with the extraction procedure detailed in (16) and the copper absorption measured.

The effect of different volumes of MIBK on the extraction of copper with ZnDBC solution

A series of solutions of pure copper of the same concentration was extracted with 10 mL of 0.05% ZnDBC in MIBK, [ZnDBC in MIBK solution (0.05%) was prepared by dissolving ZnDBC in MIBK by shaking for about 20 minutes], plus different

Table - 5: Measurement of copper content of steel samples with NaDDC.

Copper standard Concentration(ppm)	Acid solvent $H_2SO_4 + H_3PO_4 + H_2O$ Absorption		Acid solvent $H_2SO_4 + H_3PO_4 + H_2O$ Absorption	
	NoFe	20,000 µg Fe	NoFe	20,000 µg Fe
2.5 (50 µg)	0.083	0.084	0.070	0.072
5.0 (100 µg)	0.150	0.145	0.142	0.142
7.5 (150 µg)	0.222	0.224	0.200	0.205
10.0 (200 µg)	0.291	0.293	0.273	0.275
Steel sample Solutions	**Absorption**		**Absorption**	
B.C.S. No. 257/1	0.207	0.192	0.199	0.192
	0.203	0.190	0.202	0.197
B.C.S. No. 239/2	0.171	0.156	0.165	0.155
	0.173	0.163	0.180	0.155
B.C.S. No. 253/1	0.172	0.170	0.180	0.170
	0.178	0.175	0.181	0.175

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

Table - 6: Calculated values of the copper content in steel by weight in HCl + HNO_3 mixture using NaDDC as the chelating agent.

Steel Sample	Certificate value%	Standard with Fe value found%	Difference %	Standard wihtout Fe value found%	Difference %
B.C.S. No. 257/1	0.13	0.137	+0.007	0.141	+0.011
	0.13	0.141	+0.011	0.145	+0.015
B.C.S. No. 239/2	0.18	0.190	+0.010	0.195	+0.015
	0.18	0.183	0.003	0.190	+0.010
B.C.S. No. 253/1	0.39	0.403	+0.013	0.420	+0.030
	0.39	0.416	+0.026	0.427	+0.037

Table -7: Calculated values of the copper content in steel by weight in H_2SO_4+ H_3PO_4 mixture using NaDDC as the chelating agent.

Steel Sample	Certificate value%	Standard with Fe value found%	Difference %	Standard wihtout Fe value found%	Difference %
B.C.S. No. 257/1	0.13	0.126	-0.004	0.137	+0.007
	0.13	0.125	-0.005	0.133	+0.003
B.C.S. No. 239/2	0.18	0.175	-0.005	0.191	+0.011
	0.18	0.166	-0.014	0.185	+0.005
B.C.S. No. 253/1	0.39	0.366	-0.024	0.375	+0.015
	0.39	0.380	-0.010	0.385	+0.005

Table - 8: Values for % error in HCl + HNO_3 (using NaDDC as the chelating agent)

Steel Sample	Certificate Value%	Standard with Fe Average value found %	% error	Standard without Fe Average value found%	% error
B.C.S. No. 257/1	0.13	0.139	+ 6.92	0.143	+ 10.00
B.C.S. No. 239/2	0.18	0.187	+ 3.60	0.193	+ 6.94
B.C.S. No. 253/1	0.39	0.410	+ 5.00	0.424	+ 8.58

volumes of pure MIBK. The organic solvent layer of each solution after extraction was transferred to a 25 mL volumetric flask and diluted to the mark with MIBK in order to get the same volume. The absorption of copper in these solvent solutions then was measured by atomic absorption spectro-photometry. The results are listed in Table 10.

The effect of ZnDBC concentration on the extraction of copper

To determine the concentration of ZnDBC for the extraction of copper, various concentration of ZnDBC in MIBK solution were used to extract 25 µg of pure copper. The absorbances of the organic phases were measured by atomic absorption spe-ctrophotometry. The results are given in Table 11.

Stability of copper dibenzyldithiocarbamate (CuDBC) complex

To check the stability, the absorbance due to the copper of the solutions prepared in Table 10, were measured at different times after extraction. The results are given in Table 12.

Preparation of the steel sample solutions

Dissolution using sulphuric and hydrochloric acids for the measurement of CuDBC: 0.1 g of each steel sample was accurately weighed and transferred into 100 mL beakers and dissolved with heating in 11 mL of a mixture of sulphuric acid, hydrochloric acid and water (3:3:5 v/v/v, respectively). When the reaction ceased, nitric acid was added dropwise to oxidize carbides and to clarify the solution. The heating of the solution was followed by fuming and evaporation to dryness. The residue was dissolved in 10 mL 1.5 N, sulphuric acid. When cooled, the solution was quantitatively transferred into 100 mL volumetric flasks and diluted to volume with distilled water. The volumes of the samples selected for the three standard steels for extraction was that which gave a solution containing approximately 27 µg. These were 20 mL of steel solution B.C.S. No. 257/1, 15 mL of steel solution B.C.S. No. 239/2 and 7 mL of steel solution B.C.S. No. 253/1.

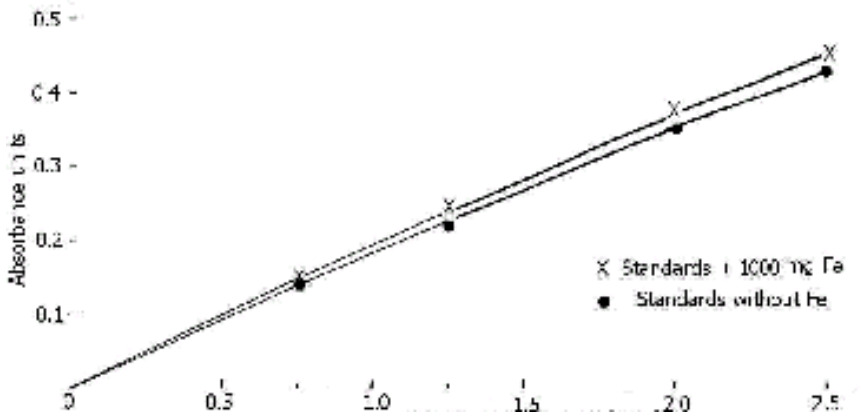
Extraction of copper with ZnDBC through solvent extraction method

Appropriate volumes of the steel solutions

Table -9: Values for % error in H_2SO_4 + H_3PO_4 mixture (using NaDDC as the chelating agent).

Steel Sample	Certificate Value%	Standard with Fe		Standard without Fe	
		Average value found %	% error	Average value Value found%	% error
B.C.S. No. 257/1	0.13	0.126	- 3.46	0.135	+ 3.8
B.C.S. No. 239/2	0.18	0.171	-5.28	0.188	+ 4.4
B.C.S. No. 253/1	0.39	0.373	+-4.36	0.380	- 2.6

containing about 27 µg of copper, prepared by the above procedure (15), were shaken for 10 minutes with 20 mL of 0.05% ZnDBC in MIBK solution in a separatory funnel. The funnel was allowed to stand for a few minutes for the layers to separate. It was not necessary to adjust the pH of the aqueous solution before extraction. The absorbance of copper in the extract was measured against a series of extracts from standard solutions (prepared in 11). The results are given in Tables 13 and 14 and plotted graphically in graph 2.



Graph - 2: Absorption of copper extracted with ZnDBC into MIBK in the presence and absence of Fe

Instrumental settings

The instrument was set up according to the optimum conditions obtained in the preliminary experiments for maximum sensitivity and reproducibility.[20] 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.

DISCUSSION

In solvent extraction techniques one of the most important considerations is the selection of a suitable organic solvent. The organic solvent used must be virtually immiscible with water and the

Table - 10: The effect of different volumes of MIBK on the extraction of copper with ZnDBC solution.

Copper content µg	0.05% ZnDBC In MIBK(mL)	Additional MIBK(mL)	Total volume (mL)	Absorbance
25	10	0	25	0.182
25	10	5	25	0.175
25	10	10	25	0.172
25	10	15	25	0.170

Table - 11: The effect of ZnDBC concentration on the extraction of copper

Copper content µg	Volume of ZnDBC - MIBK (mL)	Concentration of ZnDBC -MIBK (%)	Absorption
25	20	0.07	0.172
25	20	0.05	0.174
25	20	0.028	0.175
25	20	0.014	0.178

solubility of the complex in the solvent must be high if a good separation is to be obtained. A suitable organic solvent for atomic absorption determinations should be combustible, exhibit a reasonable aspiration rate and the combustion product should not absorb radiation from the hollow cathode lamp. The number of solvents that can be successfully aspirated into a flame is limited. Chloroform and carbon tetrachloride which were widely used in colorimetric work, then aspirated caused the flame to be extinguished. Of the flammable solvents, acetylacetone (AcAc), isobutylacetate, n-butyl ether and methyl isobutyl ketone (MIBK) were tested. They all showed a tendency to lift the flame from the burner and to make the flame luminous. It was possible by restricting the acetylene flow as much as safety possible before aspirating the solvent to hold the flame on the burner, but except for MIBK, the flame remained luminous. MIBK is only sparingly soluble in the aqueous phase and has low viscosity, giving high nebulization rate and efficiency. With this solvent the flame was steady and no absorption due to the solvent was observed. Organic solvents cause an increase in the absorption signal of the sample in the flame due to greater efficiency in producing free atoms and to more effective nebulization. Therefore, it is often necessary to adjust the fuel:oxidant ratio to obtain the optimum flame conditions for use with organic solvents.

In this research, trace amounts of copper in steel samples were determined as a copper diethyldithiocarbamate (CuDDC) complex from aqueous alkaline solution into methyl isobutyl ketone (MIBK) and by spraying the MIBK extract into the flame. Initially a series of preliminary experiments were carried out with pure copper to find out the stability and the concentration of the reagent before determination of the copper content of the steel samples. The results from Table 3 showed that the absorption increased slowly with time and this is apparent even after half an hour. The absorption of all solvent extracts was subsequently measured as soon as possible after extraction and in no case more than four hours. This time interval was necessary so that several samples and the standard solutions could be extracted and all of the absorption data obtained in one session with the atomic absorption spectrophotometry. In order to measure the copper trace in the samples and standards, attempts were made to separate copper from alkaline solution (pH 9-10). Ferric ion is held in solution by the addition of tartaric acid and other heavy metals masked by the addition of EDTA. NaDDC was added as an aqueous solution and a

Table - 12: Stability of CuDBC complex

Copper solution µg	ZnDBC-MIBK conc. %	Time after extraction (hours) 0.0	0.5	5	24
		Absorption			
25	20,000	0.172	0.172	0.173	0.170
25	20,000	0.174	0.175	0.174	0.174
25	20,000	0.175	0.176	0.175	0.173
25	20,000	0.178	0.178	0.174	0.179

Table - 13: Absorption values for copper content of steels and standards using ZnBDC as chelating agent

Copper standard concentration in ppm	Acid solvent H_2SO_4 + HCl + H_2O Absorption No Fe present	Absorption 20,000 µg Fe added
0.75 (15 µg)	0.147	0.148
1.25 (25 µg)	0.220	0.230
2.00 (40 µg)	0.355	0.375
2.50 (50 µg)	0.430	0.455
Steel samples	**Absorption**	
B.C.S.	0.243	
No. 257/1	0.236	
	0.250	
	0.240	
B.C.S.	0.255	
No. 239/2	0.260	
	0.254	
	0.258	
B.C.S.	0.256	
No. 253/1	0.254	
	0.257	
	0.250	

single extraction made with MIBK. No copper was detected by atomic absorption spectroscopy in the aqueous layer.

From Table 6 it can be seen that with a mixture of hydrochloric and nitric acids, the addition of iron to standards gives better result for the copper determination. The percentage error for each sample has been calculated and shown in Table 8, from which it is apparent that the percentage error is independent of the copper content of the steel samples. However, with a mixture of sulphuric and phosphoric acids, the addition of iron to standards makes an appreciable difference to the results obtained for copper concentrations (Table 7), although this difference does not appear in the percentage error shown in Table 9, since one is negative and the other positive. In this mixture, presence or absence of iron in standards give more accurate results than with a hydrochloric acid and nitric acid mixture. From comparison between the results obtained for the copper content of steel samples dissolved in different acid mixtures, it is apparent that sulphuric acid and phosphoric acid mixture is to be preferred as the solvent medium, even when iron is not added to the standards.

The copper content of steel sample solutions were determined by extraction as the copper dibenzyldithiocarbamate (CuDBC) complex from the acidic solution into MIBK, followed by introduction of the extract into an air-acetylene flame. Several preliminary experiments were first carried out with pure copper to determine the optimum concentration of ZnDBC, the stability of the reagent and the amount of MIBK necessary to extract copper from steel samples. The optimum condition for the flame was set on the basis of tests as discussed earlier in which the air flow rate was 5.2 L/min. and the acetylene flow rate was 1 L/min.

Although there is a slight tendency for the absorption to decrease with larger volumes of MIBK, (Table 10) this was not considered to be significant, particularly since the noise level when using an organic solvent is greater than when using water as a solvent. It appears therefore that 10 mL of

Table - 14: Calculated values of the copper content in steel by weight using ZnDBC as chelating agent.

Steel sample	Certificate value	Standard with Fe		Standard wihtout Fe	
		value found%	Difference%	Value found%	Difference%
B.C.S. No. 257/1	0.13	0.132	+0.002	0.141	+0.011
	0.13	0.127	- 0.003	0.135	+ 0.005
	0.13	0.129	-0.001	0.136	+ 0.006
	0.13	0.125	-0.005	0.126	- 0.004
B.C.S. No. 239/2	0.18	0.178	-0.002	0.191	+0.011
	0.18	0.182	+0.002	0.193	+ 0.013
	0.18	0.181	+0.001	0.192	+ 0.012
	0.18	0.184	+0.004	0.196	+0.016
B.C.S. No. 253/1	0.39	0.387	-0.013	0.397	+0.007
	0.39	0.384	- 0.016	0.394	+0.004
	0.39	0.385	-0.005	0.414	+0.024
	0.39	0.382	-0.008	0.402	+0.012

Table - 15: Values for % error in H_2SO_4 + HCl + H_2O mixture using ZnDBC as chelating agent

Steel sample	Certificate	Standard with Fe		Standard without Fe	
	Value%	Average value found%	% error	Average value found%	% error
B.C.S. No. 257/1	0.13	- 0.128	- 1.35	0.135	+ 3.85
B.C.S. No. 239/2	0.18	+0.181	+0.56	0.193	+ 7.22
B.C.S. No. 253/1	0.39	-0.385	- 1.30	0.400	+2.56

0.05% ZnDBC in MIBK is sufficient for the extraction of up to 25 µg of copper. It was subsequently discovered that it was necessary to use 20 mL of this extraction solution in order to get consistent results when extracting copper from solution of steels. The effect of ZnDBC concentration on the extraction of copper was investigated (Table 11). The results showed that there was virtually no change in the amount of copper extracted within this range of concentration (0.014%-0.07%) and for subsequent work, a 0.05% solution of ZnDBC in MIBK was used. The stability of CuDBC complex was investigated through measurement of the absorbance of the solutions given in (Table 11) by atomic absorption spectrophotometry. The results (Table 12) showed that the solution of the extracted copper in MIBK was stable for at least 24 hours.

When attempts were made to determine copper using the solutions of the steels as previously reported,[20] the results were very unsatisfactory. For example, the value obtained for the copper content

of steel B.C.S. No. 257/1 (certificate value 0.13%) was 0.095%, an error of 27%. The results for the other standard steels were similar. Further attempts were made using this extraction system and a procedure based on that suggested by Ichninose[19] for very low concentration of copper in steels (<0.005% Cu). In this method the steel is dissolved in a mixture of hydrochloric acid, sulphuric acid and water. Since in this experiment, the steel samples were dissolved in a different acid mixture, new standard solutions were prepared as detailed in experiments (10 and 11). The copper content of four separate samples of each of the standard steels was extracted into MIBK using ZnDBC as a complexing agent. The absorption of copper in the organic solvent layer of standard steel samples was compared with those obtained for standard copper solutions in the presence or absence of iron. These absorption values are shown in Table 13 and plotted graphically in graph 2 and from these data the experimental value of the copper content of steels was calculated as shown in Table 14. The results in general are good, slightly better with addition of iron to the standards. Table 15 summarizes the calculated percentage error for each sample. The conclusion is that ZnDBC in MIBK can extract copper successfully from the steel samples, especially when these samples are compared with the calibration solution containing iron, since experimental values are very near to the certificate value.

Generally speaking, in solvent extraction method, the copper is separated from the matrix solution by solvent extraction and the copper is determined by atomic absorption spectrophotometry on the organic solvent extract. The extraction procedure takes longer than the direct atomization procedure[20] and it is possible to work only with small batches of samples, since the extracted solutions are not stable over long periods and for each batch of samples it is necessary to prepare fresh extracts of the standard solutions. Another disadvantage is the volatility of the solvent which means that all solvent extracts must be kept in stoppered bottles. From the two complexing agents used, better accuracy was obtained when using ZnDBC, but the results obtained from using NaDDC were not appreciably better than those for the direct method.[20]

With ZnDBC a different acid mixture was necessary for more accurate results. This method has the advantage of extraction from the acid solution with no need to add a masking agent for iron. The conclusion is that for a rapid determination of copper in the steel samples, direct atomization of aqueous solution when dissolved in hydrochloric acid and nitric acid mixture is to be preferred if high accuracy is not required (~ 4% error). More accurate results can be obtained using a longer extraction procedure using ZnDBC (~ 1% error).

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