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The effect of ammonium pyrrolidinedithiocarbamate (APDC) complexing agent on the determination of copper trace in steel using atomic absorption spectrophotometry

N. GHARIB NASERI*

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

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ABSTRACT

A method of solvent extraction is described for concentrating and separating the copper from an aqueous alkaline solution (pH 9-10) of steel into an organic solvent prior to analysis by flame atomic absorption spectroscopy. In this research first, ammonium pyrrolidinedithiocarbamate (APDC) as a chelating agent, and tartaric acid as masking agent for ferric ion, were used then, solvent extraction, separation of copper from steel and subsequent determination of copper in the organic solvent were carried out. The copper content of four separate samples of each of the standard steels was extracted as a Cu/APDC complex into MIBK. The results obtained for steel samples were very near to the certificated values particularly when iron is added to the standard solutions. Thus, APDC could be used successfully in the extraction of copper from steel samples even when iron is not added to the standards.

Keywords: Copper, copper trace, steel, ammonium pyrrolidinedithiocarbamate (APDC) solvent extraction method, atomic absorption spectrophotometry.

INTRODUCTION

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 choice of possible chelating agents and solvent is made after a series of preliminary experiments. More detailed experiments are then carried out with those solvent extraction systems which appeared to be most promising. The extraction procedure takes longer than the direct atomization procedure 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. Ammonium pyrrolidinedithiocarbamate (APDC) was first investigated by Malissa and Schoffmann in 1955.[1]The combination of APDC as a chelating agent and methyl isobutyl ketone (MIBK) as an organic solvent in atomic absorption spectrophotometry has been reported by a number of authors[2-7]and some[4,7] found it the most useful extraction system, because APDC forms stable chelates with numerous metal over a wide pH range and MIBK exhibits ideal combustion properties in the flame. A number of advantages results from the extraction of APDC-metal complexes into a suitable organic phase. The metal may be concentrated by a factor of one hundred or more. Wanted metals can be separated from high concentrations of other solutes which cause difficulties in nebulization and atomization. The atomic absorption signal for nearly all metals is enhanced by a further factor of 3-5 when aspirated in an organic solvent instead of in an aqueous solution.[8]

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.

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

water in the ratio of 1:1:4, respectively, as described in earlier work.[9] These stock solutions were further diluted in order to make the range of standard stock solutions needed for calibration.

Preparation of working standard solutions

Two sets of working standard solutions were prepared from the stock solution of copper, one set contained copper from 15-50 µg in sulphuric and phosphoric acids mixture (prepared as discussed in earlier work)[9] and the other set at the same level as the first one, contained in addition 10,000 µg iron. Then standards were treated with the extraction procedure detailed in earlier work[10]

Fuel:oxidant ratio

Experiments to find the flow rates for air and acetylene when using a solution in methylisobutyl ketone were performed in the following way: 150 µg of copper (15 mL of 10 ppm standard solution) was extracted as APDC 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, giving the optimum condition of acetylene flow rate 1 L/min and air flow rate 5.2 (instrument flowmeter).

Preparation of Stock Solution

Stock solution containing 500 ppm copper and 10,000 ppm iron was prepared for sulphuric acid, sp. gr. 1.84, phosphoric acid, sp. gr. 1.75 and

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

and the copper absorption in the organic layer was measured by atomic absorption spectrophotometry.

Stability of copper-APDC complex

A range of standard copper solutions was prepared containing 15 to 50 µg copper and 10,000 µg iron was added to each solution. The copper then was extracted with Ammonium Pyrrolidinedithiocarbamate (APDC) solution at pH 10 into 20 mL of MIBK. The absorbance of the copper in the extracts was measured by atomic absorption spectroscopy at different times after extraction. The results are given in Table 3.

Effect of concentration of APDC on the extraction of copper

Identical solutions of pure copper each containing 10,000 µg of iron were extracted with

various volumes of ADPC solutions (1% aq.) into 20 mL of MIBK. The absorption of copper in the solvent layer was then measured by atomic absorption spectrophotometry. The aqueous layer was also tested by atomic absorption spectroscopy for copper and none was detected in any of the solutions. The results are given in table 4. From these results it was concluded that 5 mL of 1% APDC solution should be used in the extraction of copper from steel.

Extraction of copper with APDC through solvent extraction method

To a 5 mL aliquot of the steel solutions containing about 30 µg of copper [prepared as discussed earlier][10] added 10 mL tartaric acid (15% aq.) as masking agent and the solution was adjusted to pH 9-10 with aqueous NH_4OH. 5 mL APDC (1% aq. prepared by dissolving 1 g of APDC in water and adjusting the volume to 100 mL by adding more water and filtering before use) was added to the

Table - 3: Effect of stability of copper/APDC complex

Copper solutionµg	Additional Iron µg	Time after extraction (hours)				
		0.0	0.5	2	4	24
		Absorption				
15	10,000	0.135	0.135	0.133	0.127	0.130
25	10,000	0.228	0.227	0.224	0.215	0.220
40	10,000	0.360	0.361	0.360	0.335	0.345
50	10,000	0.430	0.428	0.420	0.412	0.400

Table - 4: Effect ofconcentration of APDC on the extraction of copper

Copper content (µg)	Additional iron(µg)	APDC solutionmL	Absorbance
25	10,000	2	0.220
25	10,000	5	0.228
25	10,000	10	0.230
25	10,000	20	0.230

solution then transferred to a separatory funnel. The complex (APDC/Cu) was extracted into 20 mL of MIBK by vigorously shaking for 3 minutes, then, allowed to stand for a few minutes. The aqueous phase was drawn off and the absorption of the copper in the organic solvent solution was measured by atomic absorption spectrophotometry.

Measurement of copper content of steel samples with APDC

The copper content of four separate samples of each of the standard steels was extracted as a Cu/APDC complex into MIBK. The absorption of copper in the organic solvent layer of standard steel sample was compared with those obtained for standard copper solutions in the presence and absence of iron. These results are listed in Table 5 and from these absorptions, the experimental valued of the copper content of steels was calculated as shown in Table 6. Graph 1 is a typical calibration graph.

Instrumental settings

The instrument was set up according to the optimum conditions obtained in the preliminary experiments for maximum sensitivity and reproducibility.[9] 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

Table -5: Absorption values for copper content of steels and standards

Copper standard concentration in ppm	Acid solvent H_2SO_4 + HCl + H_2O No Fe	10,000 µg Fe
	Absorption	
0.75 (15 µg)	0.117	0.119
1.25 (25 µg)	0.185	0.195
2.00 (40 µg)	0.298	0.310
2.50 (50 µg)	0.370	0.375
Steel samples	**Absorption**	
B.C.S.	0.253	
No. 257/1	0.247	
	0.252	
	0.245	
B.C.S.	0.214	
No. 239/2	0.215	
	0.212	
	0.207	
B.C.S.	0.225	
No. 253/1	0.230	
	0.228	
	0.222	

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

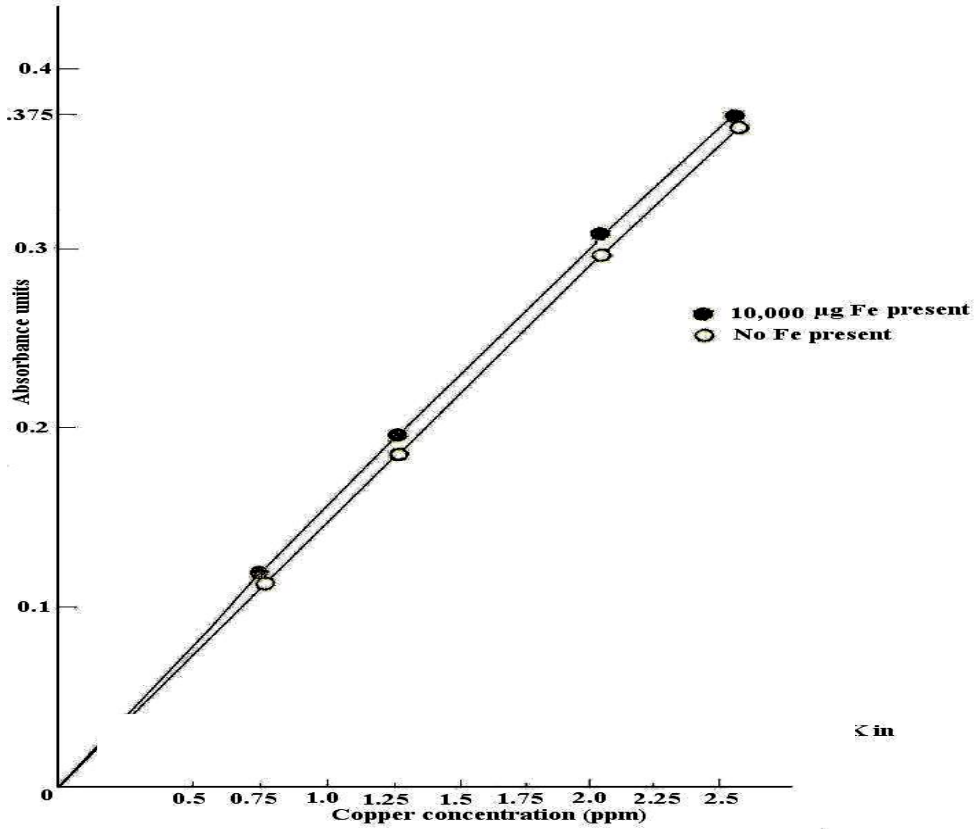
A study has been made of the extraction of copper from the solution of the steel samples using Ammonium pyrrolidinedithiocarbamate (APDC) as a complexing agent into methyl isobutyl ketone (MIBK). The concentration of APDC needed for forming a complex with copper and the stability of this reagent was investigated by a series of preliminary experiments with pure copper solutions. Maximum sensitivity was obtained when using flame conditions of air flow rate 5.2 L/min and acetylene flow rate at 1 L/min. The absorption is constant for at least two hours. Although it decreases slowly with time after this period, the difference is not considerable. Measurement of absorption should be made within two hours if possible and certainly not after four hours after extraction. The copper content of four separate samples of each of the standard steels was extracted as a Cu/APDC

Table -6: Calculated values of the copper content in steel by weight

Steel Sample	Certificate value%	Standard with Fe		Standard wihtout Fe	
		Expereriment Value %	Difference %	Expereriment Value %	Difference %
B.C.S. No. 257/1	0.13	0.133	+0.003	0.133	+0.005
	0.13	0.130	+0.000	0.130	+0.002
	0.13	0.132	+0.002	0.132	+0.004
	0.13	0.129	-0.001	0.129	+0.000
B.C.S. No. 239/2	0.18	0.185	+0.005	0.185	+0.016
	0.18	0.187	+0.007	0.187	+0.011
	0.18	0.184	+0.004	0.184	+0.009
	0.18	0.180	0.000	0.180	+0.004
B.C.S. No. 253/1	0.39	0.392	+0.002	0.392	+0.010
	0.39	0.400	+0.10	0.400	+0.020
	0.39	0.398	+0.008	0.398	+0.015
	0.39	0.387	-0.003	0.387	+0.005

Table -7: Values for % error

Steel Sample	Certificate	Standard with Fe		Standard without Fe	
		Average found value%	Average % error	Average found value%	Average % error
B.C.S. No. 257/1	0.13	0.131	0.85	0.133	2.30
B.C.S. No. 239/2	0.18	0.184	2.20	0.19	5.56
B.C.S. No. 253/1	0.39	0.394	1.03	0.41	5.13



Graph - 1: Absorption of copper extracted with APDC into MIBK in the presence and absence of iron

complex into MIBK. The results are given in Table 6. From Table 6 it is apparent that the results for steel samples are very near to the certificated values particularly when iron is added to the standard solutions. Thus, APDC could be used successfully in the extraction of copper from steel samples even when iron is not added to the standards. The percentage error for these results, are given in Table -7.

From the three complexing agents used,[10] better accuracy was obtained when using ZnDBC and APDC, but the results obtained from using NaDDC were not appreciably better than those for the direct method[10], and certainly did not justify the additional extraction procedure. 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. APDC gives results similar to that of ZnDBC but since, the extraction is made at pH 10, tartaric acid or citric acid must be added to prevent the precipitation of iron hydroxide. 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 APDC and ZnDBC (~ 1% error).

REFERENCES

1. Malissa H and Schoffmann E, *Mikrochi. Acta*(I),187 (1955).
2. Allan JE, *Spectrochim. Acta*, **17**(4), 459 (1961).
3. Mulford CE, *Atomic Absorption Newsletter*, **5**, 88 (1964).
4. Slavin W, *Atomic Absorption Newsletter*, **3**, 141 (1964).
5. Everson RJ and Parker HE, *Anal. Chem.*, **46**, 1966 (1974).
6. Kinrade JD and Van Loon JC, *Anal. Chem.,* **46**, 1894 (1974).
7. Wason CA, "APDC Monograph 74", Hopkin and Williams, Chadwell Heath, Essex, England, (1971).
8. Price WJ, "Spectrochemical Analysis by Atomic Absorption", London, 149 (1979).
9. Gharib Naseri N, " Determination of Copper trace in Steel by Direct Method using Atomic Absorption Spectrophotometry"**,** *Material Science Research India,* **4**(1), (in print) (2007).
10. Gharib Naseri N, "The effect of two comlexing agents (NaDDC and ZnDBC) on the determination of copper trace in Steel using Atomic Absorption Spectrophotometry"**,** *Material Science Research India,* **4**(1), (in print) (2007)