

# 5(4-DIMETHYLAMINOBENZYLIDENE) RHODANINE AS A REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF COPPER AND MANGANESE

E. O. OJEKA and J. F. IYUN

(Received 5 April, 2004; Revision Accepted 19 July, 2004)

## ABSTRACT

The synthesis and spectral characteristics of 5(4-dimethylaminobenzylidene)rhodanine have been investigated. The extraction-spectrophotometric method for the determination of copper and manganese based on their extraction into ethanol with 5(4-dimethylaminobenzylidene)rhodanine (DMABR) from a weakly acidic medium have been developed. The maximum absorbance of the extracted species for Cu and Mn compounds occurs at 480nm. Copper and manganese compounds react with the reagent in the molar ratio 1:1; 1:2; and 1:3 (metal:ligand) at pH 1.09 to 11 in a solution containing 20 % (v/v) of ethanol. A concentration of DMABR three times greater than the metal concentration was necessary for complete complexation; to give molar extinction coefficient ( $3.8 \times 10^3$  at pH 2 and  $7.6 \times 10^3$  at pH 8) for Cu-DMABR and ( $2.76 \times 10^3$  at pH 2 and  $1.5 \times 10^3$  at pH 8) for Mn-DMABR respectively. The interferences with some metal ions have been studied. The optimum experimental conditions were suggested for the determination of these metal ions.

**KEY WORDS:** 5(4-dimethylaminobenzylidene)rhodanine ; copper ,manganese ; spectrophotometric method

## INTRODUCTION

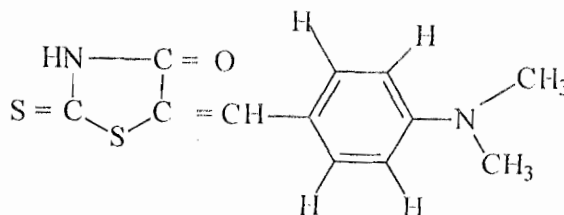
5(4-Dimethylaminobenzylidene)rhodanine abbreviated as (DMABR) is one of the widely used spectrophotometric reagents for gold (III). The information available in literature is very scanty (Welcher, 1947; Sandell, 1959; Perrin, 1964; Beamish, and VanLoon, 1972). In weakly acid medium it gives red or red-violet precipitates with Au(III), Pd(II), Hg(I), Hg(II), and Pt(IV) (Sandell, 1959; Perrin, 1964; Beamish (1966)). In these methods the sensitivity is very poor and the colour fades after about five minutes. In some instances the complex is formed only after heating for a long period, whereas others suffer from interferences from other metal ions. Furthermore, Cave and Hume (1952) during colorimetric determination of silver obtained analytical data having highest accuracy. Shiundu et al. (1990) used flow injection method for the spectrophotometric determination of Pd(II) and it was reported that Co(II), Fe(III), Ni(II) and Mn(II) did not interfere at the optimum pH even when present at a level of 0.01M i.e. hundred times of Pd (II).

A search of the literature showed that no previous attempt has been made to employ this reagent for the spectrophotometric determination of Cu and Mn. The present article describes the extraction-spectrophotometric determination of copper and manganese utilizing 5(4-dimethylaminobenzylidene)rhodanine abbreviated as DMABR.

Azo compounds based on rhodanine, thiorhodanine, and isorhodanine were synthesized for the first at the L'vov medical institute in Russia as potential medicinal preparations. The best azorhodanines exist largely as the diketo tautomers in acid and neutral media (Savvin and Gureva 1987).

The spectrophotometric study of the reaction of copper (II) and manganese (II) with DMABR in HCl medium and its analytical application are discussed. The

studies were done with 20% (v/v) ethanol the conditions for obtaining a non-saturated solution. DMABR is structurally represented as,



## MATERIALS AND METHODS

### Materials

4-Dimethylaminobenzylidene aldehyde, copper(II) sulphate and manganese (II) chloride were of analytical-reagent of BDH grade.

**Preparation of DMABR reagent solution, ( $3.78 \times 10^{-5}$  M):** It was obtained by dissolving 0.05g DMABR in  $100\text{cm}^3$  of absolute ethanol and allowed to stand overnight in the dark. The solution was filtered and the filtrate was diluted to  $500\text{cm}^3$  with ethanol. The solution was stable for months.

**1000 ppm standard metal salt solutions:** These were prepared by dissolving the required amount of their salts in  $1000\text{cm}^3$  distilled water in volumetric flasks

### Apparatus

Infrared spectra were obtained from hydrocarbon mulls utilizing, an ATI Mattson Genesis FTIR Spectrometer, while Unicam 8625 UV/VIS spectrometer and Pye uncam 929 AA atomic spectrometer were

**Table 1: Absorbance of DMABR in Acidic and Basic media**

DMABR in Moles x 10 <sup>5</sup>	pH	Absorbance in nm at 470	Absorbance in nm at 480
7.56	0.65	0.160	0.162
15.12	1.00	0.253	0.277
22.68	2.00	2.265	2.461
30.24	5.00	2.408	2.491
	Basic		
7.56	7.0	0.226	0.214
15.12	8.0	1.100	0.995
22.68	11	1.742	1.492
30.24	13	2.243	1.828

**Table 2: Absorption spectra of manganese (II) complex at pH 2.**

DMABR cm <sup>3</sup> of moles	Mn (II) cm <sup>3</sup> of 1x10 <sup>-5</sup> moles	Absorbance 480 nm	Absorbance 495 nm
2	1	0.108	0.100
4	2	0.185	0.186
6	3	0.221	0.213
8	4	0.497	0.483
10	5	0.838	0.790
12	6	1.338	1.232

**Table 3: Composition of Copper (II) - DMABR complex**

Mole-Ratio Cu (I)-DMABR complex	Ph 2	
	pH 2	pH 8
1:0	0.006	0.458
1:1	0.259	0.715
1:2	0.508	1.093
1:3	0.571	1.150
0:4	0.374	1.150

used to determine the absorbance measurements. pH measurement were made with a Philips PW 9408 pH meter with glass-calomel electrodes. The <sup>1</sup>H nmr spectra were recorded at Varian mercury YH 200 spectrometer operating at 200 MHz.

#### Synthesis of 5(4-Dimethylaminobenzylidene) rhodanine

DMABR was synthesized according to the method reported by Feigl ((1929). Rhodanine reagent was first prepared by reacting 25 cm<sup>3</sup> of CS<sub>2</sub> with 20 cm<sup>3</sup> of ether in the presence of ethanol followed by addition of 20 cm<sup>3</sup> of conc. ammonia. The carbamate salt formed was reacted with sodium chloroacetate earlier prepared. The coupling reaction was done by adding 8g rhodanine in 150 cm<sup>3</sup> IM NaOH to 10 g of 4-dimethylaminobenzaldehyde dissolved in 100 cm<sup>3</sup> of water. The product has a melting-point 285-289 °C; and elemental analysis gave the following results: C 53.35, H 4.98, N 22.76 and S 25.52%; C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>S<sub>2</sub>O requires C 53.39, H 4.97, N 22.80 and S 25.50.

#### Properties of DMABR

It is a red powder with melting point 285-289°C. The reactions with noble metals are highly sensitive in acid and strongly acid media. Excess of alkali, alkaline-earth and non-ferrous metal ions do not interfere. In solution, it gives stable red-violet colour with metals under study. It can exist in various tautomeric forms in solution. Absorption maximum of the reagent was at 500 nm. Its solubility in ethanol was 8.25g per 100 cm<sup>3</sup>; and 2.98g per 100 cm<sup>3</sup> in water at 256 0.2°C.

#### Preparation of DMABR-Metal complexes

30 cm<sup>3</sup> of 0.0000378 mole ligand (0.05g/500 cm<sup>3</sup>) in ethanol was added to 0.005 mole of copper (II) sulphate or manganese (II) chloride solution. (copper or manganese). The mixture was refluxed for 45 min. at 55°C and evaporated to dryness. The isolated complexes were washed with boiling water and ethanol; and dried in vacuum over P<sub>2</sub>O<sub>5</sub>. The absorbance of the solid complex was measured at 480 nm against a reagent blank prepared simultaneously with the samples.

### Spectrum of DMABR in Acidic and Basic media in the pH range 0.65 to 13

Serial dilution of  $3.78 \times 10^{-5}$  molar reagent solution was done to obtain varying concentrations of the reagent in  $2 \text{ cm}^3$  buffer at different pH values were observed at  $\lambda_{\text{max}}$  of 470 and 480 nm respectively in 20% (v/v) ethanol-water media.

### Absorption spectra of manganese (II) at constant pH of 2

The sample solution of DMABR - Mn was diluted to  $25 \text{ cm}^3$  and left for 1 hr, for stabilization of colour. Absorbance measurements were made at  $\lambda_{\text{max}}$  of 480 and 495 nm respectively. The following conditions were applied for the condition of high acidity of pH 2:

[DMABR] =  $3.78 \times 10^{-5}$  moles; [Mn] =  $1 \times 10^{-5}$  moles; pH = constant at 2.

### Composition of DMABR-Copper or Manganese (II) Complexes

The composition of DMABR complexes was established by Job's method of continuous variation and molar ratio-methods. The mole-ratio method was applied to two series of solutions containing the complex, one at pH 2 and the other at pH 8.0. Each final solution was  $3 \times 10^{-6}$  M (with the total concentration of  $1 \times 10^{-3}$  M metal and DMABR,  $2 \times 10^{-3}$  M or 0.529 g/litre) in absolute ethanol.  $2 \text{ cm}^3$  of the required buffer was added and the solution was diluted to  $25 \text{ cm}^3$  for absorbance reading at 480 nm using ethanol as reference.

### Determination of DMABR by Titration Method

Solutions containing 1:1, 2:1, and 3:1 molar ratios of ligand to metal ion were prepared by pipetting  $25 \text{ cm}^3$  of the metal solution into the titration vessel. 25, 50, and  $75 \text{ cm}^3$  DMABR ligand solution were added. After thermal equilibrium was reached, standard 0.1 KOH 0.1M HCl were added separately in small increments and the corresponding absorbance values at pH 2 and 8 were recorded as soon as constant values were obtained. Results are presented in Tables 3 and 4 respectively.

### Stoichiometric studies of DMABR-metal complexes

#### Reactivity of DMABR with Copper (II) in the pH range 3 to 8

$2 \text{ cm}^3$   $1 \times 10^{-3}$  moles metal ions were mixed with  $5 \text{ cm}^3$  of 0.12 and 0.15 M HCl followed by  $2 \text{ cm}^3$   $3.78 \times 10^{-5}$  M DMABR, and  $2 \text{ cm}^3$  of 20%, and 40%  $\text{C}_2\text{H}_5\text{OH}$ .  $2 \text{ cm}^3$  of buffer of 3 to 8 pH values were added, and the volume was diluted to  $20 \text{ cm}^3$ . Absorbances were measured at 460, 470, 480 and 495 nm respectively.

### Application of DMABR to the determination of manganese in tap water and effluent samples from waste water

#### Procedure

To  $20 \text{ cm}^3$  of waste water sample and tap water respectively was added  $5 \text{ cm}^3$  10 percent hydroxylammonium chloride in a volumetric flask.  $1 \text{ cm}^3$  of acetic acid-sodium acetate (Walpole) buffer of pH 5 was added and mixed.  $1 \text{ cm}^3$   $0.0000378 \text{ M}$  DMABR solution was added followed by dilution to  $25 \text{ cm}^3$  with ethanol. The absorbance was measured at 480 nm against a reagent blank prepared by using ethanol as reference.

### Periodate Oxidation of Manganese by Colorimetric Standard Method (Sandell, 1959)

#### Procedure

Dilute solutions of manganese (II) containing 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1.0 ppm and  $20 \text{ cm}^3$  dilute solutions of manganese and waste water samples were transferred into  $100 \text{ cm}^3$  volumetric flasks.  $10 \text{ cm}^3$  phosphoric acid and  $10 \text{ cm}^3$  concentrated HCl were added. The solution was made to  $50 \text{ cm}^3$  mark and stirred until all soluble salts dissolved. The solution was heated 5 min and cooled.  $50 \text{ cm}^3$  of the clear supernatant liquid was pipetted into a clean  $250 \text{ cm}^3$  beaker.  $15 \text{ cm}^3$   $\text{H}_3\text{PO}_4\text{-HNO}_3$

Mixture were added and the solution was diluted to  $150 \text{ cm}^3$  with water. 0.4g potassium periodate was added and the solution was boiled for 5 min at  $45^\circ\text{C}$  and cooled. The solution was transferred to  $250 \text{ cm}^3$  volumetric flasks, diluted to mark and mixed thoroughly. The absorbance was read at 550 nm. The coloured solution was decolourised by dropwise addition of hot oxalic acid, 0.01%  $\text{H}_2\text{O}_2$ . The transmittance of this solution was again measured against the standard manganese solution which has also been decolourised.

### DISCUSSION

The addition of ethanolic solution to aqueous mineral acid solution was to enhance metal extraction resulting from decrease in hydration. This is because the mole fraction of water decreases in the formation of extractable metal complexes. The prepared metal complexes exist in the solid form for a short period; turning to gels.

It was observed that the absorbance of the metal-ligand complexes and the blank were temperature dependent and the temperature was therefore controlled to  $25 \pm 1^\circ\text{C}$ .

From Table 1 and figure 1, in strongly acidic media, of pH(0.65-2.0) absorption maxima occurs at 480 nm and shifts to longer wavelength with increasing pH

Table 4: Composition of Manganese (II)-DMABR complex

Mole-Ratio Mn (II)-DMABR complex	Absorbance at 480 nm pH 2	Absorbance at 480 nm pH 8
1:0	-0.008	-0.003
1:1	0.150	0.176
1:2	0.227	0.200
1:3	0.434	0.241

**Table 5: Absorbance of DMABR with Copper( II) at pH 5**

HCl ( M)	Solvent	pH	460 nm	470 nm	480 nm	495 nm
0.15	Benzene	5	0.014	0.011	0.010	0.005
0.15	20% ethanol	1.09	0.058	0.058	0.058	0.031

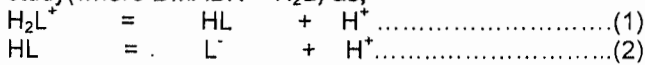
**Table 6: Absorbance of Copper ( II)-DMABR at pH 3 and 8**

HCl ( M)	Solvent	pH	460 nm	470 nm	480 nm	495 nm
0.12	Benzene	8	0.036	0.031	0.026	0.018
0.12	20 % ethanol	3	0.209	0.205	0.181	0.145

**Table 7: Absorbance of Manganese ( II)-DMABR complex at pH 2 and 11**

HCl ( M)	Solvent	pH	460 nm	470 nm	480 nm	495 nm
0.5	40% ethanol	2	0.067	0.069	0.069	0.063
0.5	40% ethanol	11	0.123	0.123	0.119	0.086

in alkaline media. These pH effects are probably due to protonation of basic groups or deprotonation of acidic group and/or various tautomeric processes. The figure exhibits three inflections indicating the possible existence of three equilibria in the pH range under study (where DMABR =  $H_2L$ ) as,



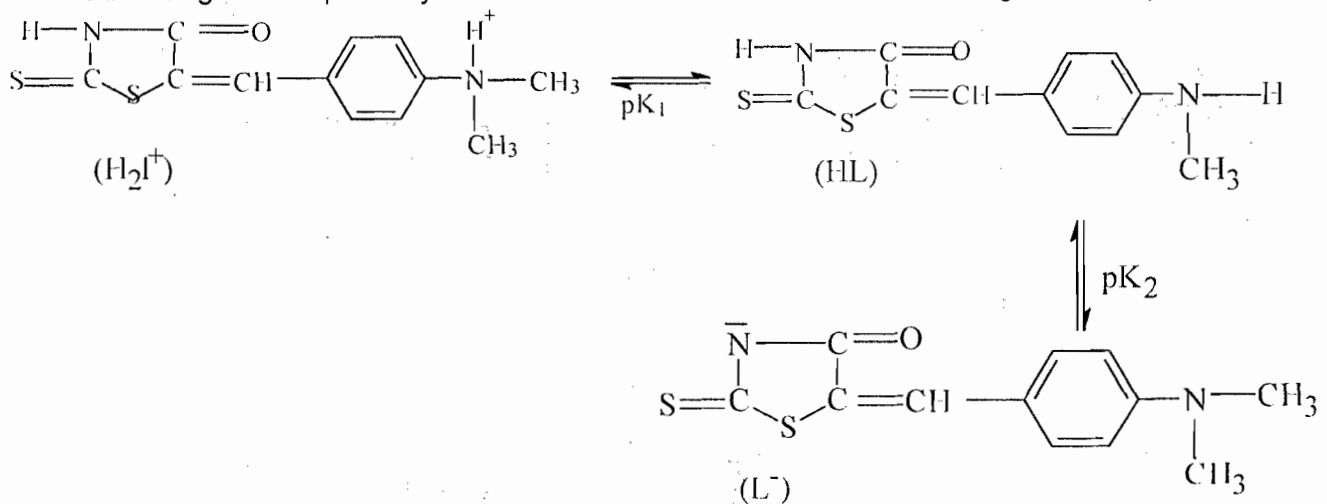
The  $pK$  values obtained in our previous studies are,  $pK_1$  7.01 and  $pK_2$  9.52 (Ojeka 2003).

Spectrum of manganese (II) at constant pH of 2. The metal chelates are assumed to be formed at both low and high pH. The absorbance tends to increase with increase in volume ( $cm^3$ ) of the metal ion. Job's method was confirmed by titration procedure in the stoichiometric studies presented in Tables 3 and 4 respectively. There is a shift in wavelength absorption band from high acidic medium to neutral solution, due to protonation of the reagent, by the hetero-atoms of the

rhodanine. The complex is formed with metal-ligand ratios of 1:1, 1:2, and 1:3. The 1:1 complex is formed with a deficient of reagent while 1:3 is formed with an excess of the reagent at the highest wavelength of 480 nm. Efforts to plot Job's curves failed.

A concentration of the ligand three times greater than the metal concentration was necessary for complete complexation. The 1:2 and 1:3 complexes are favoured by the acidic medium. Titration of the 2:1 mixture of Mn-DMABR gave precipitation of  $Mn(OH)_2$  at pH of 11. Thus, the most suitable conditions for spectrophotometric determination of these metals include the use of an excess of the ligand and a relatively high pH value; which favour the formation of 1:3 metal-ligand complex in this study.

Table 2 and figure 2 respectively show the extent of absorbance and wavelength of absorption



In the solvent extraction of DMABR in Tables 5, 6 and 7, respectively, coloured complexes formed were soluble in various organic solvents. Experimental results indicate that acidic conditions are optimum for Copper(I) and Copper(II), and little reaction occurs under basic conditions. Products formed under alkaline conditions except for Mn(II) decompose rapidly. There is a general decrease in absorbance values for Mn(II) in concentrated HCl/solvent medium than in alkaline medium probably because of higher complexing power of the chloride ions in solution; as chlorocomplexes of metals are formed in solutions comparatively low HCl concentrations. The dissociation constant of DMABR is expected to decrease with increasing acid strength due to protonation:



A higher degree of protonation in more concentrated acid solutions gave rise to higher solubility for DMABR in the aqueous phase. At high pH of 8.0, addition of  $\text{H}^+$  does not appear to promote deprotonation of  $\text{OH}^-$  grouping  $\text{Cu(II)}$ , as the absorbance decreases with increasing  $\text{H}^+$ . This is contrary to what obtained with copper(I) and Mn(II). At pH 0.65-2.5, Mn(II) reacts with the reagent in 20-40% ethanolic medium to produce a yellow colour attributable to ion-pair type of complex as  $[\text{M}(\text{H}_2\text{O})_3]^+[\text{ML}_2]^-$ . At mildly acidic condition of about pH 5-7.0, Mn(II) forms an aquo-bridging at pH 7.0. Neutral salts of these metals are expected as  $\text{M}(\text{OH})_4$  and as  $\text{M}(\text{OH})_2$  in the alkaline medium, especially copper(II).

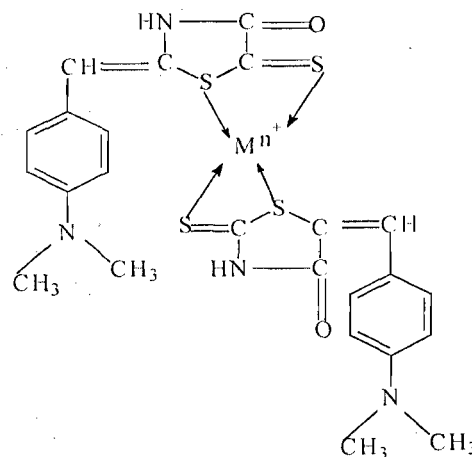
Table 8 shows interference studies; and no interference was noted at pH range 2-5. In alkaline conditions, Cu(II) interferes at 500 nm, Ag(I) at 480 nm, Fe(II) at 495 nm and Zn(II) at 520 nm. Further selectivity was achieved by multi-wavelength measurements.

#### Infrared Characterization of Mn(II) and Cu(II) complexes with DMABR

The complexation of DMABR with these metals through the nitrogen is not expected because of the steric effect of the constituents. The intensity of the thiamide band involving the  $\text{C}=\text{S}$  vibration at  $1250\text{-}1990\text{ cm}^{-1}$ , characteristics of rhodanine ring makes the coordination of metal with the thiocarbonyl sulphur most probable. The infrared spectra show no indication of an SH band in the  $2500\text{-}2600\text{ cm}^{-1}$ , but instead showed strong vibrations at about  $1413.51$  to  $1514.39\text{ cm}^{-1}$ . This is a mixed vibration of mainly NH amide band; indicating the ligand is in the thioketo rather than thiol form. The  $\text{C}=\text{N}/\text{C}-\text{N}$  stretching band was observed between  $1513.19$  and  $1655.48\text{ cm}^{-1}$ . The  $\nu(\text{C}=\text{S})$  stretching band

of the ligand at  $1055.25\text{ cm}^{-1}$  is shifted slightly lower in the complexes due to complexation. The bands at  $400\text{-}500\text{ cm}^{-1}$  correspond to metal-sulphur bonds and below  $400\text{ cm}^{-1}$  to metal-chloride bonds in Table 10. The metal-sulphur bonds are  $\text{Cu-S}(467.04\text{ cm}^{-1})$  and  $\text{Mn-S}(454.66\text{ cm}^{-1})$ . According to Horiguchi et al. (1983), Cu-S bond is at about  $300\text{ cm}^{-1}$  and Cu-Cl stretching vibration is in the range of  $200\text{-}260\text{ cm}^{-1}$ .

The suggested co-ordination nature of 5(4-dimethylaminobenzylidene) rhodanine with copper(II) and manganese(II) could be represented as shown below:



The nmr spectra of DMABR presented in figure 3 indicates that the thioketo structure in rhodanine is maintained in the ligand. No shift of the resonance frequency of the methyl protons nor of the protons of the ring  $\text{CH}_2$  group, was observed when this ligand forms complexes with metals otherwise, the ligand would change to the thiol form by a proton transfer. The duplet at 6.80 due to C(3)H/ C(5)H and quadruplet at 7.50 ppm due to C(2)H/ C(6)H(4H) as well as  $-\text{CH}=\text{C}$  arise from coupling of ring protons as well as methyl protons. The SH/ N-H protons at 2.50 ppm give a broad peak. The  $2\text{CH}_3$  protons occur at about 5 ppm.

Table 9 compares the proposed method with established periodate oxidation method for manganese(II). The periodate oxidation of manganese gave the range of 0.10-0.315 ppm in drinking water and industrial effluent samples (from NNPC, Arewa Textiles, Idea Flour Mills and Peugeot Automobile Limited

Table 8: Determination of Manganese ( II) with DMABR by Interference Method

Addition	Mn ( II) taken (g)	Mn ( II) found (g)
0.25g Fe as $\text{Fe}_2(\text{SO}_4)_3$ + 0.025 mg Ag	0.25	0.25
0.25g Fe as $\text{Fe}_2(\text{SO}_4)_3$ + 0.01mg Ag	0.10	0.10
0.25g Fe as $\text{Fe}_2(\text{SO}_4)_3$ + 0.10 mg Ag	0.10	0.11
0.25g Cu as $\text{CuSO}_4.5\text{H}_2\text{O}$	0	0

**Table 9: Application of DMABR to the determination of manganese in Drinking water and industrial waste water samples**

Sample	Mn (II) concentration $\mu\text{g per cm}^3$	
	Established periodate oxidation method Mn (II) found $\pm$ SD	DMABR proposed procedure Mn (II) found $\pm$ SD
Drinking water	0.010 $\pm$ 0.002	Trace
A	0.315 $\pm$ 0.003	Trace
B	0.288 $\pm$ 0.003	Trace
C	0.180 $\pm$ 0.001	Trace
D	0.220 $\pm$ 0.000	Trace

SD = standard Deviation

**Table 10: Infrared spectra of DMABR and its copper (II) and manganese(II) complexes ( $\text{cm}^{-1}$ )**

Compound	$\gamma(\text{N-H})$	$\gamma(\text{C=O})$	$\gamma(\text{C=C})$	$\gamma(\text{C-N})$	$\gamma(\text{C=S})$	$\gamma(\text{C-S})$	$\gamma(\text{M-S})$
DMABR	3357.77	1680.25	1461.49	1376.55	1211.50	1055.25	-
(DMABR) <sub>2</sub> Mn <sup>++</sup>	3400	1735.83	1457.19	1288.69	1161.38	1016.79	454.66
(DMABR) Cu <sup>+</sup>	3429.43	1695.31	1433.30	1285.26	1191.37	921.08	451.51
(DMABR) <sub>2</sub> Cu <sup>++</sup>	3465.44	1632.82	1454.81	1385.12	1264.75	1042.77	467.04

Kaduna) analysed. The proposed method however, failed with the effluent analysis and may not be recommended for the analysis of trace metals in effluents.

A comparative study of the colour reactions of metals with the azo derivatives of rhodanine and its analogues has shown these reagents to be of practical value especially for the determination of the concentration of noble metal ions. We have established the fact that this ligand can be used to determine the reactivity of non-ferrous metals in addition to noble metals with modification in the experimental parameters.

The apparent molar absorptivity increases with pH but the solubility of DMABR decreases with poor reproducibility. Furthermore, it is necessary to work within a small pH range due to sharp change in the absorbance of the blank solution with pH changes. Complex formation and redox processes taking place are also dependent on pH.

## CONCLUSION

Many methods are available for the determination of trace amounts of copper and manganese, but all of these suffer from pronounced drawbacks. These methods include peroxydisulfate and periodate; permanganate and 4,4'-tetramethyldiaminotriphenylmethane amongst others for manganese (Greenberg et al. 1985; Sandell, 1959). For copper some methods include bathocuproine, dithizone, hydrazine, bicyclohexanone, 1,5-Diphenylcarbohydrazide (Turkington and Tracy 1958; Sandell 1959; Virmani and Narula 1989).

Unlike in other rhodanines proposed for silver (Sandell 1959) which form chelates in colloidal solutions, DMABR formed homogenous solutions of these metals. It is easy to synthesise and purify. Its reagent blank has low and constant absorbance over a wide range of pH.

## REFERENCES

- Beamish, F. E., 1966. *The Analytical Chemistry of the Noble Metals*. Pergamon, Oxford.
- Beamish, F. E. and Van loon, J. C., 1972. *Recent Advances in the Analytical Chemistry of the Noble metals*. Pergamon, Oxford.
- Cave, G. B. C. and Hume, D. N., 1952. Colorimetric Determination of silver with p-Dimethylaminobenzylidenerhodanine. *Anal. Chem.*, 24: 1503 - 1505
- Feigl, F., 1929. Synthesis of Rhodanine derivatives. *Anal. Chem.* 74: 380-385
- Greenberg, E. A., Trussell, R. R. and Clesceri, S. L., 1985. *Standard Methods For Examination of Water and Wastewater*, 16th Ed.; American Public Health Association. Washington.
- Horiguchi, D., Saito, M., Imamura, T. and Kina, K., 1983. Infrared spectra of metal complexes. *Anal. Chim. Acta.* 151: 457-458
- Ojeka, E. O., 2003. Ph.D Thesis Ahmadu Bello University, Zaria, Nigeria
- Perrin, D.D., 1964. *Organic complexing Reagents*. Interscience, New York.
- Sandell, E. B., 1959. *Colorimetric Determination of Traces of Metals*. 3 ed, Interscience, New York.
- Savvin, S. B. and Gureva, R. F., 1987. 5-Azo Derivatives of Rhodanine and its Analogues in the Analytical Chemistry of the Noble metals, *Talanta* 34(1): 87-101.

Shiundu, P. M., Wentzell, P. D. and Wade, A. P., 1990. Spectrophotometric Determination of Palladium with Sulfochlorophenolazorhodanine. *Talanta* 37(3) : 329 - 336.

Turkington, R. W and Tracy, F. M., 1958. Spectrophotometric Determination of Ultramicro Amounts of copper with 1,5-Diphenylcarbohydrazide. *Anal. Chem.*, 30: 1699-1672.

Virmani, O. P and Narula, A. K., 1989. A Textbook of Applied Chemistry: Theory and Practice, Wiley Eastern Ltd; New Delhi .pp 1-50.

Welcher, F. J., 1947. Organic Analytical Reagents, Van Nostrand., New York.