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Synthesis and analytical application of Schiff's bases as chromogenic reagents for the determination of copper

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ABSTRACT

Schiff's bases o-Vanillidine-2-amino-benzothiazole (VBT), o-Vanillidine-2-amino-4-methylbenzothiazole (VMBT), o-Vanillidine-2-amino-6-chlorobenzothiazole (VCBT), and o-Vanillidine-2-amino-6-bromobenzothiazole (VBBT) were prepared and characterized by elemental analysis, m.p and spectral studies. The four newly synthesized Schiff's bases were used as chromogenic reagents in the spectrophotometric determination of Copper. At pH 5.89 these Schiff's bases react with Copper ions at room temperature to form 1:2 [Metal: Ligand] complexes. Beer's law is obeyed over the range $0.4\mu\text{g mL}^{-1}$ to $3.8\mu\text{g mL}^{-1}$ of copper. Metal ions like zinc, cadmium, cobalt, iron, lead and mercury do not interfere. The proposed method offers the advantages of sensitivity, rapidity, selectivity and simplicity without any prior separation and extraction. The method has been successfully applied for the determination of traces of copper in industrial effluent samples. © 2011 Trade Science Inc. - INDIA

KEYWORDS

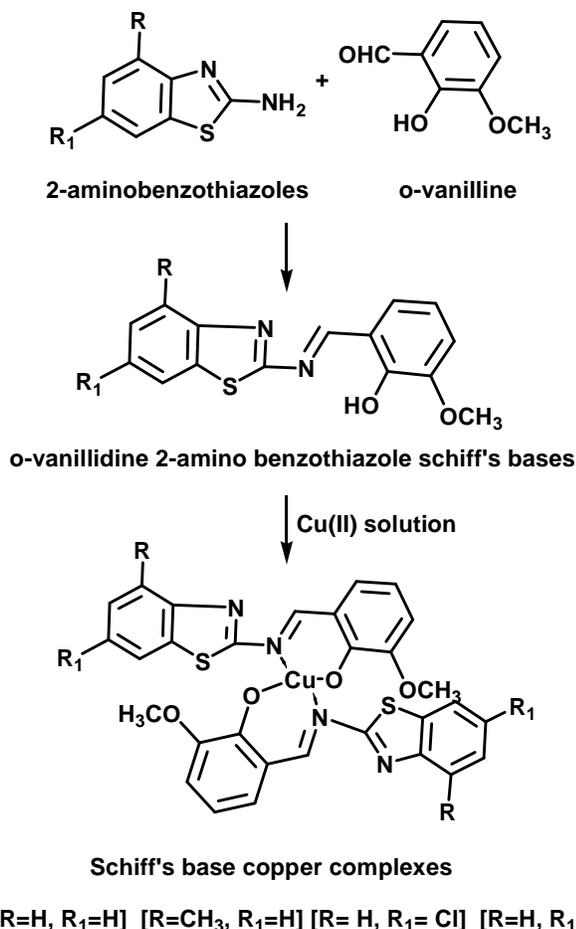
Analytical reagent;
2-aminobenzothiazole;
Copper determination;
Schiff's base;
Spectrophotometer;
o-vanillin.

INTRODUCTION

Copper is an essential micro-nutrient required in the growth of both plants and animals. In animals, it helps in the production of blood haemoglobin and in plants; copper plays a role in seed production, disease resistance and regulation of water. Both humans and animals need some amounts of copper in their diets, but very high concentrations of copper can be toxic causing adverse effects. The most common symptoms of copper toxicity are injury to red blood cells, injury to lungs, as well as damage to liver and pancreatic functions. Copper deficiency leads to defect in the pigmentation, bone formation, reproduction and in the growth^[1].

But, it is highly toxic above certain limits to organisms like certain algae, fungi and many bacteria or viruses^[2,3]. In addition, accumulation of copper in human liver is a characteristic of Wilson disease, which produces neurological and psychiatric defects^[4]. Copper in water exist as a divalent ion, Cu^{+2} . Levels over 0.05mg/L are not naturally encountered in ground water. The U.S. Environmental Protection Agency (EPA) has set a guidance level for the USA limiting copper in drinking water to 1.3 mg/L. The World Health Organization, an organization that many countries of the world rely upon for health guidance, has established a 2 mg/L copper guidance level. Because of increasing industrialization and intensification of production, there exists a high degree

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Scheme 1 : Chemical reaction for the synthesis of schiff's bases and their copper complexes

of risk and danger to natural systems and in this regard also to the groundwater. Due to the increasing awareness of the environmental impact of heavy metals determination of metal ions in environmental samples has been one of the most important topics. Copper in environmental samples are due to discharge of mine tailings, disposal of fly ashes, and disposal of municipal and industrial wastes^[5].

Most metal ions can be detected in environmental samples using analytical methods such as inductively coupled plasma atomic spectrometry flow injection atomic absorption etc^[6]. As compared with other techniques spectrophotometry is very simple and less expensive for determination of elements in a variety of samples.

In search of new sensitive and selective organic reagents, a thorough study of various benzothiazole azo dyes and benzothiazole Schiff's bases has been made^[7-16]. Schiff's bases have great concern of many analytic

chemist. Benzothiazole Schiff's bases, having multidentate coordination sites are attractive analytical reagents, since many of them form complexes with transition metal ions, they form stable 1:2 [metal:ligand] complexes^[17-19]. Synthesis characterization and antifungal activities of schiff's bases derived from benzothiazole, salicylaldehyde are common. But uses of schiff's bases as analytical reagents are less common^[20-25].

This work has been aimed to develop a sensitive and specific spectrophotometric method for the determination of copper, based on the formation of colored complexes, which are formed by the reaction of the copper ion with o-vanillidine-2-amino-benzothiazole and its derivatives. Four new schiff's bases, o-vanillidine-2-amino-benzothiazole (VBT), o-vanillidine-2-amino-4-methylbenzothiazole (VMBT), o-vanillidine-2-amino-6-chlorobenzothiazole (VCBT), and o-vanillidine-2-amino-6-bromobenzothiazole (VBBT) and their respective copper complexes were synthesized and characterized by elemental analysis, mp., mass, ¹H NMR, IR and U.V spectra. Optimum conditions for the determination of copper ions such as wave length; pH and ranges of applicability of the Beer's law are included. A further advantage of this method is that, an extraction procedure is not required and the analytical procedure is therefore very simple. This method is relatively free from interference of the metal ions like zinc, cadmium, cobalt, lead mercury and iron. The method has been successfully applied for the determination of copper in some industrial effluent samples.

EXPERIMENTAL

Apparatus

Infrared Spectra were recorded in KBr disk on a Perkin Elmer FT-IR. ¹H NMR spectra on a Bruker advanced 600, MHz spectrometer in CDCl₃ and thermo DFS double focusing magnetic sector mass spectrophotometer for mass spectral measurements. The pH is determined with a model 7007 Digisun electronic pH meter with combined glass calomel electrode. Graphite furnace Atomic Absorption Spectrometer is used for the analysis of cations in water samples. Shimadzu UV double beam spectrophotometer was used for spec-

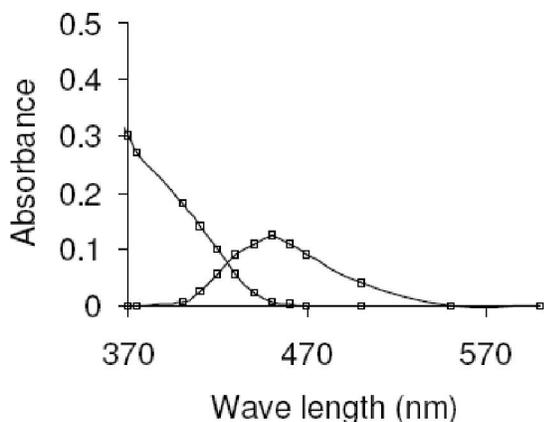


Figure 1 : Absorption spectra of VMBT and Cu-VMBT

trophotometric measurements.

Reagents

All the reagents were of analytical grade and were prepared with doubly distilled water. 0.05 % (w/v) Schiff's base solutions were prepared by dissolving appropriate amounts of VBT, VMBT, VCBT and VBBT in methanol. *o*-vanillin was purchased from Sigma Aldrich (Germany), 0.2 M acetic acid and 0.2 M sodium acetates were used for pH adjustments.

2-aminobenzothiazole, 2-amino-4-methylbenzothiazole, 2-amino-6-chlorobenzothiazole and 2-amino-6-bromobenzothiazoles were prepared starting from the corresponding α -Phenyl thioureas^[26]. The α -phenyl thiourea and α -phenyl 4-methylthioureas were cyclized with thionyl chloride, to yield the corresponding benzothiazoles^[27]. α -phenyl-6-chloro and -6-bromothioureas were cyclized with concentrated sulphuric acid and hydrobromic acid to yield 2-amino-6-chloro benzothiazole and 2-amino-6-bromobenzothiazole^[28]. The reagents were further purified by recrystallization and verified by melting points.

Synthesis of the reagents

(1) Synthesis of *o*-vanillidine-2-amino-4-methylbenzo-thiazole (VMBT)

2-amino-4-methylbenzothiazole (1.66 g, 10 mmol) was dissolved in absolute ethanol (15 mL) and then *o*-vanillin (1.10 g) was added to this solution along with a drop of piperidine. The mixture was refluxed for 3 hours and kept for eight hours. The yellowish orange solid obtained was filtered and washed several times with cold ethanol, dried and recrystallized from carbon tetrachloride to yield yellow crystalline solid.

TABLE 1 : Spectral data for the determination of copper ions using VBT, VMBT, VCBT and VBBT Schiff's bases as spectrophotometric reagents

Parameters	Cu-VBT	Cu-VMBT	Cu-VCBT	Cu-VBBT
Color	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow
λ_{\max}	450	450	450	450
Stability	30 minutes	30 minutes	30 minutes	30 minutes
Molar absorptivity, (λ_{\max}) L mol ⁻¹ cm ⁻¹	2.87×10 ³	2.94×10 ³	2.2×10 ³	1.53×10 ³
Beer lambert's range (μ g mL ⁻¹)	0.116-0.81	0.075-0.78	0.12-0.9	0.3-0.9
Limit of Detection	0.038	0.098	0.07	0.045
Sensitivity	2.2×10 ⁻³	2.14×10 ⁻³	2.9×10 ⁻³	4.12×10 ⁻³
Standard deviation	0.01352	0.03092	0.02506	0.02511
Limit of quantification	0.13	0.33	0.24	0.15
Regression (r ²)	0.9996	0.9855	0.9955	0.9995
Slope	1.0616	0.9373	1.0522	1.6713
Intercept	0.00047	0.00365	-0.0049	0.00035
Correlation coefficient	0.9998	0.9927	0.9978	0.9998

(2) Analysis of VMBT

C₁₆H₁₄N₂O₂S requires 64.41% C, 4.73% and 9.39% N; found 64.48% C, 4.7% H and 9.36% N; yellow crystalline solid, m.p 176C. IR (KBr) ν cm⁻¹: 3434 (O-H), 1596 (C=N), 1258 (C-O). ¹H NMR (CDCl₃, TMS, δ) ppm: 2.76 (s, -CH₃), 3.96 (s, -OCH₃), 6.8-7.4 (m, aromatic protons), 9.3 (s, -CH=N), 12.53 (s, -OH). The -OH signal at 12.53 ppm disappeared upon the addition of D₂O to the solution, indicating that it is an acidic proton. Mass spectrum M⁺ ion peak 298.

(3) Synthesis of VBT, VCBT and VBBT Schiff's bases

Pure *o*-vanillidine-2-amino-benzothiazole (VBT) prepared from 2-aminobenzothiazole (1.5 g) with *o*-vanillin (1.10g), *o*-vanillidine-2-amino-6-chlorobenzothiazole (VCBT) prepared from 2-amino-6-chlorobenzothiazole (1.84g) with *o*-vanillin (1.10g), and *o*-Vanillidine-2-amino-6-bromobenzothiazole (VBBT) prepared from 2-amino-6-bromobenzothiazole (2.29 g) with *o*-vanillin (1.10 g) respectively in absolute ethanol. The yellow solids of VBT, VCBT and VBBT were dried and recrystallized from carbon tetrachloride.

(4) Analysis of VBT

C₁₅H₁₂N₂O₂S requires 63.36% C, 4.25% H and

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TABLE 2 : Effect of interfering ions or substances. (0.59 $\mu\text{g mL}^{-1}$ Copper added)

Ions or substances	Tolerance limit ($\mu\text{g mL}^{-1}$)	Copper found ($\mu\text{g mL}^{-1}$) with VBT	Error ($\mu\text{g mL}^{-1}$)	Copper found ($\mu\text{g mL}^{-1}$) with VMBT	Error ($\mu\text{g mL}^{-1}$)	Copper found ($\mu\text{g mL}^{-1}$) with VCBT	Error ($\mu\text{g mL}^{-1}$)	Copper Found ($\mu\text{g mL}^{-1}$) with VBBT	Error ($\mu\text{g mL}^{-1}$)
Cl ⁻	70	0.059	0.0	0.059	0.0	0.059	0.0	0.059	0.0
SO ₄ ²⁻	103	0.050	-0.009	0.052	-0.007	0.049	-0.01	0.048	0.059
NO ₃ ⁻	90	0.059	0.0	0.059	0.0	0.059	0.0	0.059	0.0
F ⁻	38	0.063	0.004	0.645	0.586	0.064	0.005	0.067	0.008
PO ₄ ³⁻	122	0.068	0.009	0.07	0.011	0.073	0.014	0.072	0.013
DMG	1194	0.050	-0.009	0.049	-0.01	0.050	-0.009	0.052	-0.007
Thiourea	170	0.0	-0.059	0.0	-0.059	0.0	-0.059	0.0	-0.059
Hg ⁺²	1.25	0.052	-0.007	0.055	-0.004	0.054	-0.005	0.055	-0.004
Pb ⁺²	1.08	0.044	-0.015	0.042	-0.017	0.042	-0.017	0.044	-0.015
Fe ⁺²	2.02	0.052	-0.007	0.054	-0.005	0.054	-0.005	0.053	-0.006
Cd ⁺²	2.12	0.054	-0.005	0.056	-0.003	0.053	-0.006	0.054	-0.005
Zn ⁺²	2.02	0.049	-0.01	0.048	-0.011	0.048	-0.011	0.044	-0.015
Co ⁺²	1.95	0.056	-0.003	0.057	0.002	0.057	-0.002	0.055	-0.004
Ni ⁺²	1.09	0.045	-0.014	0.042	-0.017	0.044	-0.015	0.040	-0.019

9.85% N; found 63.36% C, 4.24% H and 9.84% N; yellow crystalline solid, m.p 164°C. IR (KBr) $\nu\text{ cm}^{-1}$: 3432 (O-H), 1593(C=N), 1255(C-O). ¹H NMR (CDCl₃, TMS, δ) ppm: 3.9 (s, -OCH₃), 6.9 to 8.0 (m, aromatic protons), 9.3 (s, -CH=N), 12.49(s, -OH). Mass spectrum M⁺ ion peak 284.

(5) Analysis of VCBT

C₁₅H₁₁ClN₂O₂S requires 56.52% C, 3.48% H and 8.79% N; found 56.50% C, 3.49% H and 8.79% N; yellow crystalline solid, m.p 224°C. IR (KBr) $\nu\text{ cm}^{-1}$: 3440(O-H), 1596(C=N), 1247 (C-O). ¹H NMR (CDCl₃, TMS, δ) ppm: 3.9 (s, -OCH₃), 6.9 to 8.0 (m, aromatic protons), 9.3 (s, -CH=N), 12.38 (s, -OH). Mass spectrum M⁺ ion peak 318.

(6) Analysis of VBBT

C₁₅H₁₁BrN₂O₂S requires 49.60% C, 3.05% H and 7.71% N; found 49.58% C, 3.02% H and 7.74% N; yellow crystalline solid, m.p 234°C. IR (KBr) $\nu\text{ cm}^{-1}$: 3432(O-H) 1592 (C=N), 1259 (C-O). ¹H NMR (CDCl₃, TMS, δ) ppm: 3.15(s, -OCH₃), 6.8 to 8.0 (m, aromatic protons), 9.3(s, -CH=N), 12.38 (s, -OH). Mass spectrum M⁺ ion peak 364.

(7) Synthesis of copper complexes of schiff's bases

Methanolic solution of each Schiff's base (10mmol) was mixed with Copper acetate (5 mmol) in methanol (10 mL) solution keeping metal ligand ratio 1:2 with

continuous stirring. The mixtures were then refluxed for 2 hrs, and then heated on a water bath till the volume of the solution was reduced to 10mL. The brown colored copper complex precipitated was filtered and washed with methanol and acetone. Recrystallized from chloroform and then dried in vacuum desiccator. Scheme 1 represents the synthesis of Schiff's bases and their copper complexes.

(8) Analysis of VBT copper complex

C₃₀H₂₂CuN₄O₄S₂ requires 57.18% C, 3.52% H, 10.08% Cu and 8.89% N; found 57.1% C, 3.5% H, 10.05% Cu and 8.89% N; brown solid, m.p above 260°C, ϵ_{max} : 2.87 $\times 10^3$ L mol⁻¹ cm⁻¹ (methanol) at 450 nm. IR (KBr) $\nu\text{ cm}^{-1}$: 1532 (C=N), 1339 (C-O). ¹H NMR (CDCl₃, TMS, δ) ppm: the signal at 12.49 for -OH is absent in Copper complex and other signals are same as that of the Schiff's base (VBT).

(9) Analysis of VCBT copper complex

C₃₀H₂₀ClCuN₄O₄S₂ requires 51.54% C, 2.88% H, 9.09% Cu and 8.01% N; found 51.52% C, 2.86% H, 9.0% Cu and 8.0% N; brown solid, m.p above 260°C, ϵ_{max} : 2.2 $\times 10^3$ L mol⁻¹ cm⁻¹ (methanol) at 450 nm. IR (KBr) $\nu\text{ cm}^{-1}$: 1573 (C=N), 1304 (C-O). ¹H NMR (CDCl₃, TMS, δ) ppm: The signal at 12.38 for -OH was absent in Copper complex and other signals were same as that of the Schiff's base.

TABLE 3 : Results obtained for the determination of copper in industrial effluents

Industrial effluents	AAS method copper found ($\mu\text{g mL}^{-1}$)	VBT as analytical reagent copper found ($\mu\text{g mL}^{-1}$)	% RSD	VMBT as analytical reagent copper found ($\mu\text{g mL}^{-1}$)	% RSD	VCBT as analytical reagent copper found ($\mu\text{g mL}^{-1}$)	% RSD	VBBT as analytical reagent copper found ($\mu\text{g mL}^{-1}$)	% RSD
Glowtronics	0.02	0.026	0.52	0.024	0.51	0.024	0.69	0.022	0.54
Marc batteries	0.02	0.024	0.53	0.022	0.53	0.025	0.69	0.0223	0.53
Allcoats	0.03	0.031	0.50	0.036	0.49	0.033	1.25	0.0321	0.49
Tritan valves	0.35	0.38	0.46	0.356	0.48	0.362	0.59	0.0359	0.49

^aAverage of the five determination

(10) Analysis of VBBT copper complex

$\text{C}_{30}\text{H}_{20}\text{BrCuN}_4\text{O}_4\text{S}_2$ requires 45.73% C, 2.56% H, 8.06% Cu and 22.91% N; found 45.71% C, 2.55% H, 8.01% Cu and 22.89% N; brown solid, m.p above 260°C , ϵ_{max} : $1.53 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$ (methanol) at 450 nm. IR (KBr) $\nu \text{ cm}^{-1}$: 1538 (C=N), 1304 (C-O). ^1H NMR (CDCl_3 , TMS, δ) ppm: The signal at 12.38 for –OH was absent in Copper complex and other signals were same as that of the Schiff's base.

(11) Preparation of metal standard solution

Copper (II) Standard solution of the concentration 10^{-5}M was prepared from analytical grade copper sulphate crystals.

METHODS

General procedure for the spectrophotometric determination of copper ions

Standard solutions of Schiff's bases of concentration 10^{-4}M were prepared in A.R methanol. Absorption measurements were made at 450nm by keeping reagent blank from a 25mL solution prepared by taking 1mL of the Schiff's bases of the above concentration, 1mL of $0.075 \mu\text{g mL}^{-1}$ to $0.9 \mu\text{g mL}^{-1}$ of copper solution, 2 mL of 5.89 buffer solution and made up to the mark with methanol.

RESULTS AND DISCUSSION

IR spectra

IR spectra of the complexes were compared with those of the free ligands. The C=N stretching frequencies in the free ligands were observed around 1590 cm^{-1} . The shift of this band towards a lower frequency in all copper complexes suggests that coordination has taken

place through the nitrogen of the azomethine group. The shift of the phenolic C-O stretch towards higher frequencies in all Copper complexes suggests Cu-O bond formation. Therefore it is believed that chelation of the metal ions in their Schiff's base complexes occurs through nitrogen and oxygen.

^1H NMR spectra

^1H NMR spectra of the schiff's bases exhibit a multiplet around 6.9 to 7.69 δ for the protons of the aromatic ring. A signal at 2.7 due to hydrogen of $-\text{CH}_3$ is observed only in VMBT Schiff's base. The azomethine hydrogen ($-\text{CH}=\text{N}-$) leads to singlet of integration intensity equivalent to one of the hydrogen around 9.3 δ . The signal around 3.9 δ is due to the hydrogen of the $-\text{OCH}_3$. The spectra show a singlet equivalent to a hydrogen around 12.5 δ corresponding to free –OH in the Schiff's bases^[29], disappearance of the signal at 12.5 δ upon the addition of D_2O to the solution indicating that it is an acidic proton. The higher δ value of the –OH group is attributed to the possible hydrogen bonding in the Schiff's bases. Absence of the signals around 12.5 δ were observed in all copper complexes indicating the involvement of the –OH group in chelation with copper. There is no other appreciable change in signals of the complexes as observed when compared with the Schiff's bases.

Absorption spectra

Under the experimental conditions, absorption spectra of schiff's bases VMBT, VBT, VCBT and VBBT and their corresponding copper complexes were scanned at pH 5.89. Absorption spectra of VMBT and VMBT copper complexes are shown in the figure 1. Absorbances were decreased from 370 nm to 500 nm in all the four Schiff's bases. Copper complexes of four Schiff's bases show maximum absorptions at 450 nm.

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Effect of pH

The effects of pH on the absorbance of four schiff's base copper complexes at 450 nm were studied under different pH conditions. Maximum absorbance for the complex was obtained at pH 5.89. Hence pH 5.89 was selected for the determination of copper. It is also found that the addition of 2mL of pH 5.89 buffer solution was sufficient for the pH adjustments.

Characteristics of the copper complexes

Light yellowish orange solutions, of VMBT, VBT, VCBT and VBBT solutions change to brownish yellow solutions immediately on the addition of copper ion at 5.89 pH in methanol solution with maximum absorption at 450 nm and is stable for at least half an hour.

A typical plot showed unequivocally, that the stable 1:2 [M-L] complexes are formed at pH 5.89 (λ_{max} 450 nm). Calibration graph obtained by the recommended procedure was linear over the range 0.4 $\mu\text{g mL}^{-1}$ to 3.8 $\mu\text{g mL}^{-1}$ in the final solution.

Analytical applications

To test the validity of the method, the experimental data have been statistically interpreted through the linear regression method. The high correlation coefficient (r) around 0.99 proves a linear dependence of the absorbance on metal ion concentration. Correlation coefficients (r), slopes and intercept for the copper complexes are listed in the TABLE 1.

Effect of interfering ions

An extensive study was made on the effect of interfering ions on the determination of Copper in 5.8×10^{-5} M of copper solution buffered at pH 5.89. The tolerance amounts of interfering ions are as listed in TABLE 2. The tolerance limit of interfering ions was taken as that value which caused an error of not more than $\pm 5\%$ in the absorbance. Most of the cations do not interfere with the determination of copper.

Copper determination from the industrial effluents

The effluent samples were collected from four different electroplating industries of Hebbal industrial area of Mysore city in India. These solutions were completely evaporated; they were digested with 10 mL of conc. HNO_3 , until all the brown fumes of nitric acid sub-

side^[30,31]. The residues obtained were extracted with dilute acetic acid and made up to 25 mL with redistilled water in a volumetric flask. The estimations of copper ions were carried out as described under general procedure using VBT, VMBT, VCBT and VBBT as analytical reagents and absorption measurements were made at 450 nm against the reagent blank and the results are presented in the TABLE 3. The results obtained by the proposed method agreed with the values obtained by Atomic absorption spectrophotometric method (AAS).

CONCLUSION

Four new Schiff's bases VMBT, VBT, VCBT and VBBT and their copper complexes were synthesized and characterized. These Schiff's bases react with copper (II) ions in aqueous methanol solution to form brownish yellow complexes at pH 5.89, with a stoichiometric ratio of 1:2 [Copper to ligand]. These Schiff's bases are sensitive spectrophotometric reagents for the determination of copper. The method is relatively free from interference with most of the metal ions like zinc, cadmium, cobalt, lead mercury and iron. Satisfactory results were obtained when the method was applied to the determination of copper in the industrial effluents.

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