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Spectrophotometric Determination of 2-Mercaptobenzothiazole in Cooling Water System

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The simple and convenient determination of 2-mercaptobenzothiazole (MBT) with copper(II) in cetyltrimethylammonium bromide (CTAB) media has been studied. The UV-visible spectrum of Cu(II)-MBT complex in CTAB media had a good sensitivity and reproducibility. The Cu(II)-MBT complex in CTAB solution is stable at pH 9.0 and could be quantitatively complexed if Cu were added to the sample solution more than 125 equivalent of MBT (to the mol). The optimum concentration of CTAB was 0.01 %. The calibration curve of Cu(II)-MBT complex with good linearity ($R^2 = 0.9995$) was obtained at the concentration range between 2.9×10^{-6} and 2.9×10^{-5} M in 0.01 % CTAB media. The detection limit was 9.7×10^{-7} M (0.162 mg L^{-1}). 2-Mercaptobenzothiazole in water cooling of tabriz thermal power plant could also be determined. Based on the experimental results, this proposed technique cold be applied to the simple and convenient determination of 2-mercaptobenzothiazole in real samples.

Key Words: 2-Mercaptobenzothiazole, Cetyltrimethylammonium bromide, UV-Visible spectrophotometry.

INTRODUCTION

2-Mercaptobenzothiazole (2-MBT) was originally used in the late 1940's as an accelerant in the vulcanizing 'process in rubber manufacture. Since that time, it has found widespread use as an antioxidant in the rubber industry, as an anticorrosion agent in metal processing and related applications[1], as a preservative in textile-manufacturing[2] and as a fungicide and bacteriostatic agent[1]. More recently, 2-MBT has been used in the synthesis of the antisapstain chemical TCMTB[3]. The main North American manufacturers of 2-MBT are BF Goodrich, Goodyear Tire, Uniroyal Chemical and Monsanto Chemical[4].

Technical 2-MBT is a yellowish to tan crystalline powder with a distinct, disagreeable odour. The solubility of 2-MBT in water under various conditions has been measured, as follows: 332 mg/L, pH unspecified[5]; 51 mg/L at pH 5, 118 mg/L at pH 7 and 900 mg/L at pH 9 [5]; 120 mg/L at 24 °C[6], 54 mg/L at 5 °C[6] and 100-120 mg/L at 20°C[7]. Solubility has also been measured in other solvents, including ethyl alcohol (20 g/L), acetone (100 g/L)[8], benzene and chloroform[9].

There are several methods of determination of MBT in water samples.The Southern Research Institute used high pressure liquid chromatography (HPLC) to monitor the purity of radiolabeled 2-MBT used in pharmacokinetic studies in mice and rats[10-12]. Gradient elution with 20 mM acetic acid in 40 and 85 % aqueous acetonitrile was used with radioactivity monitoring and UV absorbance at 254 nm. The more polar metabolites of 2-MBT in the urine were similarly analyzed except a combination of isocratic and gradient elution of 20 mM phosphoric acid in 20, 30, or 40 % aqueous acetonitrile was also used.

A Japanese group[13] was able to achieve detection limits of 1.0 μg/g for fish tissues and 10 ppb for water samples through extraction with methyl isobutylketone and analysis by HPLC.

Another Japanese group measured 2-MBT in water and sediment by extracting samples with methylene chloride and analyzing the extracts by gas-liquid chromatography using a flame photometric detector. Detection limits of 40 ppb for water and 2 ppb for sediment were achieved[14].

A USEPA sponsored study of the determination of 2-MBT in waste waters reported that recoveries of 79 % at the 5 ppb level were possible following extraction of samples with methylene chloride, extract partitioning on silica gel and analysis by HPLC with UV detection[15].

Finally, Environment Canada has recently developed a liquid chromatography method for determining 2-MBT levels in effluents and sediments[16]. The sample is extracted with methylene chloride, filtered and concentrated. The residue is dissolved in acetonitrile and the sample is then analyzed for 2-MBT by HPLC. Detection limits are 25 ppb.

In the present study, the convenient and simple determination of 2-mercaptobenzothiazole was spectrometrically performed with Cu complex in cationic CTAB media without an extraction procedure.

EXPERIMENTAL

A MiltonRoy 601 (UV-Visible) spectrometer was used to measure the absorbance of Cu(II)-2-mercaptobenzothiazole complex in CTAB media. To adjust the pHs and prepare the buffer solution, Metrohm-827 pH meter was used.

All chemicals, such as $CuSO_4$ (Riedel-de Haen) and 2-mercaptobenzothiazole (Accelerator), methanol (Merck), borax buffer (Merck) were analytical or guaranteed-grade reagents. Standard 2-MBT was made from 5.988 M stock solution. A 0.01 % (w/v) cetyltrimethylammonium bromide (CTAB) (Merck) solution was prepared by dissolving 0.01 g of CTAB in a 100 mL volumetric flask with stirring; Cu(II) solution was prepared by dissolving in water to give a 0.005 M solution. Borax buffer (pH 9.0) was prepared by mixing 0.025 M borax and 0.1 M HCl.

Calibration curve: Standard 2-MBT solutions were prepared in range 2.9×10^{-6} M to 2.9×10^{-5} M. Several aliquots of 2-MBT standard solutions were taken in 50 mL volumetric flasks and 2.0 mL of 0.01 % CTAB and 1.0 mL of 0.005 M

Cu(II) were added to each flask. Then it was filled to the mark with borax buffer solution (pH 9.0) and the calibration curve of 2-MBT was constructed by a UV-visible spectrophotometer. The regression equation was obtained with the method of least squares. Using this linear equation, we determined the correlation coefficient (R^2) and the detection limit. The detection limit is defined as the sample concentration giving a signal equal to the blank average signal plus three times the standard deviation of the blanks[17].

The calibration curve of Cu(II)-MBT complex with good linearity ($R^2 = 0.9995$) was obtained at the concentration range between 2.9×10^{-6} and 2.9×10^{-5} M in 0.01 % CTAB media. The detection limit was 9.7×10^{-7} M (0.162 mg L^{-1}).

Application to real sample: The water of cooling system was taken as a real sample. The standard addition method was used to determine 2-MBT in real sample. A calibration curve was constructed at optimum conditions according to calibration curve procedure in experimental section. The calibration curve of Cu(II)-MBT complex with good linearity ($R^2 = 0.996$) was obtained at the concentration range between 2.9×10^{-6} and 2.9×10^{-5} M in 0.01 % CTAB media.

RESULTS AND DISCUSSION

Absorption spectra of Cu(II)-MBT complex: After Cu(II), MBT and CTAB were taken in a 50 mL volumetric flask so that their concentrations were 5×10^{-3} M and 1.2×10^{-5} M and 0.01 %, respectively, the solution was diluted to the mark with borax buffer (pH 9.0). Then, the absorption spectrum of Cu(II)-MBT complex was obtained (Fig. 1). The analytical sensitivity and the reproducibility in this spectrum were good in CTAB media. The phenomenon seems to have been caused by the electrostatic and hydrophobic interactions between Cu(II)-MBT complex and surfactant[18].

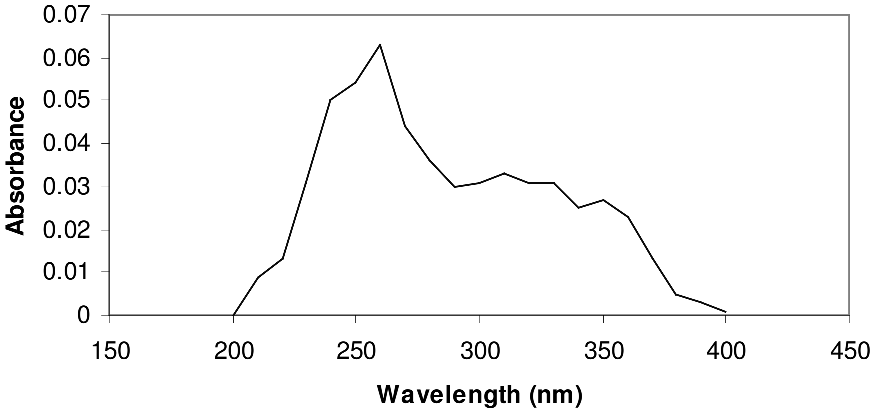

Fig. 1. UV-Visible spectra of Cu(II)-2-mercaptobenzothiazole (0.6×10^{-5} M) in 0.01 % CTAB media at pH 9.0

pH effect: The influence of pH on the absorbance of Cu(II)-MBT (0.6×10^{-5} M) complex in 0.01 % CTAB media was investigated (Fig. 2). Cu(II)-MBT complex showed the maximum absorption at pH 9.0. From this result, it is realized that Cu(II)-MBT complex was quantitatively formed and well dissolved in CTAB media at pH 9.0. It is assumed that the reaction to form this complex could have competed against hydroxide precipitation above pH 9.0 and at acidic pH, as the sulfur atom in the chelating site of MBT has more affinity power with proton at a higher concentration of protons.

Concentration of CTAB: When the concentration of CTAB surfactant exceeds its critical micelle concentration, the homogeneous micelle solution is formed at a point where Cu(II)-MBT complex can be well dissolved. Due to high viscosity, the concentrated CTAB media was difficult to handle, whereas those with low viscosity under diluted conditions could not form a micelle or make a homogeneous solution of complex as the polarity of aqueous solution was not lowered. With the concentration of CTAB varying from 0.005 to 0.03 % at pH 9.0, the absorbance of Cu(II)-MBT (0.6×10^{-5} M) complex was investigated and the results are shown in Fig. 3. The maximum absorbance was obtained when the concentration of CTAB was 0.01 %.

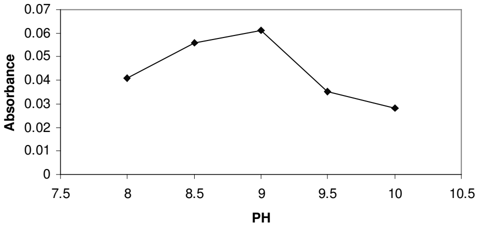

Fig. 2. Effect of pH on the absorbance of Cu(II) -2-mercaptobenzothiazole (0.6×10^{-5} M) in 0.01 % CTAB media

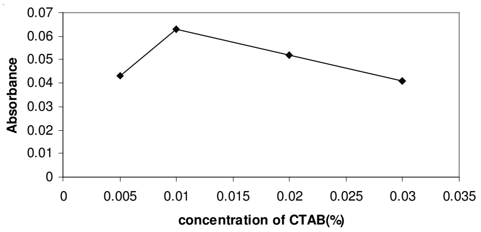

Fig. 3. Effect of the concentration of CTAB on the Cu-2-mercaptobenzothiazole (0.6×10^{-5} M) complex at pH 9

Concentration of copper: It is known that Cu(II) is stoichiometrically combines with MBT to form 1:2 complex[19]. For a metal complex to be formed quantitatively, however, one must add more chelating agent to the sample solution. Fig. 4 shows how the absorbance of Cu(II)-MBT complex changes with the concentration of Cu. It is found that when Cu was added to more than 125 equivalent of MBT (to the mol), the absorbance was high and constant.

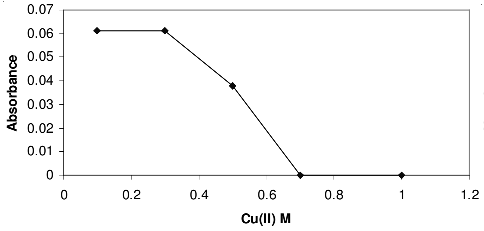

Fig. 4. Effect of the concentration of Cu on the Cu-2-mercaptobenzothiazole (0.6×10^{-5} M) complex at pH 9

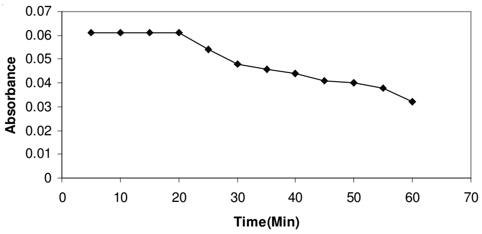

Fig. 5. Effect of time on the stability Cu-2-mercaptobenzothiazole (0.6×10^{-5} M) complex at pH 9

To investigate the stability of Cu(II)-MBT complex in CTAB media at pH 9.0, the absorbance was measured as the function of time (Fig. 5). The absorbance is constant from the beginning of measurement to 20 min and after 20 min, the absorbance was decreased.

Conclusion

By using of Cu-MBT complex in CTAB bromide media, MBT could be determined simply, conveniently. Results from the proposed method shows that the calibration curve of Cu(II)-MBT complex with good linearity ($R^2 = 0.9995$) was obtained at the concentration range between 2.9×10^{-6} and 2.9×10^{-5} M in 0.01 % CTAB media. The detection limit was 9.7×10^{-7} M (0.162 mg L^{-1}). The proposed technique could be applied to the determination of 2-mercaptobenzothiazole in real samples.

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