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1. Introduction

Metals can get into cooling system water from corrosion of the materials used to construct the equipment (cooling tower, heat exchanger, and piping), or from the use of conditioning chemicals containing metals. Copper is a common material of construction in cooling systems. Because of its excellent heat transfer efficiency, heat exchangers, and condensers are often made from copper. Copper piping is also commonly found in cooling systems. Moreover, Copper is a metal that has a wide range of applications due to its good properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. Copper is resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it is susceptible to corrosion. The use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected. The possibility of the copper corrosion prevention has attracted many researchers so until now numerous possible inhibitors have been investigated. Amongst them there are inorganic inhibitors [1], but in much greater numbers there are organic compounds and their derivatives such as azoles, amines, amino acids [2,3] and many others. It is noticed that presence of heteroatoms such as nitrogen, sulphur, phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. This is explained by the presence of vacant d orbitals in copper atom that form coordinative bonds with atoms able to donate electrons. Interaction with rings containing conjugated bonds, electrons, is also present. Based on these results more and more compounds containing numerous heteroatoms and functional groups are developed synthesized since it is noticed they are responsible for good properties regarding corrosion inhibition because they enable chemisorption.

2. Inorganic copper corrosion inhibitors

The use of inorganic inhibitors as an alternative to organic compounds is based on the possibility of degradation of organic compounds with time and temperature. Three different inorganic inhibitors are investigated: chromate CrO$_4^{2-}$, molybdate MoO$_4^{2-}$ and tetraborate...
B4O7^2- in concentration of 0.033M in solution containing 850g/l LiBr and has pH 6.9. Chromate is generally accepted as efficient corrosion inhibitor that can passivate metals by forming a monoatomic or polyatomic oxide film at the electrode surface, but it is also known that it can promote corrosion acting as a cathodic reactive. [1]

3. Organic copper corrosion inhibitors

3.1 Amines
Copper corrosion inhibition in de-aerated, aerated, and oxygenated HCl [4] and NaCl [5] solutions by N-phenyl-1,4-phenylenediamine (NPPD) is investigated. The NPPD adsorbs on the copper surface whereat Cu undergoes oxidation to Cu^+ and form insoluble complex Cu^+-NPPD on the surface. The efficiency increases with time and inhibitor concentration. The behavior of secondary amines as copper corrosion inhibitors in acid media, 0.5M hydrochloric acid and 0.5M sulphuric acid, is studied. [6] The homologous series of aromatic secondary amines with various substituents is investigated.

3.2 Amino acids
Amino acids form a class of non-toxic organic compounds that are completely soluble in aqueous media and produced with high purity at low cost. These properties would justify their use as corrosion inhibitors.
J.B.Matos [2] studied the effect of cysteine (Cys) on the anodic dissolution of copper in sulfuric acid, at room temperature using electrochemical methods. Cys (HSCH$_2$CHNH$_2$COOH) contains three dissociable protons, and in aqueous solutions ionization depends upon pH. According to the copper dissolution mechanism proposed for sulfate media in the absence of cys the main species present on the copper surface at low overpotentials is the intermediate Cu(I)ads.

3.3 Triphenylmethane derivatives
Two nitrogen containing organic compounds which are triphenylmethane ((C$_6$H$_5$)$_3$CH) derivatives, fuchsin basic FB (rosanine chloride) (C$_{20}$H$_{19}$N$_3$•HCl) and fuchsin acid sodium salt FA(C$_{20}$H$_{17}$N$_3$O$_9$S$_3$Na$_2$), are tested as new copper corrosion inhibitors. [7,8] These compounds are thought to be good candidates due to the presence of chloride ion in FB and the polar or charged nature of the more complex FA surfactant molecule.

3.4 Thiole group compounds
The inhibition of copper corrosion in 1.5% NaCl solution is studied at 25, 35 and 45°C using three inhibitors: thiosemicarbazide (inh 1), phenyl isothiocyanate (inh 2) and their condensation product 1-phenyl-2,5-dithiohydrazodicarbonamide (inh 3). [9] It is concluded that all the three compounds are efficient corrosion inhibitors whereat the inhibition efficiencies follow the sequence: inh3>inh1>inh2. The enhanced effectiveness of the inh 3 can be correlated with the structure and size of molecule, inh 3 has four nitrogen atoms, two sulphur atoms and delocalised $\delta$ electron density acting as active centres and the largest surface area. Mechanism of inhibition is proposed as adsorption only in case of inh 2; inh 1 at lower concentrations inhibits corrosion through adsorption while at higher concentrations Cu(I) complex is formed that gradually oxidises into Cu(II) complex.
3.5 Phosphates as copper corrosion inhibitors
Copper corrosion by-product release to potable water is a complex function of pipe age, water quality, stagnation time and phosphate inhibitor type. Phosphates can be phosphoric acid, combination of orthophosphoric acid and Zink orthophosphate, polyphosphate or blend of orthophosphoric acid and polyphosphate. It is noticed [10] that dosing of 1mg/l orthophosphate led to reductions in copper release ranging from 43-90% when compared to the same condition without inhibitor regardless of pipe age, water quality or stagnation period. Orthophosphate and hexametaphosphate have beneficial effects on copper release, but orthophosphate leads to greater reductions in copper release when compared to hexametaphosphate.

3.6 Azoles
Azoles are organic compounds containing nitrogen atoms with free electron pairs that are potential sites for bonding with copper and that enable inhibiting action. Also, there is a possibility of introduction of other heteroatoms and groups in molecules of these compounds so there is a wide range of derivatives that exhibit good inhibition characteristics.
El-Sayed M. Sherif [11-14] investigated the influence of 2-amino-5-ethylthio-1,3,4-thiadiazole (AETD) on copper corrosion in aerated HCl solution [11] as well as the influence of 2-amino-5-ethylthio-1,3,4-thiadiazole (AETD) [12], 2-amino-5-ethyl-1,3,4-thiadiazole (AETDA) [13] and 5- (phenyl)-4H-1,2,4-triazole-3-thiole (PTAT) [14] in NaCl solution. It is expected that these compounds show high inhibition efficiency since they are heterocyclic compounds containing more donor atoms, besides that they are non-toxic and cheap.

3.6.1 Benzotriazoles
In recent years, investigators have shown that a system of tarnish or corrosion control for copper, brass and bronze can be built around the organic compound, 1, 2, 3, benzotriazole. Benzotriazole forms a strongly bonded chemisorbed two-dimensional barrier film less than 50 angstroms thick. This insoluble film, which may be a monomolecular layer, protects copper and its alloys in aqueous media, various atmospheres, lubricants, and hydraulic fluids. Benzotriazole also forms insoluble precipitates with copper ions in solution (that is, it chelates these ion), thereby preventing the corrosion of aluminum and steel in other parts of a water system.

3.6.1.1 Inhibition mechanism of benzotriazole
Benzotriazole (BTA), whose structure is shown in Figure 1, has been used for a long time as an important corrosion inhibitor for Cu and its.

![Fig. 1. Chemical structure of benzotriazol (BTA)](image-url)
The protective barrier layer, which consists of a complex between Cu and BTA molecules can be formed by the immersion of the Cu surface in a solution of BTA or by vapor transport from impregnated paper or electrochemically. This barrier is insoluble in water and many organic solvents and grows with time to a certain thickness depending on the BTA concentration and the pH of the solution. [15]

### 3.6.2 Benzothiazole (BT)

Benzothiazole enter the environment from a variety of sources such as the leaching of rubber products, but particularly by routes associated with the manufacture and use of mercaptobenzothiazole (MBT) and MBT-based rubber additives, fine particles of automobile tires, and antifreeze. All benzothiazole used are solids at room temperature with the exception of benzothiazole (BT), which is liquid.

Benzothiazoles form a part of xenobiotic, heterocyclic, molecular structures comprising a benzene ring fused with a thiazole ring. Their general structure is shown in Figure 2.

![Fig. 2. General structure of benzothiazoles](image)

Table 1 shows that BT possesses a high solubility (4300 mg/L), this is probably due to its high polarity and the fact that it is a liquid at room temperature. BT is also considered as volatile with a vapour pressure 0.0143 mm Hg (25°C).

<table>
<thead>
<tr>
<th>R =</th>
<th>formula</th>
<th>Chemical names</th>
<th>Abreviation</th>
<th>Molecular weight (g/mol)</th>
<th>Water Solubility (mg/L) 25°C</th>
<th>Octanl/water (log10 Kow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO3H</td>
<td>C₆H₅N O₂S₂</td>
<td>Benzothiazol Sulfonic acid</td>
<td>BTSA</td>
<td>215</td>
<td>2.35</td>
<td>-0.99</td>
</tr>
<tr>
<td>OH</td>
<td>C₆H₅NOS</td>
<td>Hydroxybenzothiazole</td>
<td>OHBT</td>
<td>151</td>
<td>2354</td>
<td>2.00</td>
</tr>
<tr>
<td>NH₂</td>
<td>C₆H₅N₂S</td>
<td>Aminobenzothiazole</td>
<td>ABT</td>
<td>150</td>
<td>310.3</td>
<td>2.86</td>
</tr>
<tr>
<td>SH</td>
<td>C₆H₅N₂S</td>
<td>Mercaptothiazole</td>
<td>MBT</td>
<td>167</td>
<td>120</td>
<td>2.17</td>
</tr>
<tr>
<td>H</td>
<td>C₆H₅NS</td>
<td>Benzothiazole</td>
<td>BT</td>
<td>135</td>
<td>4300</td>
<td>3.22</td>
</tr>
<tr>
<td>CH₃</td>
<td>C₆H₅NS</td>
<td>Methyliothiazole</td>
<td>MeBT</td>
<td>149</td>
<td>366.3</td>
<td>3.04</td>
</tr>
<tr>
<td>SCH₃</td>
<td>C₆H₅N₂S</td>
<td>Methyliothiazole</td>
<td>MTBT</td>
<td>181</td>
<td>125</td>
<td>3.12</td>
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<tr>
<td>SCH₂SCN</td>
<td>C₆H₅N₂S</td>
<td>Thioacetylthiothiazole</td>
<td>TCMTB</td>
<td>238</td>
<td>125</td>
<td>4.66</td>
</tr>
<tr>
<td>S-S-BT</td>
<td>C₆H₅N₂S</td>
<td>Dithiobisbenzothiazole</td>
<td>MBTS</td>
<td>332</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Structural formulas, chemical names, abbreviations and some properties of studied benzothiazoles
All benzothiazole used are solids at room temperature with the exception of benzothiazole (BT), which is liquid. Table 1 shows that BT possesses a high solubility (4300 mg/L), this is probably due to its high polarity and the fact that it is a liquid at room temperature. BT is also considered as volatile with a vapour pressure 0.0143 mm Hg (25°C).

4. MBT; most effective benzothiazoles for copper alloys inhibition

MBT is the most important member of the benzothiazole group of heterocyclic aromatic compounds. In fact, its discovery in ca. 1920 led to the major use in the production of rubber additive chemicals but predominately, as vulcanization accelerator in rubber industry. MBT is also applied for various purposes, such as bio-corrosion inhibitor in industrial cooling and in the galvanic industry, and coating agent of metallic surfaces. It is also used as an external chemotherapeutic and antifungal drug in medical application. [16] Both MBT and OHBT can exist in two tautomeric forms (Figure 3).

![Figure 3. Two tautomeric forms of MBT and OHBT](image)

OHBT has a good solubility of 2354 mg/L in water. MBT, MTBT and TCMTB are moderately soluble with respective solubilities of 120 mg/L, 125 mg/L and 125 mg/L. These values of solubility and their respective vapour pressure (0.000464, 0.00026, and 3.12 $10^{-7}$ mm Hg) show that these benzothiazoles are be considered as not volatile from aqueous solutions (or volatile with difficulty). [16]
4.1 Physical and chemical properties
The structural formula of 2-MBT is shown below:

(CAS Registry No: 149-30-4)

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; 51 mg/L at pH 5, 118 mg/L at pH 7, and 900 mg/L at pH 9; 120 mg/L at 24°C, 54 mg/L at 5°C, and 100-120 mg/L at 20°C. Solubility has also been measured in other solvents, including ethyl alcohol (20 g/L), acetone (100 g/L), benzene, and chloroform. 2-MBT has a specific gravity of 1.42-1.5 at 25°C, a vapour pressure of 24 mm Hg at 20°C, and a melting point of approximately 180°C. Decomposition occurs above 260°C. [17].

4.2 Toxicity
Some authors have shown that MBT is mainly responsible for toxic effects in MBT production activated sludge. MBT has been also shown to induce tumors, to be toxic (at 600 mmol L$^{-1}$) to aquatic organisms, and may also hamper waste treatment. MBT and MBTS have been reported as one of the most frequent allergens causing shoe dermatitis. Hinderer et al. proved that MBTS induced genetic damage to mammalian cells. MBT interfered with the nitrification processes and exhibited biocidal effects.[16]

4.3 Other applications
MBT is found widely in a variety of rubber articles in the modern environment both at home and at work. Examples of such articles are rubber tires and tubes for your car, rubber boots and shoes, rubber soles, gloves, garden hoses, elastic and rubberized clothing such as brassieres, girdles, support stockings, swimwear, swim caps and elastic bands as well as in rubber pillows, sponge makeup applicators, toys, balloons, baby bottle nippers, latex condoms, examination and surgical gloves, dental dams and rubber handles on tools such as tennis racquets and golf club handles. [18]

4.4 An effective corrosion inhibitor for copper alloys
MBT is a particularly effective corrosion inhibitor for copper and copper alloy. In circulating cooling water system, low concentrations (such as 2 mg/L) of 2-Mercaptobenzothiazole (MBT) will be able to make copper and copper alloy corrosion rate dropped very low. In direct currency cooling water system that the cooling equipment made of copper and copper alloy, because of the high usage and cost, MBT is rarely used as copper corrosion inhibitor.

Measurements of polarization curves show that the MBT at low concentrations is an anodic type inhibitor. MBT has many advantages: 1) effective corrosion inhibition control for
copper and copper alloy; 2) low dosage. Shortcoming is very sensitive to chlorine and chloramines, it is easily destroyed by oxidation.

4.5 Analytical methods of detection
The Southern Research Institute used high pressure liquid chromatography (HPLC) to monitor the purity of radio labeled 2-MBT used in pharmacokinetic studies in mice and rats. 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. The detection limits of the method were not indicated in the available summaries.

A Japanese group[19] was able to achieve detection limits of 1.0 ug/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.[20]

Finally, Environment Canada has recently developed a liquid chromatography method for determining 2-MBT levels in effluents and sediments. 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.[17]

The simple and convenient determination of 2-mercaptobenzothiazole (MBT) was spectrometrically performed with Cu complex in cationic CTAB media without an extraction procedure. This method has been studied in Tabriz Thermal Power Plant and we are reviewed details of this method in this part.

4.5.1 Spectrophotometric determination of 2-MBT in cooling water

4.5.1.1 Experimental
Instrumentation: 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.

Reagents and solutions: All chemicals, such as CuSO4 (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 ~ 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. [18].

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

### 4.5.1.2 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 $5 \times 10^{-3}$ M and $1.2 \times 10^{-5}$ 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 (Figure 4). 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 hydro-phobic interactions between Cu(II)-MBT complex and surfactant [21].

![Absorbance vs Wavelength](https://www.intechopen.com)

**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 (Figure 5). Cu(II)-MBT complex showed the maximum absorption at pH 9.0. From this result, we realize that Cu(II)-MBT complex was quantitatively formed and well dissolved in CTAB media at pH 9.0. We assume 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 hard 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 Figure 6. The maximum absorbance was obtained when the concentration of CTAB was 0.01%.

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

Fig. 6. Effect of the concentration of CTAB on the Cu-2-mercaptobenzothiazole (0.6×10^{-5} M) complex at PH 9.
Concentration of Cu: It is known that Cu(II) is stochiometrically combines with MBT to form 1 : 2 complex [22]. For a metal complex to be formed quantitatively, however, one must add more chelating agent to the sample solution. Figure 7 shows how the absorbance of Cu(II)-MBT complex changes with the concentration of Cu. We found that when Cu was added to more than 125 equivalent of MBT (to the mol), the absorbance was high and constant.

![Fig. 7. Effect of the concentration of Cu on the Cu-2-mercaptobenzothiazole (0.6×10⁻⁵ M) complex at pH 9.](image)

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 (Figure 8). The absorbance is constant from the beginning of measurement to 20 min and after 20 min, the absorbance was decreased.

![Fig. 8. Effect of time on the stability Cu-2-mercaptobenzothiazole (0.6×10⁻⁵ M) complex at pH 9.](image)
4.5.1.3 Conclusions

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 (R²=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 MBT in real samples.

5. References


Thermal power plants are one of the most important process industries for engineering professionals. Over the past few decades, the power sector has been facing a number of critical issues. However, the most fundamental challenge is meeting the growing power demand in sustainable and efficient ways. Practicing power plant engineers not only look after operation and maintenance of the plant, but also look after a range of activities, including research and development, starting from power generation, to environmental assessment of power plants. The book Thermal Power Plants covers features, operational issues, advantages, and limitations of power plants, as well as benefits of renewable power generation. It also introduces thermal performance analysis, fuel combustion issues, performance monitoring and modelling, plants health monitoring, including component fault diagnosis and prognosis, functional analysis, economics of plant operation and maintenance, and environmental aspects. This book addresses several issues related to both coal fired and gas turbine power plants. The book is suitable for both undergraduate and research for higher degree students, and of course, for practicing power plant engineers.

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