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Determination of Sulphide in Arabian Seawater using UV- Visible Spectrophotometer

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ABSTRACT

High concentration of sulphide in cooling water being utilized for condenser tubes cause stress cracking corrosion, microbially induced corrosion and pitting corrosion phenomenon. Fouling of condenser tube by sulphide is highly undesirable because it reduces the heat transfer capabilities, increases backpressure in the condenser thus affecting the turbine performance. In this work, a method was established for determination of sulphide ion in Arabian sea water using Ultraviolet-Visible Spectroscopy technique. The experiments conducted show precise values for sample (seawater) as well as for absorbencies of standard solutions. Maximum absorbance of methylene blue complex has determined after scanning the equipment from 400 to 700 nm and was found around at 600 nm. Two different sampling points (Machli Chowk & a Conventional Power Plant) were selected to get the average concentration of sulphide in Arabian Sea. The average sulphide concentration in Machli Chowk sample was found out to be 0.287±0.031 ppm and average sulphide concentration near a conventional power plant was found out to be 0.31±0.029 ppm. Average sulphide concentration was also compared with the Sindh Environmental Quality Standards (SEQS) to validate the results which recommends less than 1 ppm for sulphide concentration in seawater.

Keywords: *Concentration of Sulphide, Methylene Blue Method, Arabian Sea,Corrosion & its Types,Sources of Sulphide, UV-Visible Spectrophotometer*

1. Introduction

Most of the metals react directly with sulphur to form metal sulphide e.g. CdS, Ag_2S, ZnS, FeS_2 etc. This sulphide contributes no color to the salts. In gaseous form sulphur appears as H_2S which is poisonous and corrosive in nature and has smell like rotten eggs. On the basis of chemical bonding, sulphide is classified into three different classes as follows:

a. Inorganic Sulphide: These are the negatively charged ionic compounds e.g. H_2S.
b. Organic Sulphide: These compounds contain a Sulphur atom which is covalently bonded with two organic groups e.g. diethyl sulphide.
c. Phosphorus Sulphide: These are the compounds in which Sulphur atom is attached with phosphorus by a bond that has both covalent and ionic characteristics e.g. P_4S_{10}

From above three categories present in sea water, inorganic sulphide (H_2S, S^{2-}) is very harmful for the condenser tubes as well as for heat exchangers. [1] Dissolved sulphide is very dangerous because it causes corrosion on different metals. In sea water average concentration of sulphate is about 3 ppm [2]. Under anaerobic conditions, sulphate is reduced to sulphide in the presence of sulphate reducing bacteria which ultimately increases the concentration of sulphide in sea water that leads towards the corrosion of metals. Also sulphide prevents the formation of protective corrosion film on metal surface.

1.1 Sulphate Reduction

Sulphate reduction occurs in three steps as follows [3]:

$$\text{Sulphate } (SO_4^{2-}) \xrightarrow{\text{Sat}} \text{Adenosine 5-Phosphosulphate (APS)}$$

$$\text{Adenosine 5-Phosphosulphate (APS)} \xrightarrow{\text{Apr, 2e}} \text{Sulphite } (SO_3^{2-})$$

$$\text{Sulphite } (SO_3^{2-}) \xrightarrow{\text{DSr, 6e-}} \text{Sulphide } (HS^{2-})$$

First sulphate is converted to APS by an enzyme Sat (ATP sulphurylase). APS is then reduced to sulphite by using an enzyme Apr (Adenylyl Sulphate reductase) and acquiring the input of two electrons. Sulphite is further reduced to sulphide by another enzyme DSr (dissimilatory sulphite reductase) by acquiring input of six electrons.

1.2 Sources of Sulphide in Sea Water

Following are the different sources of sulphide present in sea water [4].

a. Volcanic activity: Volcanic gases release from sea contains SO_2, HCl, H_2S and HF.
b. Sedimentary rocks: It is present as sulphate in sedimentary rocks as well as in pyrite shale as FeS_2.
c. Sewage: It is present in the form of inorganic sulphate or combined in organic matter which further decomposes into H_2S. Concentration of Sulphur compound in sewage is 6-10 ppm).
d. Input from rivers: Sea is connected to different rivers which contains a high amount of sulphide in it.
e. Dimethylsulphide [$(CH_3)_2S$ or DMS]: Dimethylsulphide is produced by the decomposition of dimethylsulfoniopropionate (present in unicellular algae called phytoplankton). DMS is a major biogenic gas emitted in sea.

1.3 Forms of Sulphide in Seawater

Sulphide present in sea water in different types of forms as follows [5].

i. Sulphate (SO_4^{2-})
ii. Sulphide (H_2S)
iii. SO_2
iv. Dimethylsulphide
v. FeS_2

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2. Corrosion and its Types

Corrosion is the deterioration and loss of a material and its critical properties due to chemical, electrochemical and other reactions of the exposed material surface with the surrounding environment.

Integrity of steam generator tube depends mainly on condenser tube condition in a power plant. Sulphide is one of the troublesome contaminant which is very aggressive towards the admiralty brass (69% Cu, 30% Zn, 1% Sn & As) tubes of the condenser. It induce different types of corrosion in metals such as:

2.1 Stress Corrosion Cracking (SCC)

SCC is a localized form of corrosion due to the loss of metal damage. It is manifested as cracks where stresses are dominant in material [6].

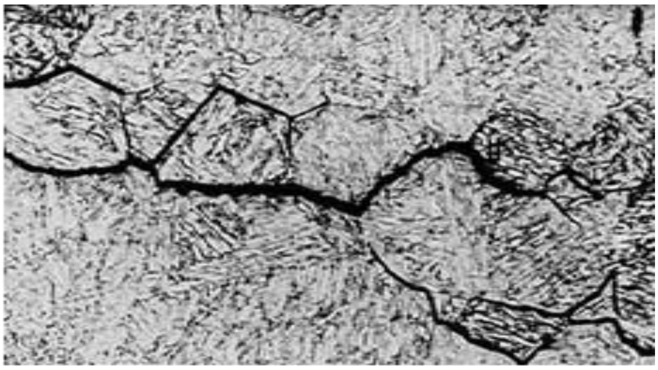

Fig. 1: Stress cracking corrosion of stainless steel [6]

2.2 Microbially-Induced Corrosion (MIC)

It is also known as biogenic caused by sulphate reducing bacteria (SRB). Free floating bacteria present in sea water can stick to the surface within minutes of encounter and start producing sliming EPS (extracellular polymeric substance). After that highly organized growth of biofilm will start producing. After forming a biofilm on the surface, clumps of cells are released to colonize on a new surface. Attachment, growth and detachment process of SRB on metal surface is also known as biofilm life cycle. If MIC occurs, it will increase galvanic, crevice and pitting corrosion rates in the material. So, this type of corrosion is very harmful to the materials[6].

Fig. 2: Microbiologically induced corrosion on a metal surface [6]

2.3 Pitting Corrosion

When oxidation of sulphide occurs, it will form thiosulphate ($S_2O_3^{2-}$) to induce pitting corrosion[6].

$$2S^{2-} + {}^{3}/_{2}\, O_2 \rightarrow S_2O_3^{2-}$$

Fig. 3: Pitting corrosion on steel [6]

3. Materials & Methods

Following reagents are used to carry out analysis of sulphide determination.

i. $Na_2S.9H_2O$ (0.0042 M).
ii. Deionized Water.
iii. $FeCl_3.6H_2O$ (0.111 M).
iv. N-N, dimethyl-p-phenylenediamine sulphate (0.00854 M).
v. M HCl Solution. (From 12 M conc. HCl, 50% V/V)

The sulphide concentration in sea water can be determined by UV-Visible Spectrophotometer. The task can be accomplished by mixing measured quantity of ferric chloride, N-N, dimethyl-p-phenylenediamine sulphate and $Na_2S.9H_2O$. This sample solution is also known as methylene blue complex.

Amino acid stock solution was prepared by adding 0.2 g of N-N, dimethyl-p-phenylenediamine sulphate salt in to 6 M HCl Solution (50 ml) in 100 ml flask and fill up to the mark with de-ionized water.

Ferric chloride solution was prepared by adding 3g of $FeCl_3.6H_2O$ salt into 6 M HCl Solution (50 ml) in 100 ml flask and fill up to the mark with de-ionized water.

3 ml of amino acid stock solution, 1.5 ml of ferric chloride solution and a calculated amount of $Na_2S.9H_2O$ was added into the 25 ml flask to make methylene blue complex of required concentration. Each flask was diluted up to the mark with DI water.

3.1 Wavelength Determination for Maximum Absorbance of Sulphide

Maximum absorbance of S^{2-} is determined after scanning the equipment from 400 to 700 nm. Maximum value is obtained at 600 nm. Therefore, all the experiments were conducted on this wavelength.

Initially 12 and 18 ppm methylene blue complex were prepared as above and wavelength varied for visible spectrum (400 to 700 nm). The observed absorbencies for 12 and 18 ppm solution as shown in Table 1. Graphically, it can be seen in Figure 4.

Table 1: Data Recorded for Visible Spectrum Scan

λ(nm)	Absorbance	
	12ppm	18ppm
400	-0.05	0.036
430	-0.01	0.089
460	0.023	0.124
490	0.04	0.144
520	0.062	0.171
550	0.102	0.226
580	0.124	0.225
600	0.135	0.263
610	0.102	0.216
640	0	0.058
670	-0.01	0.035
690	-0.01	0.024
700	-0.02	0.019

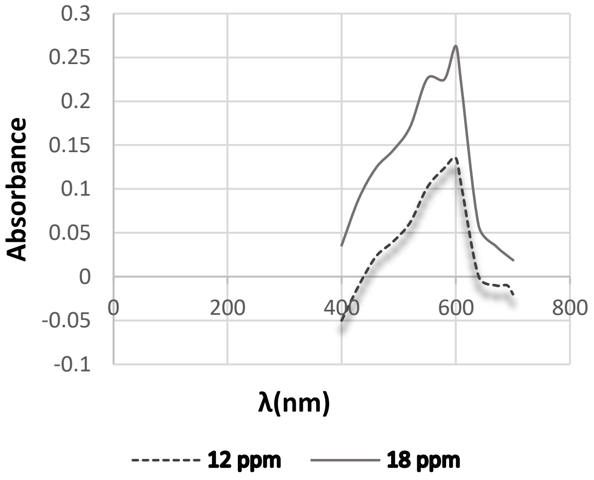

Fig. 4: Maximum absorption of 12ppm & 18ppm complex solution

3.2 *Reduction in the Absorbance with Time due to loss of Sulphide in Solution Prepared*

When fresh solution of sulphide was prepared it should be analyzed immediately due to the instability of sulphide solution which makes it unreliable to use as a standard solution for calibration. When the same solution used over a period of time during a calibration run, the absorbance of solution decreases due to loss of sulphide as shown in Figure 5 for 12 and 18 ppm solution.

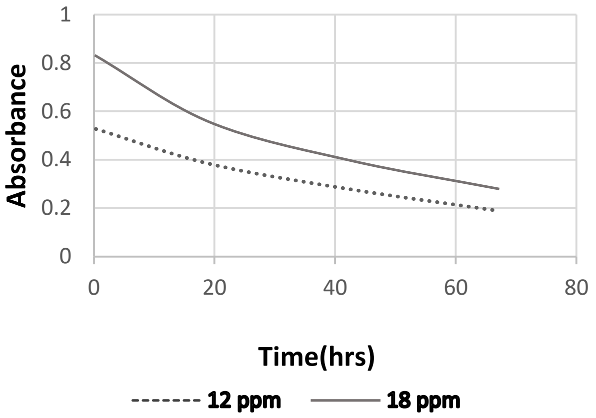

Fig. 5: Effect of Time vs Absorbance

3.3 *Determination of Sulphide Concentration (0 to 18ppm)*

First, 50 ppm of $Na_2S.9H_2O$ solution was prepared which is diluted to 2, 4, 6, 8, 12, 18 ppm range and their absorbance are recorded as shown in Table 2.

Table 2: Average absorbance of standard solution of sodium sulphide

Conc. (ppm)	Trial # 1	Trial # 2	Trial # 3	Average Absorbance	Standard Deviation (±S.D)
0	0	0	0	0	0
2	0.105	0.105	0.106	0.105	0.00057
4	0.176	0.173	0.175	0.175	0.0013
6	0.291	0.29	0.288	0.290	0.0013
8	0.361	0.361	0.362	0.361	0.00057
12	0.527	0.526	0.524	0.526	0.0013
18	0.829	0.827	0.83	0.829	0.0013

Results are plotted to check the linearity of the curve as shown in Fig. 6.

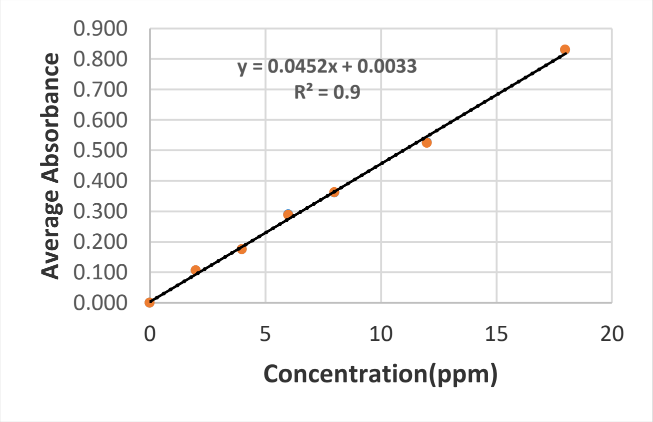

Fig. 6: Concentration vs Average Absorbance

The absorbance of sea water samples collected from Machli Chowk and their concentration are shown in the following Table 3.

Table 3: Absorbance of sea water sample collected from Machli Chowk

Sample	Trial # 1	Trial # 2	Average Absorbance (y)	Concentration (ppm) =(y-0.0033)/0.0452	Standard Deviation (±SD)
1	0.015	0.013	0.014	0.24	0.03
2	0.012	0.011	0.0115	0.18	
3	0.012	0.010	0.011	0.17	

Thus the average concentration of sulphide in Machli Chowk sample comes out to be 0.1967±0.03ppm.

The absorbance of sea water samples collected near a Conventional Power Plant and their concentration are shown in the following Table 4.

Table 4: Absorbance of sea water sample collected near a Conventional Power Plant

Sample	Trial # 1	Trial # 2	Average Absorbance (y)	Concentration (ppm) =(y-0.0033)/0.0452	Standard Deviation (±SD)
1	0.017	0.016	0.015	0.26	0.029
2	0.010	0.014	0.012	0.19	
3	0.012	0.014	0.013	0.21	

Thus the average concentration of sulphide collected near a conventional power plant in sample comes out to be 0.22±0.029 ppm.

3.4 *Removal of Statistical Error*

The concentration of sulphide result very low in sea sample (0.2 ppm). Therefore, a standard curve from 0 to 2 ppm should be drawn.

3.5 *Determination of Sulphide Concentration (0 to 2ppm)*

First, 5 ppm of $Na_2S.9H_2O$ solution was prepared which is diluted to 0.1, 0.2, 0.4, 0.6, 0.8, 1 and 2 ppm range and their absorbance are recorded as shown in Table 5.

Table 5: Average absorbance of standard solution of sodium sulphide

Conc. (ppm)	Trial # 1	Trial # 2	Average Absorbance	Standard Deviation (±S.D)
0	0	0	0	0
0.1	0.003	0.004	0.0035	0.0005
0.2	0.008	0.009	0.0085	0.0005
0.4	0.017	0.018	0.0175	0.0005
0.6	0.025	0.027	0.026	0.001
0.8	0.034	0.037	0.0355	0.0015
1	0.044	0.046	0.045	0.001
2	0.096	0.094	0.095	0.001

The results are plotted to check the linearity of the curve as shown in Fig. 7.

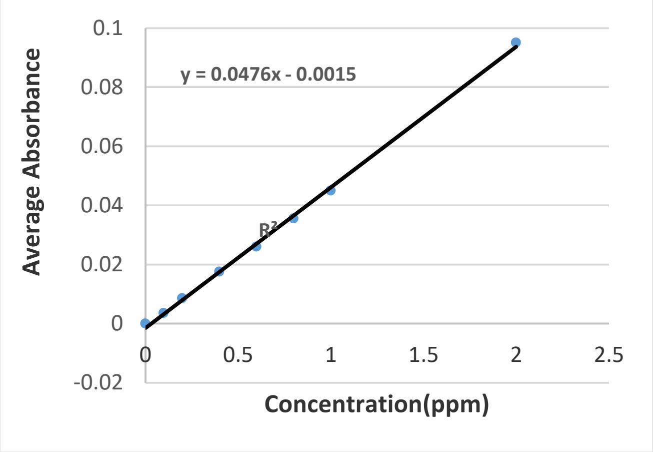

Fig. 7: Concentration vs Average Absorbance

The absorbance of sea water samples collected from Machli Chowk and their concentration are shown in the following Table 6.

Table 6: Absorbance of sea water sample collected from Machli Chowk

Sample	Trial # 1	Trial # 2	Average Absorbance (y)	Concentration (ppm) =(y-0.0033)/0.0452	Standard Deviation (±SD)
1	0.015	0.013	0.014	0.33	0.031
2	0.012	0.011	0.0115	0.27	
3	0.012	0.010	0.011	0.26	

Thus the average concentration of sulphide in Machli Chowk sample comes out to be 0.287±0.031 ppm.

The absorbance of sea water samples collected near a conventional power plant and their concentration are shown in the following Table 7.

Table 7: Absorbance of sea water sample collected near a Conventional Power Plant

Sample	Trial # 1	Trial # 2	Average Absorbance (y)	Concentration (ppm) =(y-0.0033)/0.0452	Standard Deviation (±SD)
1	0.017	0.016	0.015	0.35	0.029
2	0.010	0.014	0.012	0.28	
3	0.012	0.014	0.013	0.30	

Thus the average concentration of sulphide collected near a conventional power plant in sample comes out to be 0.31±0.029 ppm.

4. Comparision with SEQS Value

Sulphide release to the environment according to Sindh Environmental Quality Standards (SEQS) for municipal and liquid effluents is 1ppm.

Average sulphide concentration is determined experimentally around 0.3 ppm which is quite reasonable and within limits of SEQS.

5. Conclusions

The following conclusions are obtained from the experiments:

a. Dissolved sulphide and bi-sulphide present in sea water produced stress corrosion cracking, microbial induced cracking and pitting corrosion as well.

b. Methylene blue method for determination of sulphide can be effectively used for concentration >= 0.1ppm.

c. Variation of concentration of sulphide in the sample was due to the loss of sulphide with time and in the atmosphere during filtration and handling. So, fresh sea water samples should be taken each time before the analysis.

d. Sulphide concentration in sea water ranges between 0.3 to 0.4 ppm. So, standard curve of low concentration should be drawn for lower concentrations to remove statistical errors and get accurate results.

e. Pre-treatment of sea water for sulphide determination should be avoided as loss of sulphide could occur during that time period which will not give the accurate results.

f. Sulphide in sea water with concentration greater than 0.01 ppm was susceptible to the accelerated damages on the equipment specially made by copper-nickel alloy. But sulphide will attack on condenser tubes vigorously after exposure to 0.2 ppm sulfides concentration in sea water [7].

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