



## 5-CHLOROMETHYL-8-HYDROXYQUINOLINE; A NOVEL COLOURIMETRIC SENSOR TO DETECT Fe(II) IONS

**K.A.P. Gaminda<sup>1</sup>, D.T Abeyasinghe<sup>1\*</sup>, C.D Jayasinghe<sup>2</sup>, M. D. P. de Costa<sup>3</sup>, R. Senthilnithy<sup>3</sup>**

<sup>1</sup>Department of Chemistry, The Open University of Sri Lanka, Sri Lanka

<sup>2</sup>Department of Zoology, The Open University of Sri Lanka, Sri Lanka

<sup>3</sup>Department of Chemistry, University of Colombo, Sri Lanka

### INTRODUCTION

Iron is the most abundant transition metal in the human body. It exists in different oxidation states, such as the ferrous form (Fe(II)) and the ferric form (Fe(III)). Iron is categorized as an essential metal ion. It plays a significant role in various biological processes such as oxygen transport and storage using globin-heme proteins (hemoglobin, myoglobin, and neuroglobin), DNA synthesis and repair, cell growth and replication through iron-dependent proteins, electron transfer, enzymatic reactions, and energy production. (Cipurković et al., 2021; Zheng et al., 2020) However, Fe(II) is toxic to the cells at higher concentrations due to its reactivity with hydrogen peroxide. This reactivity forms the hydroxyl radical, the hazardous form of reactive oxygen species available in the cells. These free radicals cause significant harm to the cells due to their high reactivity (Sun et al., 2020) The elevated Fe(II) concentration in the human body affects the increase in the aging process and degenerative diseases such as cancer, neurological disorders (Alzheimer's and Parkinson's), and hepatitis. (Cipurković et al., 2021; Zheng et al., 2020) Therefore, efforts have been made to develop novel sensors capable of detecting Fe(II) ion contaminations in the environment. Among these novel sensors, colorimetric sensors attracted the research interest of the scientists due to their simplicity, rapid detection, sensitivity, versatility, and real-time monitoring of the metal ions compared to the other conventional methods. Various Fe(II) detecting colorimetric methods were developed using 1, 10 -phenanthroline and reported. In this study, the 8-Hydroxyquinoline (8-HQ) derivative was synthesized and utilized to develop a colorimetric sensor to detect Fe(II) in the aqueous solutions.

8-HQ is a potent metal chelator utilized in various fields such as the development of medicinal drugs (antiviral drugs), fluorescence markers, transition metal chelators, organic light-emitting diodes (OLED), etc. (Rohini et al., 2020). The 8-HQ is a bicyclic complex containing a pyridine ring fused with phenol (Rohini et al., 2020). Due to the presence of the hydroxyl group at the 8th position, 8-HQ is susceptible to electrophilic aromatic substitution, diazonium coupling, and molecular rearrangements. (Saadeh et al., 2020) The proximity of the hydroxyl group and the pyridine nitrogen makes 8-HQ a monoprotic bidentate chelating agent. Hence, 8-HQ forms different types of complexes (four- and six-covalent) with metal ions. (Saadeh et al., 2020) Scientists identified that excited-state intramolecular proton transfer (ESIPT) from 8-HQ moiety to the quinoline N atom is responsible for the weak fluorescence of the 8-hydroxyquinoline. (Rohini et al., 2020; Zhang et al., 2005). However, the complex formation of the 8-HQ with the metal ions blocks the ESIPT, restores the fluorescence, and causes fluorescence enhancement (Rohini et al., 2020; Zhang et al., 2005). This feature was utilized to develop fluorescence chemosensors for metal detection via ESIPT suppression. The introduction of functional groups at the C-2 and C-7 positions in 8-HQ is extensively studied to improve the metal binding (Rohini et al., 2020; Zhang et al., 2005). The photoinduced electron transfer (PET) process leads to fluorescence quenching which was recently recognized due to the attachment of methylene amine at the C-2 or C-7 position of the 8-HQ. Upon the metal-binding, PET suppression was utilized to develop fluorescent sensors to detect transition metal ions in fluorescence enhancement mode (Rohini et al., 2020; Zhang et al., 2005).



However, the 5- chloromethyl-8-hydroxyquinoline (5Cl8HQ), an 8-HQ derivative, exhibited remarkable colorimetric change in Fe(II) ions. This study mainly focuses on developing 8-HQ derivatives as a novel colorimetric chemosensor to detect environmental contamination of Fe(II) ions.

## METHODOLOGY

### Synthesis of 5-Chloromethyl-8-hydroxyquinoline hydrochloride

A weight of 7.37 g (0.0508 mol) of 8-hydroxyquinoline (8-HQ) was mixed with 8.0 ml of concentrated hydrochloric acid (Conc. HCl), and 8 mL of 37% formaldehyde (HCOH) in a round bottom flask immersed in a water bath and the temperature of the mixture was maintained at 50°C. Afterward, the mixture was treated with hydrogen chloride gas and stirred for 6 hours. The resulting yellow color solid was allowed to settle down at room temperature overnight. Then the solvent was removed by filtering to give 5-chloromethyl-8-hydroxyquinoline (5Cl8HQ) as a yellow solid (Burckhalter & Leib, 1961; Lashgari et al., 2016). Finally, the yellow solid obtained was washed three times with acetone. The yellow solid was dried using a vacuum oven. Then the solid was further characterized using FT-IR.

## RESULTS AND DISCUSSION

### Analysis based on the FT-IR spectroscopy

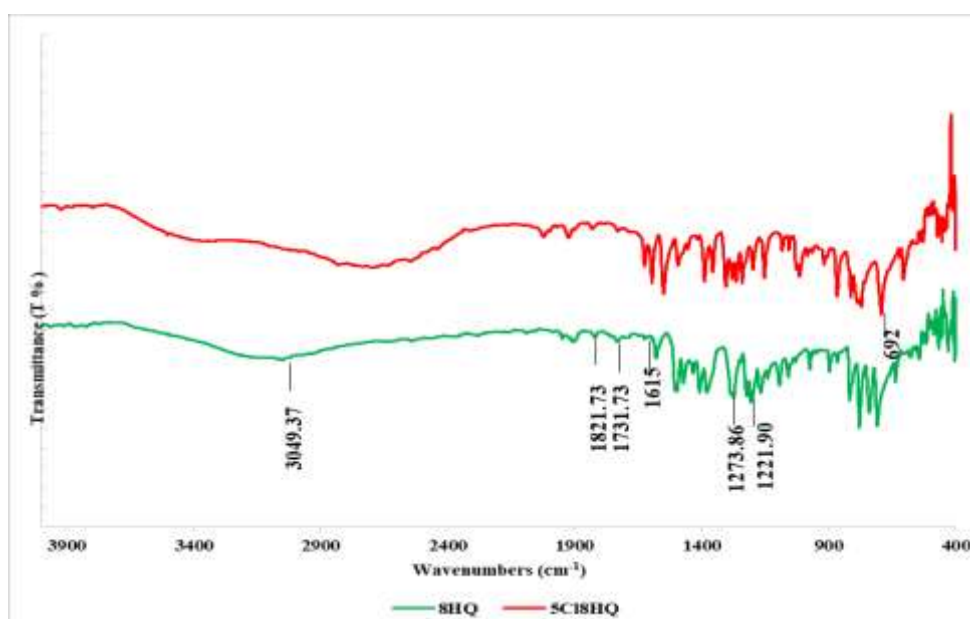


Figure 1: FT-IR spectra of the 8-HQ and 5CL8HQ.

The Fourier-Transform Infrared spectroscopy of the 8-Hydroxyquinoline and its derivatives were measured in the wavenumber region 4000  $\text{cm}^{-1}$  – 400  $\text{cm}^{-1}$ . Figure 1 compares the FTIR spectra of 8-Hydroxyquinoline and its derivatives. The FT-IR spectra are approximately similar, and new peaks obtained for the derivatives indicate the formation of new bonds, proving that new substances have been formed.

Table 1: Summary of the FT-IR peaks of the 8-Hydroxyquinoline and its derivatives.

Chemical bond	C=C	C-H	Aromatic	C-O	O-H	C-N	C-Cl	C=N
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			C-H					
Wave number (cm <sup>-1</sup> )	1615	1821	3049	1221	3342	1273/ 1251	692	1731

The peak at 692 cm<sup>-1</sup> in the FT-IR spectra of 5Cl8HQ, which is characteristic of the C-Cl stretching, indicates the successful synthesis of the 5Cl8HQ using 8- Hydroxyquinoline. This distinctive vibrational peak suggests the formation of the 5Cl8HQ (Lashgari et al., 2016).

The melting point (mp) of the 5Cl8HQ was estimated as 280 °C, which was lower than the previously reported value of 283 °C. (Kolobielski, 1966). This lower melting point of the 5Cl8HQ indicates that the synthesized derivative might be contaminated with impurities. Further purification of the derivative is required to improve the sensitivity and selectivity of 5Cl8HQ.

### COLORIMETRIC DETECTION OF THE FE(II) BY THE 5CL8HQ

The compound 5Cl8HQ exhibited a remarkable property used to investigate the possibility of detecting Fe(II) contaminations. In the presence of Fe(II) ion, the 5Cl8HQ solution exhibited a colorimetric change from yellow to green color and a gradual increase of the absorption at 245 nm. The color intensity tends to increase with increasing metal concentration, and none of the metals, such as Al<sup>3+</sup>, Zn<sup>2+</sup>, and Pb<sup>2+</sup> were capable of changing the sensor's color from yellow to green.

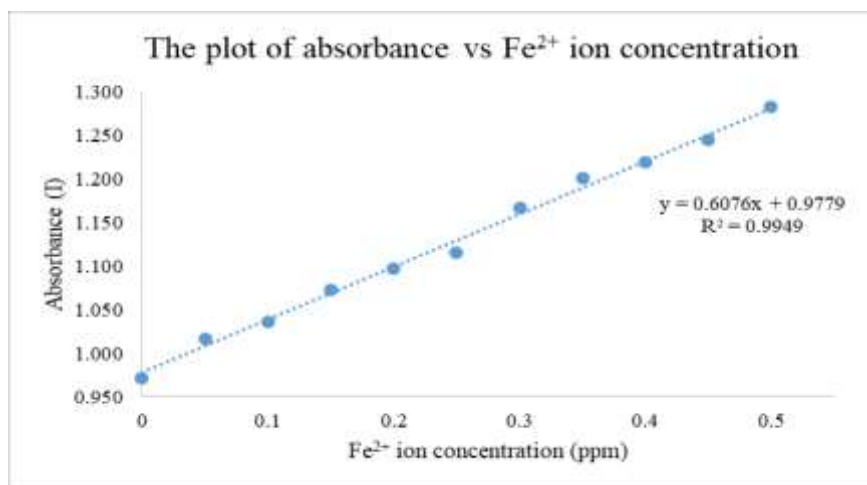


Figure 2: Plot of the UV-vis absorbance at 245 nm as a function of Fe(II) ion concentration.

### CONCLUSIONS/RECOMMENDATIONS

The 5Cl8HQ sensor exhibits an excellent linear relationship from 0.00 ppm to 0.50 ppm with a LOD of 0.04 ± 0.10 ppm. Compared to the other 8-HQ derivatives, 5Cl8HQ is entirely dissolved in water, and this facilitates the detection of the Fe<sup>2+</sup> ions in aqueous solutions without additional purifications or concentration of the samples. However, further purifications and structural characterizations are required to understand the mechanism involved in detecting the Fe(II) ions by 5Cl8HQ.

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