International Journal of Current Advanced Research
ISSN: O: 2319-6475, ISSN: P: 2319-6505, Impact Factor: 6.614
Available Online at www.journalijcar.org
Volume 10; Issue 05 (C); May 2021; Page No.24417-24421
DOI: http://dx.doi.org/10.24327/ijcar.2021.24421.4844

Research Article

SYNTHESIS, CHARACTERIZATION AND ANALYTICAL APPLICATIONS OF 2-CHLOROQUINOLINE-3-CARBALDEHYDE THIOSEMICARBAZONE

Omprakash Tukaram Sangule

Department of Chemistry, Smt. Kasturbai Walchand College, Sangli-416416

ARTICLE INFO

Article History:
Received 10th February, 2021
Received in revised form 2nd March, 2021
Accepted 26th April, 2021
Published online 28th May, 2021

Key words:

2-Chloroquinoline-3-carbaldehyde, Thiosemicarbazone, Fe (III), Ni (II), Beer's law, antimicrobial activity.

ABSTRACT

Quest of researchers for innovative analytical reagent is unending. Among the analytical reagents available in the market has one or more limitations. 2-Chloroquinoline-3-carbaldehyde Thiosemicarbazone (2-Chloro-QAT) is found to a better an analytical reagent for transition metals. It is synthesized from 2-Chloroquinolone-3- Carbaldehyde and Thiosemicarbazide. Further, it was characterized by elemental analysis, antimicrobial activity UV Visiblespectra, IR spectra and XRD analysis. As it forms colored complexes with Fe (III) and Ni (II), it was used for their analysis from samples. Practically it was used to determine Fe (III) content from water and Ni (II) content from Chocolate. Amount of both the ions were calculated by both calculation and graphical method. From Beer's plot, Fe (III) content in water sample and Ni (II) content from Cadbury chocolate were determined. Results obtained by both the methods were pretty good.

INTRODUCTION

Thiosemicarbazone (TSC) remained in limelight since 20^{th}century. It is a ligand, which donates electron through Nitrogen and Sulphur atom to metal and forms metal ligand complexes. Metal complexes of TSC has two aspects namely Pharmaceutical and analytical one. In Pharmaceutical aspects TSC shows antibiological [1-3] and anticancer activity [4-6].Literature survey reveals that its drug action increases in presence of metal. In mid of 20^{th} century, it was used against Tuberculosis and leprosy [7-8], then for smallpox [9], antitumor [10]and antifungal [11-12]. In all above cases activity of TSC increases in presence of Metals [13]. Another aspect of TSC isan analytical reagent. Analytical reagent available in market has one or more limitations. On the other hand,TSC forms colored complexes with transition metals and can be innovative analytical reagent. Uniqueness of TSC is that they are selective and sensitive for many transition metals. They are sensitive and selective enough to detect µg quantity of metals from samples. People are working on synthesis and characterization of transition metal complexes [14-17].In the present work, we focused on synthesis, characterizationandanalytical applications of 2-Chloroquinoline-3-carbaldehyde Thiosemicarbazone(2-Chloro-QAT) with Fe (III) and Ni (II) from available samples.

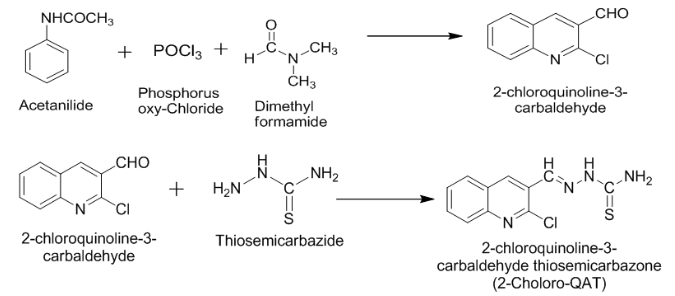
Corresponding author:* **Omprakash Tukaram Sangule
Department of Chemistry, Smt. Kasturbai Walchand College, Sangli-416416

Experimental

Synthesis of 2-Chloro-QAT, its characterization and analytical applications are included in experimentation. For the same analytical grade chemicals were purchased from Merck ltd. They were used as received. Buffer required for experiment was prepared by standard procedure [18]. Required UV-Visible spectrophotometric analysis was carried on ELICO spectrophotometer models 171. IR spectra was taken on Perkin Elmer 221 IR spectrophotometer and X-RD was taken on PW-3710 differactometer.

Synthesis of 2-Chloroquinoline-3- Carbaldehyde Thiosemicarbazone

2-Chloro-QAT was synthesized by refluxing equimolecular quantities of 2-Chloroquinoline-3-Carbaldehyde and thiosemicarbazide in minimum quantities of alcohol[19]. 2-Chloro-QAT formed was filtered, dried and recrystallized. It was white colored solid having melting point 225^0C and molecular weight by formula was found to be 264.73. It was used for further experimentation purpose. 2-Chloroquinoline-3-Carbaldehyde required for synthesis of 2-Chloro-QAT was prepared was prepared by standard method using Vilsmeier's reaction[20]. It was reaction between acetanilide and phosphorous oxy chloride in dimethyl formamideas an solvent. Reaction of synthesis can be shown as below. [21-23]



Characterization of 2-Chloroquinoline-3- Carbaldehyde Thiosemicarbazone

2-Chloroquinoline-3- Carbaldehyde Thiosemicarbazone after synthesis was characterized by various parameters like elemental analysis, antimicrobial activity, IR spectra and X-RD method. Elemental analysis was carried by standard method [24]. For antimicrobial activity, gram negative bacterial strain *Klebsiella pneumoniae* was used. It was conducted by disc diffusion method and antibacterial activity was measured in term of zone of inhibition. [25]. UV-Visible spectra of 2-Chloro-QAT was taken at different wavelength in UV-Visible range. IR spectra of 2-Chloro-QAT was taken in the range of 4000-700 cm^{-1}. The characteristic bands observed is shown in fig.1. Expected functional groups are shown in Table2. To determine type of structure of 2-Chloro-QAT, X-RD spectra of 2-Chloro-QAT was taken on diffractometer type PW 3710 based with tube anode Cu and wavelength 1.54. It is shown in in fig.2

Determination of Iron content from water sample

Fe (III) content from the Panchganga river water was determined by using 2-Chloro-QAT.Water sample may contains organic and inorganic matter including Fe (III) to be determined. Organic matter in it was destroyed using following procedure. Collected water sample was filtered, heated to evaporate major quantity of water. To it few drops of per chloric acid was added and heating continued. Again after evaporation of water in major quantity, few drops of Concentrated $HNO_3$was added and further heated to evaporation in such a way that maximum water is lost from it. After cooling, it was diluted to 100 cm^3 using double distilled water. This diluted water sample was used for further experimental purpose.

Absorption spectra of Fe (III) - 2-Chloro-QAT

To measure λ_{max} for Fe (III) - 2-Chloro-QAT solution was prepared containing standard Fe (III) and reagent (2-Chloro-QAT). Under optimum pH, absorbance was measured at various wavelength using reagent blank and noted. A graph of absorbance vs. wavelength was plotted and $\lambda_{max}$was calculated and found to be 370nm. This wavelength was used for further experimentation.

Beer's law forFe (III) - 2-Chloro-QAT

To determine iron from sample, various solutions were prepared containing different amount of standard iron, but same amount of reagent. Equal volume of buffer of optimum pH 5 was added in each solution. Simultaneously, sample solution was prepared by the same procedure except standard iron solution, sample solution was taken. Finally each solution was diluted to 10 cm^3using Dimethyl Formamide (DMF) and absorbance was measured at 370 nm using reagent blank. A graph of absorbance vs. Fe (III) in ppm was plotted and from that concentration of unknown was calculated. It is shown in fig.3. To confirm results of graphical method, calculation method was also used. Amount of Fe (III) from sample was calculated by $C_1/C_2= D_1/D_2$, where C_1, C_2 is concentration of known and unknown respectively. D_1 and D_2 means Optical density of known and unknown respectively.

Determination of Ni (II) content from Chocolate

2-Chloro-QAT was tested as an analytical reagent for Ni (II).For the same we used Cadbury chocolate available in market. As it contains both organic and inorganic matter like Ni (II). So as to get rid of organic content, it was refluxed in silica crucible. It was kept in furnace for heating purpose at 800^0C for 24 hrs. It was cooled and few drops of concentrated HNO_3 was added and again refluxed at same temperature for 12 hours. Further, it was cooled, a few drops of perchloric acid was added and refluxed for same temperature for 12 hrs. After cooling, it was diluted to 100cm^3 by double distilled water. Ni (II)ions get dissolved in water. This diluted sample solution was used for determination Ni (II) content from Cadbury chocolate using 2-Chloro-QAT as an analytical reagent in Beer's-Lambert's law.

Absorption spectra of Ni (II) - 2-Chloro-QAT

To measure λ_{max} for Ni (II) - 2-Chloro-QAT same procedure was followed as explained in Absorption spectra of Fe (III) - 2-Chloro-QAT.Instead of Standard Fe (III), standard Ni (II) was used and from the graph $\lambda_{max}$for Ni (II) - 2-Chloro-QAT was found to be 370 nm

Beer's law forNi (II) - 2-Chloro-QAT

To determine concentration of Ni (II) from sample using Beer's law same procedure was followed as explained in Beer's law for Fe (III) - 2-Chloro-QAT. Instead of standard Fe (III) here standard Ni (II) was used and diluted sample solution was used to determine Ni (II) from cadbury chocolate. Graph of Absorbance vs. Ni (II) in ppm was plotted. Nature of graph is straight line passing through origin. Absorbance of sample was extrapolated from the plot and Ni (II) content from sample was determined. It is shown in fig.4

RESULTS AND DISCUSSION

2-Chloro-QAT was synthesized and characterized by UV-Visible spectra, elemental analysis, antimicrobial activity, IR spectra and X-RD method. Further it was tested for analytical reagent using iron and nickel sample.

Characterization of 2-Chloro-QAT

UV-Visible Spectra

2-Chloro-QAT shows λ_{max} at 260 nm indicating that 2-Chloro-QAT shows absorption maxima in UV range

Elemental Analysis

Elemental analysis of 2-Chloro-QAT is shown in Table 1indicating that it contains carbon, nitrogen, hydrogen, chlorine and sulphur. Their expected and actual percentage is nearly same, indicating confirmation of elemental analysis.

Table 1

Sr. No.	Chemical Analysis	Percentage found	Expected percentage
1	Carbon	49.80	49.90
2	Hydrogen	03.20	03.40
3	Nitrogen	21.80	21.17
4	Sulphur	12.00	12.10
5	Chloride	13.20	13.42

Antimicrobial Activity

As 2-Chloro-QAT shows positive antimicrobial activity against gram negative bacterial strain *Klebsiella pneumoniae* indicating 2-Chloro-QAT has bactericidal action. As it shows large zone of inhibition (1.2 cm) indicating that it has strong antimicrobial activity. Probable reason is that the cell wall of gram negative bacteria contains thinner peptidoglycan layer than gram positive bacteria.[18]

IR Spectra

IR Spectra of 2-Chloro-QAT is shown in fig.1.From spectral peaks, it reveals that $\equiv C-Cl$ stretch at 560,$\equiv C-H$ (Aromatic hydrocarbon) stretch at 790, quinoline streach at 1620, -N-C=S &$\equiv C-H$ stretch at 2060; -C=CH_2, -CHO stretches at 3120 cm^{-1}. Frequencies and corresponding expected functional group is shown in Table 2

Table 2 Expected Functional groups at various frequencies

Sr. No.	Frequencies, Wave Number	Expected elements or Functional groups
1	3400	Simple H bonded –NH_2, -NH_3
2	3380	-C=N stretch
3	3290	-OH, C=CH_2, -CHO weakly
4	2200	-N-C=S stretch
5	1700	Aldehyde- $>C=O$strech
6	1600	Pyridine, Quinoline etc
7	1540	-C=S, -NH Medium
8	1480	-C=S, -NH, Pyridine
9	1280	-C=S Strong
10	1140	Other olefin $\equiv C-H$Medium
11	1110	Other olefin $\equiv C-H$ Medium
12	800	Five adjacent aromatic –C-H
13	750	$\equiv C-Cl$

From the above results, it can be concluded that 2-Chloro-QAT contains –Cl, NH_2, -SH, Quinoline ring in its structure.

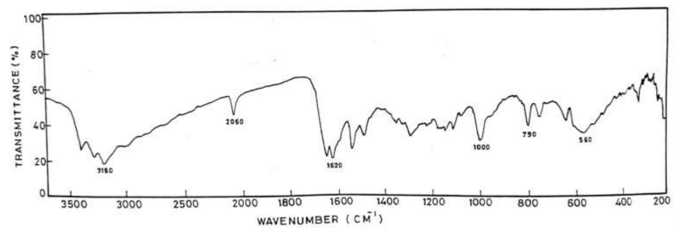


Fig 1 IR Spectra of 2-Chloroquinoline-3-Carbaldehyde Thiosemicarbazone

X-RD of 2-Chloro-QAT

X-RD is shown in fig.2 Values of $Sin^2\Theta$ observed and $Sin^2\Theta$ calculated are nearly equal, consequently values of d observed and d calculated are also equal indicating system is orthorhombic.

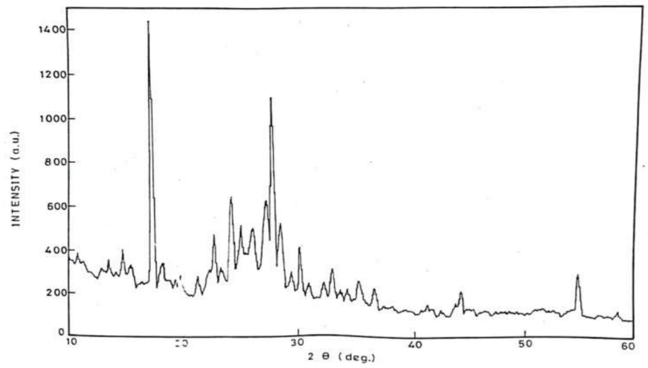
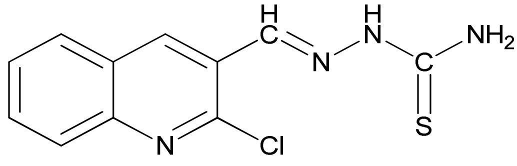


Fig 2 X-RD of 2-Chloroquinoline-3-carbaldehyde Thiosemicarbazone

Above characterization reveals that 2-Chloro-QATshould have following structure.



2-chloroquinoline-3- carbaldehyde thiosemicarbazone (2-Choloro-QAT)

Analytical application of 2-Chloro-QAT
Determination of Iron from sample using 2-Chloro-QAT

2-Chloro-QAT forms colored complex with Fe (III), we analyzed amount of Fe (III)fromthe Panchganga river water using 2-Chloro-QAT as an analytical reagent. Reason behind selection of this sample was soil of Kolhapur region is rich in iron content. Besides this industrial belt of Kolhapur also contains iron related industries. Industrial effluent from these industries after treatment is dumped into the Panchganga river. So, naturally there are chances of presence of iron content in river water sample. Keeping this in mind, we analyzed water sample of the Panchaganga river.As mentioned in experimentation, for determination of Fe (III) content principle of Beer's -lambert law was used.

From Beer's plot (fig.3) amount of Fe (III) was calculated and it was found to be 0.90 ppm/cm^3. To confirm results even calculation method was also used. Amount of Fe (III) found using calculation method was 0.92 ppm/cm^3.

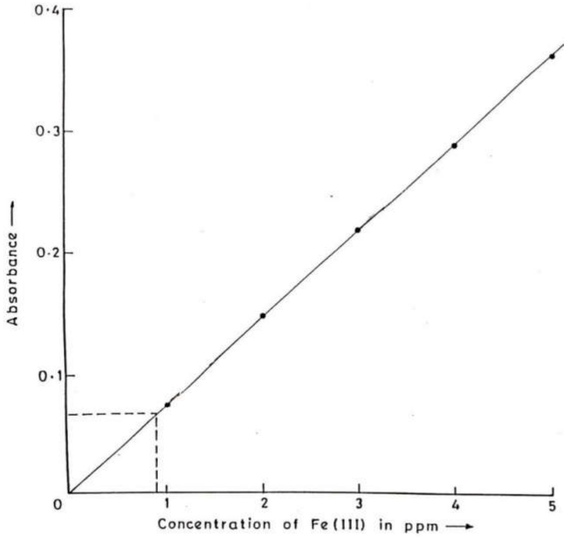


Fig 3 Beer's law for Fe (III)-2-Chloro-QAT
(Concentration of Fe (III) from sample by graph=0.9 ppm)

Comparing results of both the method, it can be said that results obtained by both the methods are almost same confirming 2-Chloro-QAT is good analytical reagent for determination Fe (III) from sample.

Determination of Nickel from sample using 2-Chloro-QAT

2-Chloro-QAT forms colored complex with Ni (II), we analyzed amount of Ni (II)fromthe Cadbury chocolate using 2-Chloro-QAT as an analytical reagent. As mentioned in experimentation, for determination of Ni (II) content, principle of Beer's -lambert law was used.

From Beer's plot (fig.4) amount of Ni (II) from sample was calculated and it was found to be 4.15 ppm/cm^3 (8.30 mg/g) To confirm results even calculation method was also used. Amount of Ni (II)found using calculation method was 4.16 ppm/cm^3(8.32 mg/g). Comparing results of both the method, it can be said that results obtained by both the methods are almost same, confirming 2-Chloro-QAT is good analytical reagent even for determination Ni (II) from sample.

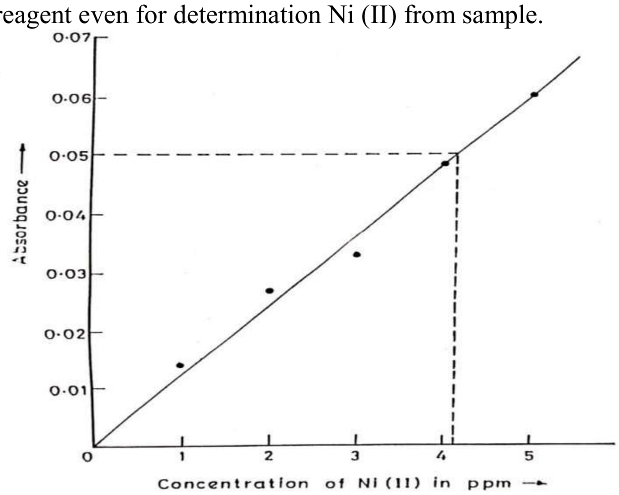


Fig 4 Beer's law for Ni (II)-2-Chloro-QAT
(Concentration of Ni (II) from sample by graph=04.15ppm)

CONCLUSION

2-Chloro-QAT is easy to prepare. It can be prepare in any laboratory with adequate facilities. Besides this chemicals required for analytical purpose can be easily available in any laboratory having adequate facility. As 2-Chloro-QAT forms colored complexes with Fe (III) and Ni (II), it can be used to find out Fe (III) and Ni (II) from various samples. Above all,2-Chloro-QAT can be used as an analytical reagent for various transition metals. As 2-Chloro-QAT shows antimicrobial activity and literature survey reveals that thiosemicarbazones are active against tumor, fungal and disease caused by bacteria. Further, its activity increase in presence of metals. Analytical reagent for various transition metals and use of 2-Chloro-QATwith metals as a drug are the areas yet to be exploited for it.

Acknowledgement

Author is thankful to HOD and teaching staff of department of Chemistry, Shivaji University, Kolhapur for constant encouragement and providing laboratoryfacility during this work. Author is also thankful to Dr. (Mrs.) V. A. Jadhav for guiding to this work.

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How to cite this article:

Omprakash Tukaram Sangule (2021) 'Synthesis, Characterization And Analytical Applications of 2-Chloroquinoline-3-Carbaldehyde Thiosemicarbazone', *International Journal of Current Advanced Research,* 10(05), pp. 24417-24421.
DOI: http://dx.doi.org/10.24327/ijcar.2021.24421.4844

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