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PREPARATION AND IDENTIFICATION OF NEW ORGANIC REAGENT 2-{(6-MTHYL BENZOTHIAZOL AZO) -1- NAPHTHOL -4-SULFONIC} AND USE IT IN DETERMINATION FOR COPPER ION BY FLOW INJECTION TECHNIQUES

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ABSTRACT

The research includes preparation and identification of new aza reagent 2-{(6-mthyl benzothiazol azo) -1- naphthol -4-sulfonic} by infrared (FTIR), spectrophotometric Uv- vis, melting point. This reagent used for estimation copper (II) in new design of (FIA) system, the various parameters (chemical and physical) affecting on estimation have been investigated such as flow rate was 9 ml/min, reaction coil 35 cm, volume reagent 335.5 µl, volume sample 196.25. µl, pH was 7 and reagent concentration 10-4 M, after that preparation the calibration curve in flow injection analysis system, the average desperation coefficient was 1.117 and reliability were studied. Compared between two methods (spectrophotometric method and FIA method).

KEYWORD: Copper ion, Determination, Flow Injection.

INTRODUCTION

Flow injection analysis which is simply technique, speed and low of cost as it is based on the use of a few amounts of reagent[1] and repetition high in the analysis process in a way semi-automatic or and automatic highly efficient and sensitive to chemical analyzes and the number of modeling large and fast distinct and limits of detection of low-lying.[2] The content of Cu ion in the Earth's crust is a small amount about 0.01% and don't increase the percentage of Cu ion in the raw material to 1.2%, and Alkoprit Cu2O and copper ores ore Alkoprit Cu2O and Alchalkwsat Cu2S and oftentimes Cu ion ores with the composition of a complex with other metals such as nickel, zinc, gold, molybdenum lead and other of precious

items.[3] Cu ion considered is one of the most important elements in biological systems[4], such as the blood serum of humans contain of 0.7-1.4 ppm from copper ion.[5] The Cu ion decrease in serum lend to pathological disorders such as congestive growth, these disorders usually depends on the age, type, gender, the environment, as long as the continuation of a deficiency, or at the level of Cu ion decrease. Further, eating a large amount of Cu ion leads to the accumulation of copper ion, especially in the liver and is often followed by the accumulation of Cu ion to the liberation into the serum this usually caused a hemolytic and the occurrence of Janudice, and for humans, the main source of poisoning Cu ion when inhalation of industrial waste and other sources, entering large amounts of Cu ion to the serum human from eat the food saved or dyed[6-8] Several analytical techniques that is use to determination of Cu ion, such as spectrophotometry and flow injection analysis[9-10], atomic absorption spectrometry[11], chemiluminescence[12], Neutron activation analysis, Inductive coupled plasma–atomic emission spectrometry,[13-14] and flow injection analysis.[15] Copper is an industrially important metal, it is used in, wire making, coin making, thermal conductance, medicine, alloys, transportation industry and fashioning metal products.[16] On the other hand, toxic role of the metal ion is well recognized Copper is available in nature in carbonates, chlorides and sulfides in a most famous.[17] Copper is utilized in in industrially useful alloys and electric industries Copper is also a supplement dietary nutrient, so only few amounts of the metal are needed for well-being[18] Copper ion has a very high thermal conductivity and electrical**.** Copper is available in free state in the form of carbonates, chlorides and sulfides.[19-21]

Apparatus: Spectrophotometer ShimadzuUV-1800 spectrophotometer, Spectrophotometer Labomed.inG single, beam and analytical Balance sensitive Denver InstrumentUSA, Ismatic, files interaction with the radius of 0.5 mm homemade, pipes load of Teflon, flow cell, volume of 450 µL peristaltic pump Germany homemade valves.

Materials is used: All chemicals used are have a high purity.

Preparation of solutions

1 - Prepare a solution of 0.001 M organic reagent dissolved 0.0399 g of reagent in 25 ml distilled water then transfer the solution to volumetric flask 100 ml.

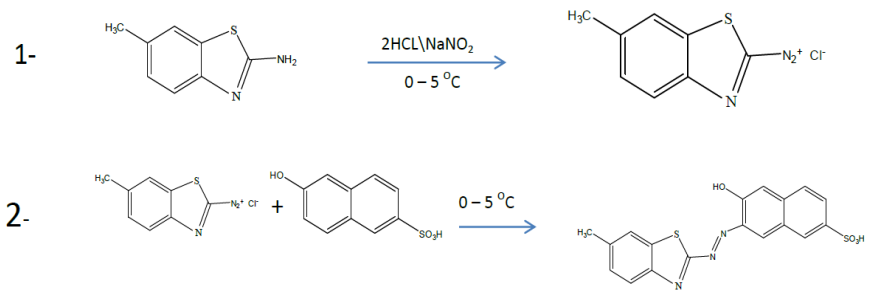
2 - Prepare 0.1 M of copper salt dissolved 1.7054 g of salt in 25 ml distilled water then transfer the solution to volumetric flask 100ml.

3 - Prepare 0.2 M of hydrochloric acid by used dilute low from concentration reagent has S.G (1.8) and purity (36-37.5)% after prepare solution standrazation with carbonate solution.

4 - Prepare 0.2 M of Acetic acid by used dilute low from concentration reagent has S.G (1.05) and purity (99.9)%.

Preparation of the new ligand (2-{(6-mthyl benzothiazol azo) -1- naphthol -4- sulfonic})

Dimpai ligand was prepared according to the following general procedure[22] (scheme 1). 2-amino - 6- methyl benzathiazol (0.164g, 1mmol) was dissolved in 30 ml of water and 1 ml of concentrated hydrochloride acid. this solution was diazotized below (0- 5) OC with 20 ml aqueous 1mmol from sodium nitrate. A drop of the reaction mixture is tested from time to time with the starch – iodide paper until nitrous acid persists in the solution during a 10 min interval. the resulting diazonium chloride solution was mixed with 1-nephthol -4- sulfonic (0.227 g 1mmol) dissolve in 50 ml alkaline ethanol cooled below (0-5) OC after leaving the refrigerator for 24 hour, the mixture was acidified with (0.1 M) hydrochloride acid unit (pH = 6) the precipitate was filtered off, and twice recrystallized from hot ethanol, and dried over anhydrous $CaCl_2$.



HL: yield 82% m.p (201-202) Oc.

Determine the max wavelength

determined max wavelength complex using ultraviolet visible spectroscopy (UV-VIS spectroscopy) to determination the λ max for complex and reagent and then determined the optimum conditions for the complexity.

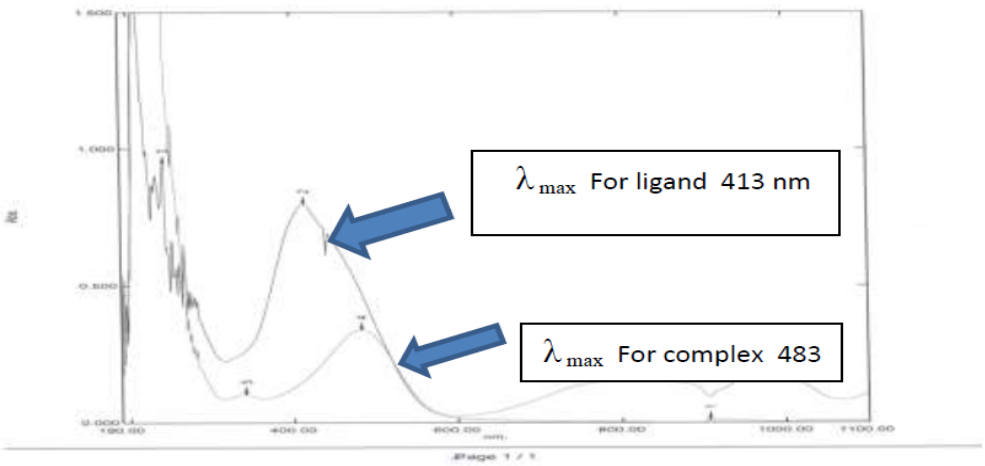


Figure. (1): UV-VIS spectra for reagent and complex.

The FTIR spectra for complexes and reagent

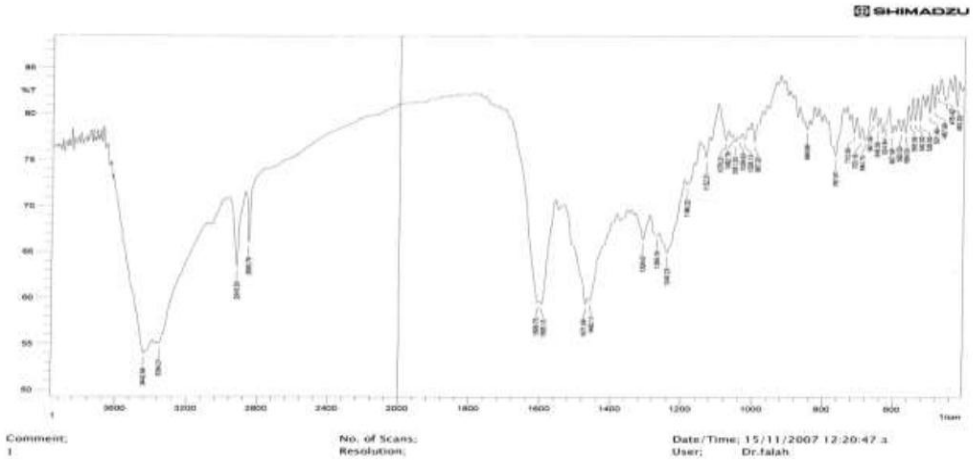


Figure. (2): FT-IR spectra for reagent.

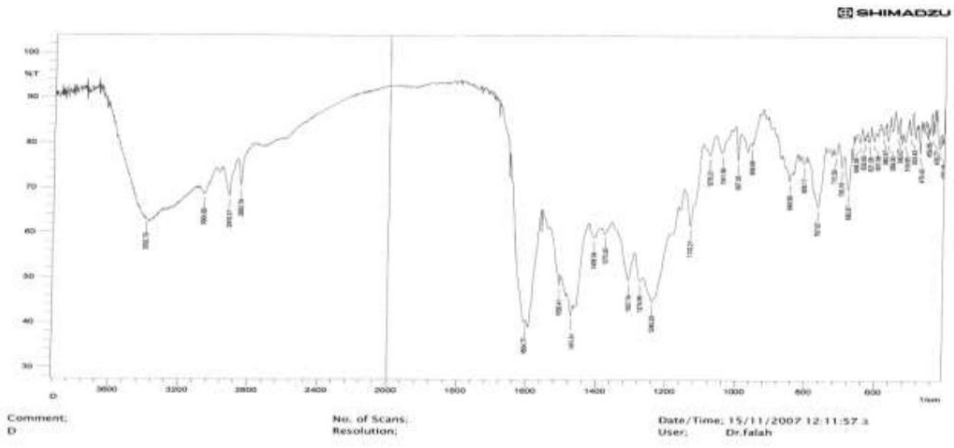


Figure. (3): FT-IR spectra for complex copper.

Table. (1): values stretching vibrations in infrared spectroscopy.

No.	Formal	υ(C-H)al	υ(C=N)	υ(N=N)
1	Reagent	2916cm^{-1}	1594cm^{-1}	1471cm^{-1}
2	copper complex	2916cm^{-1}	1594cm^{-1}	1451cm^{-1}

These spectra show a marked difference between functional group to the stretching vibration of υ(N=N) in the reagent at (1471) cm-1 shifted to lower frequencies at 1451cm-1 that mean the coordination of ligand through the nitrogen atom at the amine group.

RESULTS AND DISCUSSION

2- Determination of cupper by using new organic reagent in flow injection techinques

System that is designed to determine Cu ion in flow injection after measuring the wavelength of the complex after that determine the all optimum conditions for complexity.

Determine optimum condition

Conducted a study to determine the physical and chemical optimal complexity.

A- study chemical variables

1- Effect the reagent concentration

This study determine the ideal concentration of reagent that is used for the complexity of where the from study the ideal concentration was 10-4 M after this concentration the beak become distortion as figure.(3)

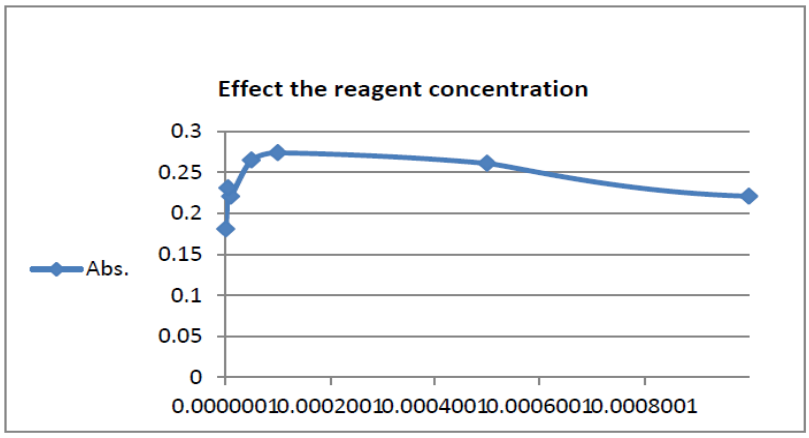


Figure. (3): Effect the reagent concentration.

Table. (2): Effect the reagent concentration.

Abs.	concentration
0.181	0.005
0.221	0.001
0.261	0.0005
0.274	**0.0001**
0.265	0.00005
0.221	0.00001
0.231	0.000005
0.181	0.000001

2- Effect the pH

Determine the optimum pH through formed the complex in the different value of pH from (4-10), the optimum pH was 7, as figure(4) after that prepared the suitable buffer from carbonate sodium and HCl.

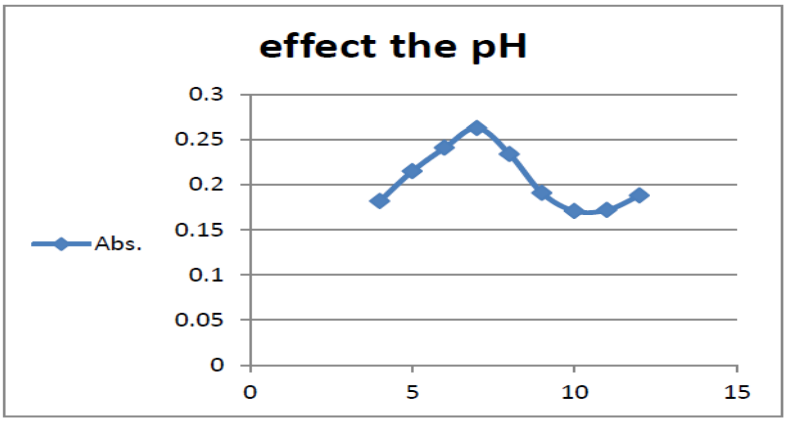


Figure. (4): Effect the pH on complex formation.

Table. (3): Effect the pH on complex.

Abs.	pH
0.182	4
0.215	5
0.241	6
0.263	**7**
0.234	8
0.191	9
0.171	10
0.172	11
0.188	12

B- physical variables

1- effect flow rate

The Flow rate studied by using different flow rate from (4 – 16) ml/min the ideal flow rate was 9 ml /min, this value give the best peak height. as figure (5)

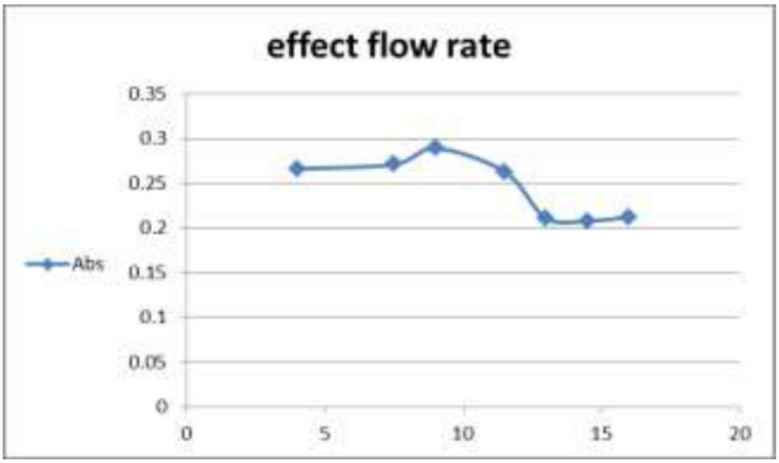


Figure. (5): Effect flow rate.

Table. (4): Effect floe rate.

Abs	flow rate(ml/min)
0.266	4
0.271	7.5
0.289	**9**
0.263	11.5
0.211	13
0.208	14.5
0.212	16

2- Reaction coil length

In this study use different the reaction coil length from (0-70) cm, this shown that the sensitivity of method increase with length of reaction coil (35) cm, shown in figure(6).

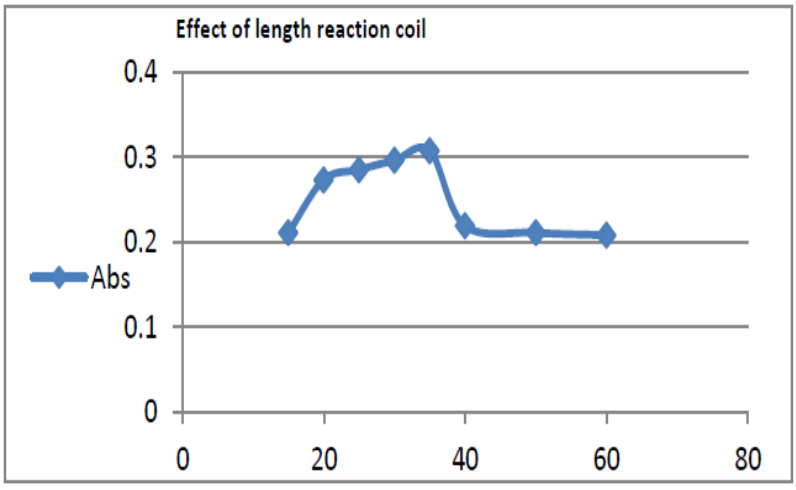


Figure. (6) reaction coil length.

Table. (5): Reaction coil length formation.

Abs	length reaction coil (cm)
0.211	15
0.273	20
0.285	25
0.296	30
0.307	**35**
0.219	40
0.211	50
0.208	60

3- Volume of the reagent: Different volume from reagent uses from (108.5 - 275.5) µl by changed the length of reagent loop, the optimum volume of reagent was 235.5 µl as shown Figure (7).

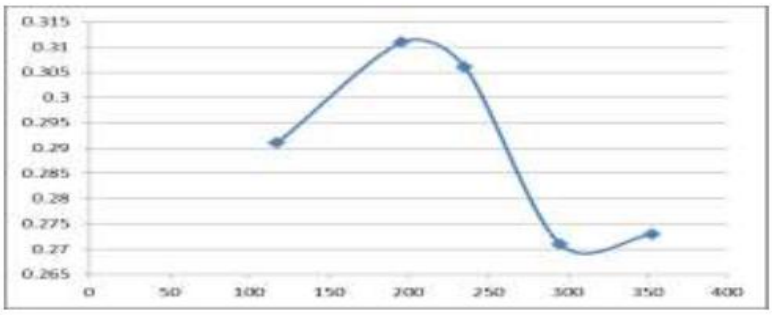


Figure. (7): effect volume of reagent.

Table. (6): Volume of reagent.

Abs.	volume of reagent (MCL)
0.288	117.75
0.309	196.25
0.322	**235.5**
0.301	295.25
0.298	353.25

4- Volume of metal ion: Study effect of sample volume through change length loop of copper ion, in the range from(108.5 - 275.5) µl from the result found the ideal volume of metal was 196.25 µl as in the figure (8).

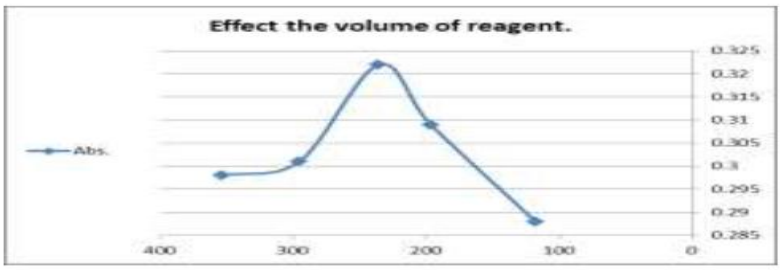


Figure. (8): volume of metal.

Table. (7): volume of ion.

Abs	volume ol ion
0.291	117.75
0.311	**196.25**
0.306	235.5
0.271	295.25
0.273	353.25

Preparation of the calibration curve

Calibration curve was prepared at the optimum conditions of complexity and only change the copper ion concentration as in the figure (9)

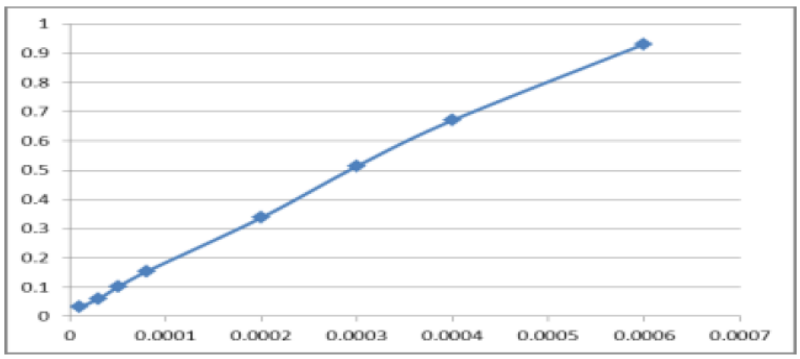


Figure. (9): Calibration curve of CU II at optimum condition.

Table. (8): Calibration curve of CU ion.

Abs.	con. Ion (m)
0.032	0.00001
0.061	0.00003
0.101	0.00005
0.154	0.00008
0.338	0.0002
0.514	0.0003
0.671	0.0004
0.931	0.0006

Reliability

To study the of flow injection analysis unit the reliability in concentration 5×10-4M copper ion for ten time out the result show in table(8).

Table. (9): Reliability.

Sample number	1	2	3	4	5	6	7	8	9	10	mean	SD	RSD %
Abs.	0.322	0.322	0.321	0.322	0.321	0.323	0.322	0.322	0.322	0.322	0.322	0.52	0.95

Dispersion: The dispersion coefficient of tow concentration of copper ion were study and the table(7) show the result.

Table. (10): Dispersion coefficient of FIA unit.

copper ion concentration	Response in (mm)		Dispersion (D) $D = \frac{H^{\circ}}{H_{max}}$
	H°	H_{max}	
5×10^{-4}M	0.328	0.322	1.0185
4×10^{-4}M	0.710	0.671	1.0588

HO :- without dispersion

H max :- with dispersion

Interference

Study overlapping some cation and anion with Cu ion in the composition of the copper complex at wavelength 483 nm, where the height of the complex copper 0.322 when the concentration of Cu ion in the complex is 1×10-6M.

The anion and cation is not interference with copper

(Na^{+}, CO^{+2}, F-Ni^{+2}, Mn^{+2}, NO_3^{-}, K^{+}, CH_3COO^{-}, tertar^{+}, $C_2O_4^{-2}$, Cl^{-})

Table. (11): Interference.

	Ion	*Conc.*	*Abs (nm)*	*Difference*	*treatment with Masking agent*
1	*Hg^{+2}*	*0.0005*	*0.322*	———	———
2	*Cd^{+2}*	*0.0005*	*0.301*	*-0.021*	*A drop of 0.1M concentration of Altertrat*
		0.005	*0.299*	*-0.023*	*Two drops of concentration of 0.1 M Altertrat*
3	*Ag+*	*0.0005*	*No R.*	*0*	
		0.005	*0.311*	*-0.011*	*Four of the concentration of 0.1M Altertrat*
4	*$Fe^{+}3$*	*0.0005*	*0.317*	*-0.005*	*A drop of 0.1 Mconcentration of oxalates*
		0.005	*0.308*	*-0.014*	*Two drops of 0.1M concentration of oxalates*
5	*Pb^{+2}*	*0.0005*	*0.311*	*-0.011*	*A drop of 0.1M concentration of oxalates*
		0.005	*0.301*	*-0.021*	*Two drops of 0.1M concentration of oxalates*

Applications

Table. (12): Applications.

Sample	take	The found value By Atomic absorbasion	The found value By flow injaction
tap water	0.2ppm	0.2ppm	0.2ppm
Aqueous solution	4ppm	3.8ppm	3.8ppm
Drug/freoglobin syrup	4ppm	3.85ppm	3.9ppm
Drug/Haematianic syrup	5Ppm	4.7ppm	4.85ppm
Drug/omega3 syrup	4ppm	3.9ppm	3.9ppm
Dialac milk	2.5 ppm	2.3ppm	2.1ppm

REFERENCES

1. O. Abdel-Hadi al-Majid C.Mohammed and A.Hussein, Journal of the Science of Mustansiriya, 2013; 24: 2, Arabic copy.
2. Z. A-A Khammas and A. A. Ghali Iraqi National Journal of Chemistry, 2013; 49: 25-37.
3. D. G. da Silva, L. A. Portugal, A. M. Serra, S. L. Ferreira and V. C, aFood Chemistry, 2013; 137: 159–163.
4. J. Rimjhem S.S. kumar A.Uma, K,S and S, Neba Res. J.pharma. 2013; 4: 8.
5. Y. Li, B. Hu, Spectrochim. Acta, Part B, 2007; 62: 1153-1160.
6. J.C.A.De Wuilloud, R. G. Wuilloud, M.F.Silva, R. A. Olsinaa and L.D Martinez, Spectrochim.
7. S. A. N. Aljadaan1 and E. A. Saeed, 2010; 36(2): 15. Acta, Part B, 2002; 57: 365-374.
8. J.D. Lee, Anew concise inorganic chemistry, Edition, van nostrand Rein hold, 1977; 346: 390.
9. I.M.Dittert, T.A. Maranh, D.L.G. Borges, M.A. Vieira, B. Welz and A.J. Curtius, Talanta, 2007; 72: 1786-1790.
10. D. Martín-Yerga, M. B. G.-García, and A. C.Talanta, 2013; 116: 1091-1104.
11. S.S. Bozkurt, K. Ocakoglu and M. Merdivan, Microchim. Acta, 2012; 177: 47-52.
12. E.M.Martinis, P. Bertón, R.A. Olsina, J.C. Altamirano and R.G. Wuilloud, J. Hazard. Mater., 2009; 167: 475-481.
13. P.R.Aranda, R.A. Gil, S. Moyano, I.E. deVito and L.D. Martinez, Talanta, 2008; 75: 307-311.
14. M.R. Sobrabi, E.F.Farokhi, A. Adnani and M.Ziaian, J. Appl. Sci., 2007; 7: 3123-3125.
15. Z.Q. Tan, J.F. Liu, R. Liu, Y.G. Yin and G.B.Jiang, Chem. Commun., 2009; 45: 7030-7032.
16. M. Garrido, M.S.Di Nezio, A.G.Lista, M. Palomeque and B.S. Fernandez, Anal. Chim. Acta, 2004; 502: 173-177.
17. Y.J. Xue-Bo, J. Chromatogr. A, 2007; 1154: 437-443.
18. A. Niazi, T. Momeni-Isfahani and Z. Ahmari, J. Hazard. Mater., 2009; 165: 1200-1203.
19. H.I.B. Ulusoy, R. Gurkan and S. Ulusoy, Talanta, 2012; 88: 516-523.
20. C-G.Yuan, K. Lin and A. Chang, Microchim. Acta, 2010; 171: 313-319.
21. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds" 6rd Ed., A John Wiley & Sons, Inc., Hoboken, New Jersey, Published Simultaneously in Canada, 2009; 1-29, 57-, 67, 313.
22. H. Chen, J. Chen and X. Jin, D. Wei, JHazard. Mater., 2009; 172: 1282-1287.