

Detection of Fe(III) Levels via. Two Different Spectrophotometric Methods in Diwaniah City/Iraq

Hasan M. Luaibi, Bassam F. Alfarhani and Muqdad Irhaeem Kadhim
Department of Chemistry, College of Sciences, University of Al-Qadisiyah, Al-Diwaniyah City, Iraq

Abstract: In this study, multiple H₂O samples were collected from different locations in Diwaniah River, Iraq. This river consider to be the major pollutes site in this city, the reson behind this is the huge amount of pollutatnts going to the river stream over years. To get a better picture about the extent of pollution, the ferric concentration levels have been determined in the river stream. Two separate spectrophotometric methods have been developed for quantification of low concentration levels of ferric in different sources of water, these two methods were, quick, simple and sensitive. The 8 hydroxy quinoline has been used in the first method and the reagent was acting as a chromogenic, the detection was based on reaction of ferric with 8 Hydroxy quinoline (8-Hy) to form a chemical complex with λ max equal to 371 nm using multi-extraction method of analysis. In method 2, KSCN (potassium thiocyanate) was act as a chromogen then will react with ferric ion in acidic pH to produce a complex (red) with λ max equal to 480 nm. In both methods Beers-Lambert law was observed with a 0.1-2.0 ppm as dynamic range of Fe³⁺. The value of recovery was 98.5-102.5% with 1.1 and 1.05% as a coefficient of variation of for method one and method two. Both methods show statically no difference in ferric concentrations, therefore, the two methods were effectively practical to determine ferric concentration in river, tap and botteled water samples.

Key words: Fe(III), 8 Hydroxy quinoline (8-Hy), potassium thiocyanate (KSCN), river water, tap water, concentration

INTRODUCTION

Iron, consider to be an energetic element which is important for development of biological system, also, it is act as O-carrier (Oxygen carrier) in transporting of the electrons and storage and that is why iron has the major influences on deregulation of metabolism. So, an unbalanced high-levels of Fe in the human-body can cause haemochromatosis and deficiency leads to anemia. Due to the previous reasons, iron should precisely quantify in chemical and biological environment (Alfarhani *et al.*, 2016; Skoog *et al.*, 2014) and samples from industry (Alfarhani *et al.*, 2018). In marine ecologies, most of heavy metals counting Fe can be distributed among several environmental systems such as water, sediment and biota (Abdo, 2013).

Depending on specific chemical forms such as suspended as particulate matters and dissolving to form either ions or complexes, mobility and toxicity these species will show different behavior (Alsuhami and Mccready, 2012).

Because of their environmental determination and possible capacity to bioaccumulate over food chain

(Adebayo *et al.*, 2011; Yang *et al.*, 2012; Tuna *et al.*, 2007), heavy metals consider to be serious danger to the construction of aquatic eco-systems. These metals might disturb the production of major producers which should be taken in-to attention straight via the enzymatic inhibition of chlorophyll synthesis or through inducing of deficiency of vital nutrients (Jiang *et al.*, 2014). Several studies concentrate on the increasing of resulting Fe conc. From anthropogenic process in H₂O, plants and soil due to their negative effects on water quality and aquatic bio-diversity (Khalil *et al.*, 2007; Segura *et al.*, 2006; Lokeshwari and Chandrappa, 2006). Conservation and restoration practices are thus crucial steps to assume to maintain both aquatic environment. AL-Diwaniyah River is among the maximum polluted locations in Iraq. The river has been used for farming washing, fishing and drinking water for long time. Recent studies confirm evidence showing a major pollution of diwaniah river stream by two main sources, domestic and industrial actions and release of agricultural wastes alongside the river stream (Jumbe and Nandini, 2009; Hseu *et al.*, 2002; Chen and Ma, 2001; Alsudani *et al.*, 2010).

The main objective of the current study was to evaluate concentrations of iron (III) in Diwaniyah water by using a simple methods in lack of advanced instruments such as, AAS (Atomic Absorption Spectroscopy), ICP (Inductively Coupled Plazma) and IC (Ion Chromatography) (Sandroni *et al.*, 2003). This study also, aimed to make a comparison between two separate methods of determination of Fe(III) in river, bottled water and drinking water.

MATERIALS AND METHODS

Experimental part

Samples locations: Several water samples (from surface) have been collected from Diwaniyah River (total number of samples equal to 120 in average of ten samples per 4 weeks), the samples were collected from August, 2016-2017 of the same month 1. The river stream pass through Diwaniyah city. The river was a main surface water that takes waste-water sewage from the management plant.

The river water samples were obtained from 60 cm (depth) below the surface of river water, the process involve using water-sampler. The collected samples were stored in acid washed PVC containers (2.5 L), the cleaning process involve using a concentrated solution of nitric acid to reserve the metal and prevent precipitation. The collected samples were kept in cold place and saved in laboratory at temperature below 4°C until further analysis. The other samples (bottled water) were obtained from city market and the tap water collected from different several houses in Diwaniyah city.

Material and chemicals used: The solvents used were consider to be high purity (HPLC-grade). While the other chemicals were in analytical-reagent grade. These chemicals were used in the analysis with no further purification process. The anaylsis done using de-ionized water. Oxine (8 hyd. quinolone) was gotten from sigma.

UV-Visible absorption-spectroscopy: All the absorption spectra were obtained using dual-beam spectrophotometer. The source used was xenon lamp with 2 nanometer band-pass. All the measurements for the solutions were made with 3 mL cuvette type quartz with path-length equal to 1 cm.

Ferric/oxine complex method for quantification of Fe(III) (method one): A ten part per million (ppm) solution of ferric standard was sited in a separatory funnel, 10 mL of oxine/chloroform was added according to the chemical equation below, the content was accurately shaken for

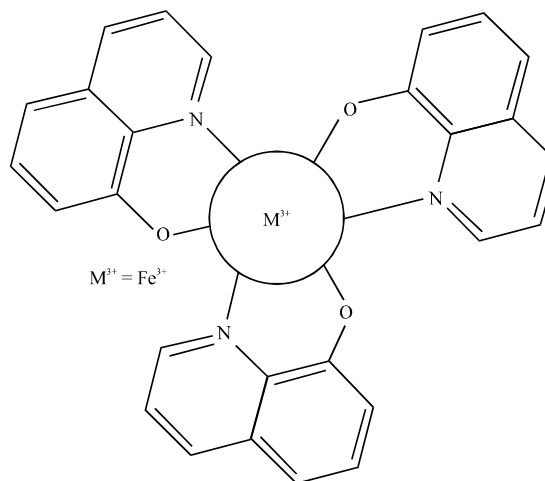
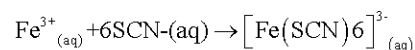


Fig. 1: Structure of Ferric-oxine

3-5 min. The upper layer, (aqueous layer) was permitted to be separated via distrubution between the aqueous-layer and the chloroform oxine-metal complex layer (lower-layer). The blank was complete by adding 10 mL of de-ionized water to 10 mL of CCl₄ in a separatory funnel. Both the immiscible layers were shaken for 3-5 min and then separated into several test-tubes. The absorption of the complex show the highest value with wavelength equal to 371 nm. Figure 1 shows the chemical structure of the complex formed.

Iron(III) determination by thiocyanate complex (method two): In the current method (Alfarhani *et al.*, 2018), the Fe(III) extracted and the solution made visible by adding, thiocyanate ions. SCN⁻ react with the Fe(III) ion to form a complex with red color according to chemical equation below:



Through comparison of the color intensity of the complex with the color of a several concentrations that represent standard solutions to build up a calibration curve with recognized Fe(III) concentrations, the concentration of Fe III in water samples could be quantify. The highest value of absorbance of the complex was found to be at 480 nm.

RESULTS AND DISCUSSION

Fe(III) concentration by method one: Five different concentrations from the ferric/oxine complex and the blank solution were made and used to build-up a curve of calibration (Fig. 2). Using the optimum condition for this

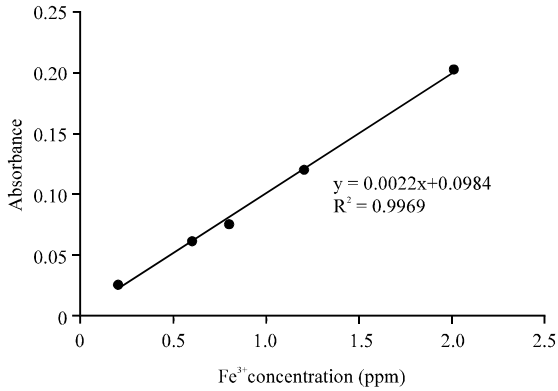


Fig. 2: Curve of calibration using method one

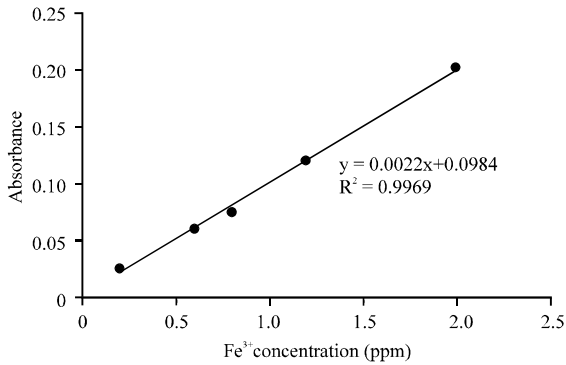


Fig. 3: Curve of calibration by method 2

method, the resultant curve of calibration for the Fe(III) was linear fitting with a least correlation coefficient value of 0.9909. In Table 1, demonstrations the results gotten from using method one, each value is an five samples average.

Fe(III) conc. by method two: The 6 concentrations from the Fe(III)-SCN-complex and a blank solutions were chemically prepared and a curve of calibration was build up for this method (Fig 3). Using the optimum conditions, the resultant curve of calibration for the ferric was linear fitting. A least correlation coefficient value of 0.99903, Table 2 represent the values obtained from applying the current method, each value is an 5 samples average.

Method 1 and 2 comparison: A statistically dependence comparison was made using a 95% CI (Confidence Interval), the obtained value was done using 5 trials ($\alpha/4$: 0.05; $N/4$: 3) where $t_{critical} = 2.780$. The obtained t_{exp} (experimental) value was less than ($t_{critical}$), hence, the average concentrations (in ppm) from both methods in Table 2 and 3 were consider to be no statically difference (100%).

Table 1 Fe(III) concentration values by method one

Samples	Ferric concentration in part per million (ppm)
*R 1	0.88±0.04
R 2	0.86±0.03
R 3	1.11±0.09
R 4	1.23±0.08
*T 1	0.14±0.02
T 2	0.24±0.01
T 3	0.33±0.07
T 4	0.75±0.09
Bottled-water	0.25±0.04

*R River samples; *T Tap-water sample; *1, 2, 3 and 4 are the sample locations in Fig. 1

Table 2: Fe (III) conc. by method two

Samples	Ferric concentration in part per million (ppm)
R 1	0.93±0.04
R 2	0.88±0.04
R 3	1.34±0.50
R 4	1.53±0.13
T 1	0.31±0.02
T 2	0.42±0.02
T 3	0.49±0.09
T 4	0.69±0.07
Bottled-water	0.18±0.02

*R River sample; *T Tap-water samples; * 1, 2, 3 and 4 are the samples locations in Fig. 1

Table 3: Statistical-comparison between method 1 and 2

Samples	t_{exp} method 1: method 2
R 1	0.467632
R 2	0.238736
R 3	0.073452
R 4	0.157365
T 1	0.256325
T 2	0.376635
T 3	0.187982
T 4	0.288374

The obtained results show that the average recoveries for both methods were 84-91% for both method one and method two, respectively, the obtained results indicate that Fe(III) concentration in river-water get higher as river stream cross Diwaniyah city, the observed results can be explained as follow as the river pass more distance a different pollutants drained to the stream that come from different sources such as: agricultural, anthropogenic and sewage. The results also, show a difference in Fe content, the reason behind this that the high temperature in the hot season will cause degradation for organic matter due to fermentation, also, Fe could be released from sediments to the water stream. The tap-water iron concentration show no difference in Fe levels among the different samples locations.

The results show that a higher level of Fe(III) where observed in a location in the end of the city, the obtained level were above the limit of the International Standards (ISs) (equal to 1 part per million). While all the tap-water and bottled water samples were below ISs. Fig. 4 shows a comparison between different Fe(III) concentration at different sample locations.

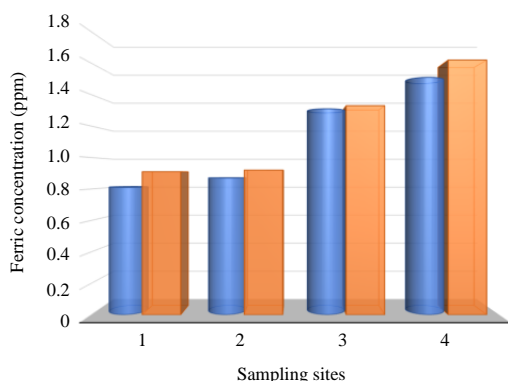


Fig. 4: A graph represent the Fe conc. At different samples locations, blue and orange bars indicate the results observed by method one and two, respectively

CONCLUSION

Diwanayah River is studied as a container for several sources of pollutants (mainly, anthropogenic and agricultural), it is show that it is vital to monitor the quality of water. This river helps as the main source of drink and irrigation for the people whom live in the vicinity and for people whom eat fish from Diwanayah River. The the waste discharges increasing will effect the river which can increase the level of the pollutants and hence, higher possibility of risk. It is essential to always monitor the conc. Of Fe(III) as an Indicators (In) for heavy metals pollution in surface of water.

REFERENCES

Abdo, M.H., 2013. Physico-chemical studies on the pollutants effect in the aquatic environment of Rosetta Branch River Nile, Egypt. *Life Sci. J.*, 10: 493-501.

Adebayo, B.K., S. Ayejuyo, H.K. Okoro and B.J. Ximba, 2011. Spectrophotometric determination of iron (III) in tap water using 8-hydroxyquinoline as a chromogenic reagent. *Afr. J. Biotechnol.*, 10: 16051-16057.

Alfarhani, B., M. Al-Tameemi, H.C. Goicoechea, F. Barbosa Jr. and A.D. Campiglia, 2018. Direct analysis of benzo [a] pyrene metabolites with strong overlapping in both the spectral and lifetime domains. *Microchem. J.*, 137: 51-61.

Alfarhani, B., M. Al-tameemi, A.V. Schenone, H.C. Goicoechea and F. Barbosa Jr. *et al.*, 2016. Room temperature fluorescence spectroscopy of benzo [a] pyrene metabolites on octadecyl extraction membranes. *Microchem. J.*, 129: 83-89.

Alsudani, H.M., R.I. Al-Bayati, M.M. Barbooti and A.A. Hassan, 2010. Determination of common cations and ammonium by ion chromatography in water samples of Baghdad City part 2. *Intl. Res. J. Biotechnol.*, 1: 028-036.

Alsuhami, A.O. and T. McCreedy, 2012. Rapid immobilization of-8- hydroxy quinoline onto Silica materials and its application for on-line solid-phase extraction of transition metals from environmental samples before ICP-OES determination. *Global Nest J.*, 14: 55-65.

Chen, M. and L.Q. Ma, 2001. Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Sci. Soc. Am. J.*, 65: 491-499.

Hseu, Z.Y., Z.S. Chen, C.C. Tsai, C.C. Tsui, S.F. Cheng, C.L. Liu and H.T. Lin, 2002. Digestion methods for total heavy metals in sediments and soils. *Water Air Soil Pollut.*, 141: 189-205.

Jiang, X., A. Teng, W. Xu and X. Liu, 2014. Distribution and pollution assessment of heavy metals in surface sediments in the Yellow Sea. *Mar. Pollut. Bull.*, 83: 366-375.

Jumbe, A.S. and N. Nandini, 2009. Heavy metals analysis and sediment quality values in urban lakes. *Am. J. Environ. Sci.*, 5: 678-687.

Khalil, M.K., A.M. Radwan and K.M. El-Moselhy, 2007. Distribution of phosphorus fractions and some of heavy metals in surface sediments of Burullus lagoon and adjacent Mediterranean Sea. *Egypt. J. Aquat. Res.*, 33: 277-288.

Lokeshwari, H. and G.T. Chandrappa, 2006. Impact of heavy metal contamination of Bellandur lake on soil and cultivated vegetation. *Curr. Sci.*, 91: 622-627.

Sandroni, V., C.M. Smith and A. Donovan, 2003. Microwave digestion of sediment, soils and urban particulate matter for trace metal analysis. *Talanta*, 60: 715-723.

Segura, R., V. Arancibia, M.C. Zuniga and P. Pasten, 2006. Distribution of copper, zinc, lead and cadmium concentrations in stream sediments from the Mapocho River in Santiago, Chile. *J. Geochem. Explorat.*, 91: 71-80.

Skoog, D.A., D.M. West, S.R. Crouch and F.J. Holler, 2014. *Fundamentals of Analytical Chemistry*. 9th Edn., Cengage Publisher, Boston, Massachusetts, USA., ISBN:9781285056241, Pages: 958.

Tuna, A.L., F. Yilmaz, A. Demirak and N. Ozdemir, 2007. Sources and distribution of trace metals in the Saricay Stream Basin of Southwestern Turkey. *Environ. Monit. Assess.*, 125: 47-57.

Yang, Y., F. Chen, L. Zhang, J. Liu, S. Wu and M. Kang, 2012. Comprehensive assessment of heavy metal contamination in sediment of the Pearl River Estuary and adjacent shelf. *Mar. Pollut. Bull.*, 64: 1947-1955.