Determination of Zinc Ions in Drinking Water Distribution Systems (PVC pipes) by Spectrophotometric Method

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Abstract

In this work, a method for the simultaneous spectrophotometric determination of zinc which was precipitated into deionized water that is in a commercial distribution systems PVC pipe, is proposed using UV-VIS Spectrophotometer. The method based on the reaction between the analytes Zn^{2+} and 2-carboxy-2-hyroxy-5-sulfoformazylbenze (Zincon) at an absorption maximum of 620nm at pH 9-10. This ligand is selective reagent. Since the complex is colored (blue), its stoichiometry can be established using visible spectrometry to measure the absorbance of solutions of known composition. The stoichiometry of the complex was determined by Job's method and molar ratio method and found to be 1:2 (M: L). A series of synthetic solution containing different concentrations of zinc were used to check the prediction ability of the complexation. Water quality samples collected a 100cm PVC system of drinking water in three sizes from different country full with deionized water for different time.

Keywords: spectrophotometric, PVC pipe, zincon, drinking water

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تقدير أيونات الزنك في الأنظمة الناقلة لمياه الشرب (أنابيب بولي فنيل كلورايد) بطريقة التحليل الطيفي المرئي

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الخلاصة

تتناول هذه الدراسة طريقة طيفية لتقدير أيونات الزنك المترسب في الماء المنزوع الأيونات الذي تم تجميعه من أنابيب البولي فنيل كلورايد التجارية الناقلة لمياه الشرب بفترات زمنية مختلفة تتراوح من (1-10) أيام وذلك بإستخدام تقنية الأشعة فوق البنفسجية-المرئية. تعتمد هذه الطريقة على دراسة أطياف معقدات أيون الزنك الثنائي مع الزنكون لأقصى إمتصاص بطول موجي 620 نانومتر عند دالة حامضية تتراوح بين 9-10. حيث إن إنتقائية الليكاند عالية لأيونات الزنك. تم دراسة التوازن للمحاليل الزرقاء اللون لمعقدات الزنك-زنكون في طيف المنطقة المرئية من خلال قياس إمتصاصية المحاليل المتكونة. وتم دراسة تكافؤية المعقد بطريقتي جوب والنسب المولية، أظهرت النتائج إن اتحاد ايون الزنك الثلاثي مع الزنكون بنسبة 2:1. تم تحليل نماذج المياه وإمكانية إحتوائها على تراكيز مختلفة من الزنك من خلال قابلية تكوين المعقدات. لثلاثة من أنابيب البولي فنيل كلورايد بطول 100 سم بأقطار مختلفة وبأزمنة مختلفة ومن مناشيء متغايرة وذلك لغرض إيجاد طريقة لتحليل الزنك في الأنابيب الناقلة لمياه الشرب.

الكلمات المفتاحية : المطيافية ، أنابيب بولي فنيل كلورايد ، زنكون ، مياه الشرب.

Introduction

Zinc is an essential element and it plays an important physiological role in human beings. It is present in many alloys and is also found in a number of pharmaceutical samples and in airborne particulates, causing environmental pollution. Human contains the second largest amount of Zn 2.00g after Fe 4.00g. It is a constituent of over 100 enzyme systems [1]. According to Schwartz term “Concentration Window” metals are (a) Essential at definite trace level, (b) Deficient than that level cause metabolic disorder, (c) Higher than that level termed “Toxic level”, and causes adverse Effects [2]. Concentration of zinc greater than 3.0

ppm affects the potable nature in alkaline waters according to IQS (Iraqi), 2009 and WHO, 2008 standards [3,4]. The determination of zinc in drinking water is also of considerable interest to investigate further. Zinc also has industrial significance. Methods available to determine zinc ion with simple colorimetric methods using different organic reagents and Zincon reagent as semi-quantitative assessments, which include in Table 1.

Table 1: Comparison of present method and other reported spectrophotometric methods

Reagent	λmax (nm)	pH	M:L	Ref
-naphthylazo)]pyridine disodium salt′-sulpho 1′-hydroxy-4′bis-[2,6-(2	565	7.5 – 9.1	1:1	5
3-hydroxybenzylaminobenzoic acid	460	5.0	N.R	6
1-ethyl-6-fluoro-4-oxo-7-piperazin-1-yl-1H-quinoline-3-carboxylic acid (Norfloxacin)	365	5.5 – 6.5	1:1	7
Benzoylpyridine thiosemicarbazone (BPT)	430	6.0	1:1	8
Methylglyoxal bis(4-phenyl-3-thiosemicarbazone)	430	5.0-6.0	1:1	9
o-{2-[α-(2-hydroxy-5-sulfophenylazo)-benzylidene]hydrazine}benzoic acid	20	9.0-10.0	1:2	P.M

M:L is Metal:Ligand, Ref is the reference, N.R is Not Reported, and P. M is Present method.
Zincon: Among the many reagents eliciting complexation-induced spectral changes, the dye of zincon; $C_{20}H_{15}N_4S.H_2O$; Figure 1, has been shown to serve as an excellent chromophore for the quantification of zinc and copper ions in aqueous solution [10].

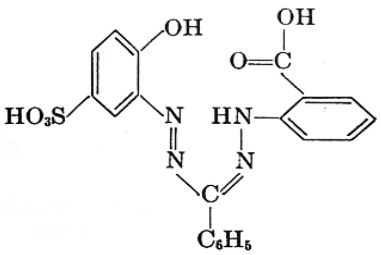

Figure 1: Structure of zincon

Zincon, MW. 480.43g, is proposed as a short name for the compound 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene. According to Chemical Abstracts' nomenclature the name is o-{2-[α-(2-hydroxy-5-sulfophenylazo)-benzylidene]hydrazine}benzoic acid. Polyvinyl chloride pipe: Polyvinyl chloride, commonly abbreviated PVC, is a widely-used plastic. It was

accidentally discovered on at least two occasions in the 19th century. Afterwards, in the early 20th century, Russian chemists attempted to use PVC in commercial products, but they faced difficulties because of the rigid and brittle nature of this polymer. It was not until 1940s that the plastic industry started using PVC in its unplasticized form for pipes, but it was soon found that PVC degraded when exposed to the light and heat that are part of the production process [11]. PVC is one of the most valuable products of the chemical industry and the second-largest thermoplastic commodity produced around the world, after polyethylenes [12]. Furthermore, it is also the most versatile of all thermoplastics. It can be converted either into rigid products or into flexible articles when compounded with plasticizers [12]. In recent years, the use of polyvinyl chloride (PVC) pipes has been increasingly considered for replacing the old steel and copper pipes in public drinking water distribution systems. Its widespread use is due to its low cost, ease of the installation, excellent structural strength, its light weight, and resistance to corrosion [13]. Drinking water distribution systems are at risk of some heavy metal which used as stable of inner Pinter, leaching from the pipe into the drinking water in the water distribution system. The majority of the cases of limited the excess heavy metal concentrations in drinking water distribution systems have been reported in Iraq, according to IQS(Iraqi), 1991 [14], they coated with four heavy metals: lead, zinc, cadmium, and nickel, although the problem may be more widespread. The present work provides an analysis of the absorption spectra of zincon in its free and metal-bound forms, and the results of this work show abvaise difference in the ratio of zinc ion to zincon which is used to determine zinc ion in PVC pipes from recently workers which consider a basic reference [10] for many researchers like as [15-19].

As a consequence of these investigations, an optimized method that allows the facile determination of Zn^{2+} is presented. Furthermore, a procedure for the quantification of Zn^{2+} in the drinking water distribution systems made from PVC pipe, which can be directly applied to assess the metal content of Zn^{2+}, is described.

Experimental

Equipment: Electronic absorption measurements were carried out by using a SHIMADZU 1800 spectrophotometer (slit width 0.1 nm and scan rate 500 nm min^{-1}) equipped with 1.00cm

quartz cells. Measurements of pH were made with a HACH digital pH-meter using a combined electrode. Chemical reagent: A Stock solutions of zinc salts were prepared from their suppliers; HiMedia Laboratory, India ($ZnSO_4.7H_2O$). Standards of working solution were made by appropriate dilution as required. A standard stock solution of Zn(II) 1×10^{-4} M was prepared by dissolving 1.4 mg of Zinc(II)-Sulfate-7-Hydrate in volumetric flask 50mL in deionised water. The working solutions were obtained by diluting the stock solution to the requisite concentrations with double distilled water. A stock Zincon solution 1×10^{-4} M was prepared from their suppliers; Riedel - DE Haen AG, Seelze -Hannover, Germany; by dissolving 2.4mg reagent in 1mL of NaOH 1M prior to dilution to 50 mL with deionized water. The stock solution was stable at 4°C for (at least) 1 week. The pH of these solutions was prepared in doubly distilled water. Clark and Lubs buffer solution of pH 9 to 10 [20] was prepared by dissolving 2.40g of sodium hydroxide NaOH in 60mL of deionized water. Then transfer the solution to a 100mL volumetric flask, and add 3.73g of potassium chloride KCl and 3.10g of boric acid H_3BO_3 with swirling the flask to dissolve the solids make up to volume with deionized water. Suitable portions of these solutions were mixed to get the desired pH, then and checking the pH. Perpetration of PVC pipes: Three PVC pipes with 100cm length were filled with deionized water and cover with a tight lid for different duration time 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 days. Then take the sample in label polyethylene containers. Commercial PVC pipe is packed for servicing industry, as following the Table 2:

Table 2: Properties of three commercial PVC pipes

No. of PVC pipe	Diameter/ inch	Length / m	Country of origin
I	25	1	Turkey
II	20	1	Turkey
III	20	1	Kingdom of Bahrain

Solution preparation: In each of set different 20 mL of volumetric flasks, 0.05 mL of buffer solution (pH 9-10), 1 mL of zincon 1×10^{-4}M and various volumes of 1×10^{-4} M zinc(II) solution were made up to the mark with double distilled water.

Calibration curve: A series of solutions containing different amounts of the metal ion were prepared as per the general experimental procedure. The absorbance of the solutions was

measured at λ_{max} = 620 nm after 15 minutes of sample incubation at room temperature. The linear relationship between the concentration of the metal ions associated with zincon and the absorbance, against the reagent blank, served as the basis for the determination of the total metal ion concentration. A calibration curve drawn between absorbance and the metal ion concentration indicates that Zn^{2+} can be determined in the concentration range 0.25×10^{-5}M to 2.25×10^{-5}M, after treating with the Least Square Method. The calibration curve is shown in the Figure 2.

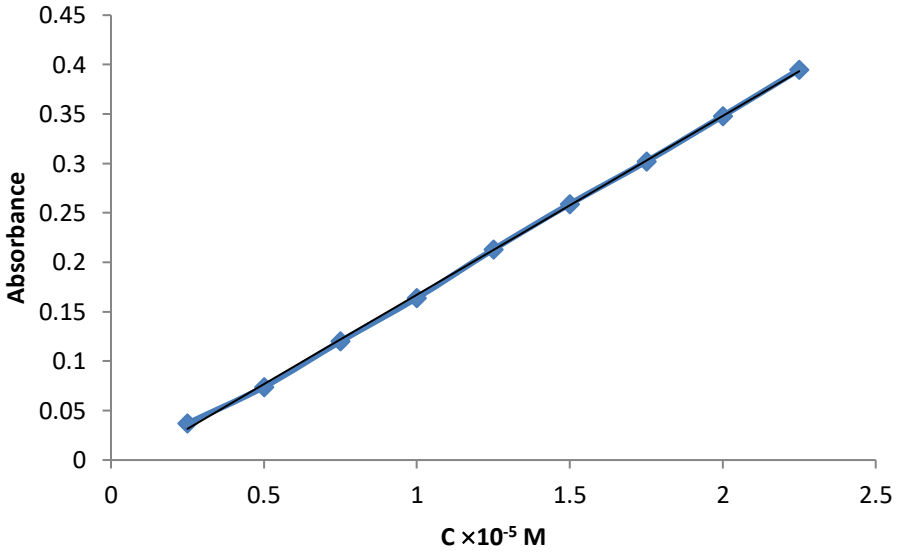

Figure 2: Analytical determination of (Zn^{2+} ~zincon) complex- under general procedure

y = 0.1809x - 0.0136 …… (1)

Coefficient of correlation = 0.9995

The curve has indicated applicability of Beer-Lambert's Law over the region 0.25×10^{-5}M to 2.25×10^{-5}M and straight line equation. The liner plot between the absorbance and the amount of zinc (II) ion is drawn and the straight line obeys the equation (1).

Results and discussion

Complex formation: Zinc(II) reacts with 2-carboxy-2′-hydroxy-5′-sulfoformazylbenzene, Zincon, and forms a blue colored complex in basic medium. The absorption spectra of the solution containing zinc(II) complex in visible region changes with pH 9-10 against the

reagent blank and also that of the reagent solution against the corresponding buffer blank were recorded in the wavelength region 580-700 nm, as illustrated in Figure 3.

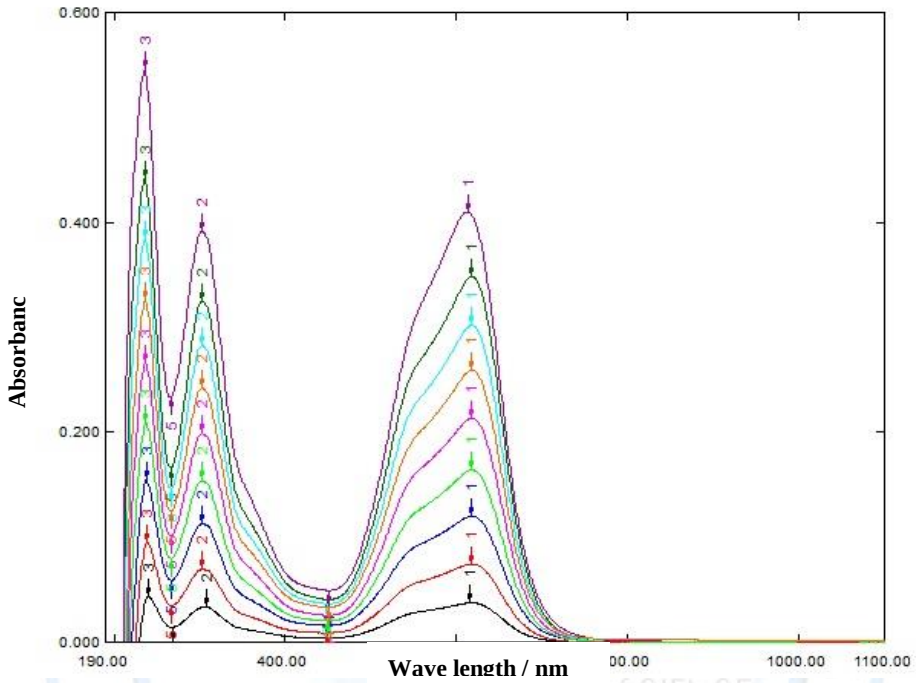

Figure 3: The absorption spectra of the solution containing zinc (II) complex

The spectrum shows that zinc (II) complex has absorption maxima at 620nm. At 620 nm, the reagent does not show considerable absorbance. Absorption spectra: Zinc(II), which reacts sensitively with zincon to form blue colored complexes in the aqueous media, is a fast process. Their absorption spectra show in Figure 4.

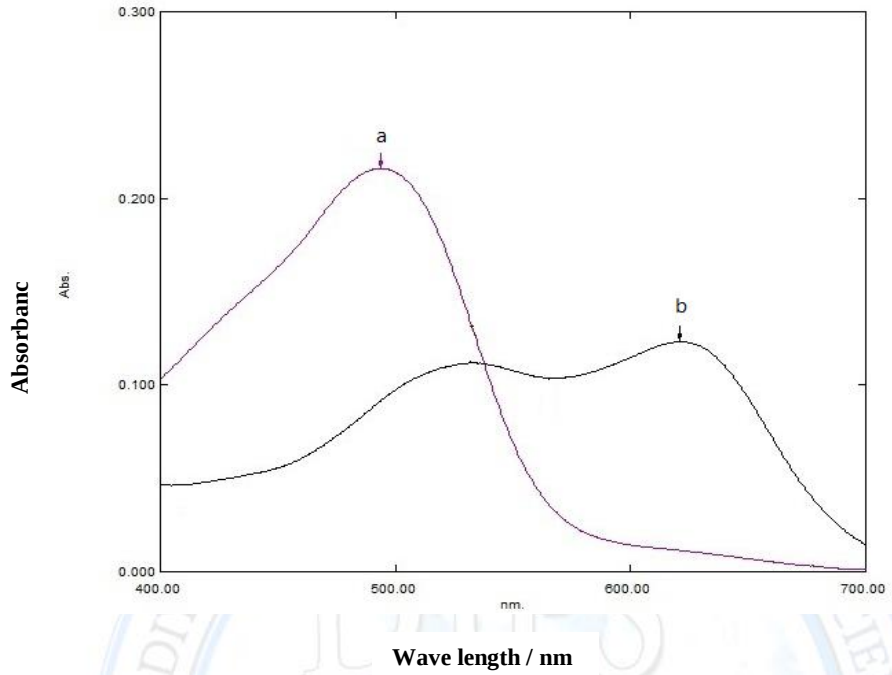

Figure 4: Absorbance Spectra for (a): 1×10^{-5} M solutions of zincon ligand against 0.025 mL NaOH (1M) + deionized water as blank, (b): Zinc complex solution at pH 9 against a solution of reagent as blank

The colored solutions were highly stable for at least 7 days under 4°C. Absorbance curve measured every 10 minutes, beginning at 400nm versus deionized water with buffer solution blank. Hence, 620nm was chosen for further studies [10]. Stoichiometry of the complex Job′s method: One method that is widely applicable is job′s method of continuous variation [21, 22].Separate standard solutions of the electropositive ion and the complexing agent are mixed in different molar proportions such that the total molarity is constsnt , i.e. the mole fraction of both the zinc ion and zincon are varied within a fixed total molarity, as shown in Table 2.

Table 3: Data of continuous variation method (Job′s method) to determination of Stoichiometry of (Zn^{2+}~zincon) complex

no.	V_{Zn2+}/mL	V_{zincon}/mL	$X_{Zn^{2+}}$	Absorbance
1	0.05	0.55	0.0833	0.277
2	0.10	0.50	0.1667	0.488
3	0.15	0.45	0.2500	0.635
4	0.20	0.40	0.3334	0.690
5	0.25	0.35	0.4167	0.625
6	0.30	0.30	0.5000	0.545
7	0.35	0.25	0.5834	0.450
8	0.40	0.20	0.6667	0.370

Absorbance readings for the series of solutions are pagainst the mole fractions of the zinc ion and zincon to give two intersecting stright lines, the point of intersection corresponding to the stoichiometry of the Zn~zincon complex in terms of the mole fraction, as shown in figure 5. The system is obeyed Beer-Lambert Law.

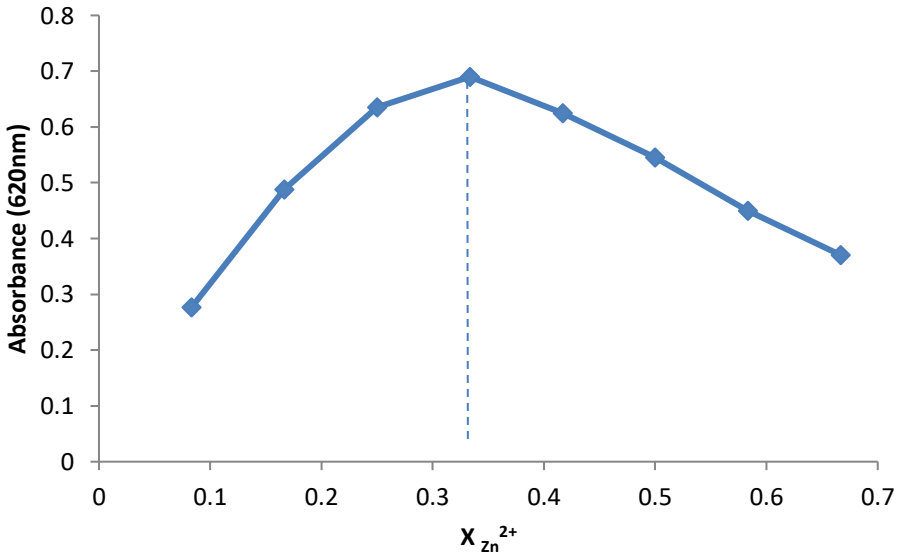

Figure 5: Continuous variation method of (Zn^{2+}~zincon) complex (Job′s method).

From Table 2 and figure 5, the value of mole fraction of zinc $X_{Zn^{2+}}$ at the point of inflection is equal to 0.33.

So that the stoichiometry of $X_{Zn^{2+}}$ is (1:2), Zn(II) to zincon.

Mole-ratio method: Another popular method for the determination of stoichiometry of complex is the mole-ratio (or the molar-ratio) method [23, 24, 25].If the molar ratio method is

used, a series of solutions are prepared in which the concentration of the other component is varied. The absorbance of the solutions are measured and plotted as a function of the ratio of ligand concentration to electropositive-ion concentration or the inverse. Alternatively, the absorbance can be plotted as a function of the concentration of the varied component in each solution or function of some other variable (such as volume) that is proportional to the concentration of the varied component. If relative stable complexes are formed and if only the complex absorbs radiation at the chosen wavelength, the absorbance of each solution increases with increased concentration of the varied component until the concentration is sufficient the cause all of the constant-concentration component to react. Further increases in concentration do not cause increased absorbance. The ratio of the ligand to the electropositive ion at the extrapolated intersection of the two linear portions of the plot corresponds to the ratio in the complex. Table 4 shows the data of Molar-ratio method to determination of (Zn^{2+}~zincon) complex stoichiometry.

Table 4: Data of Molar-ratio method to determination of Stoichiometry of (Zn^{2+}~zincon) complex

no.	V_{zincon} / mL	V_{Zn2+} / mL	Mole ratio	Absorbance at λ_{max}=620nm
1	0.4	0.05	0.125	0.203
2	0.4	0.10	0.250	0.413
3	0.4	0.15	0.375	0.570
4	0.4	0.20	0.500	0.664
5	0.4	0.30	0.750	0.675
6	0.4	0.40	1.000	0.675
7	0.4	0.50	1.250	0.673

Figure 6 drives to show Mole ratio method of (Zn^{2+}~zincon) complex**.**

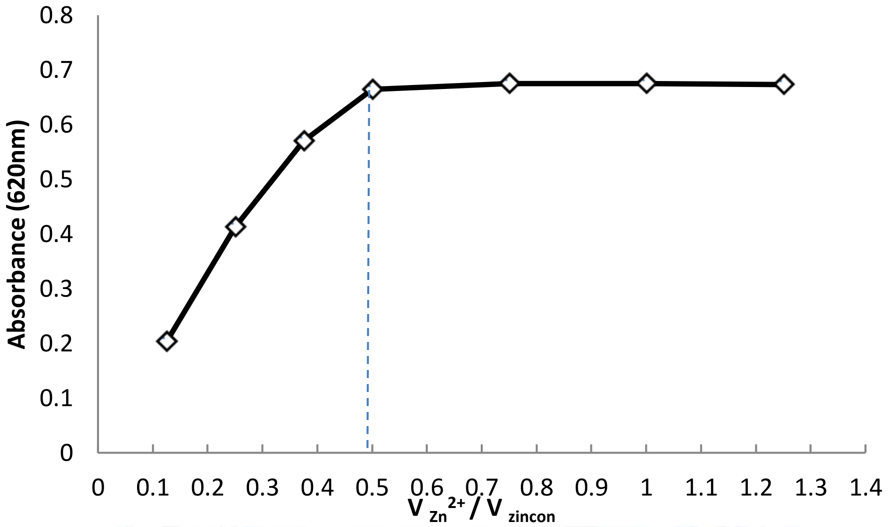

Figure 6: Mole ratio method

From Table 3 and figure 3, the value of mole ratio, at the point of inflection is equal to 0.5. That is:

$$\frac{[\mathbf{Zn^{2+}}]}{[\mathbf{zincon}]} \approx \frac{0.5}{1} \approx \frac{1}{2}$$

The stoichiometry of (Zn(II)~zincon) complex may therefore be established as (1:2)

The solution stability of a coordination compound (different from its thermal stability or its stability towards redox) deals with an equilibrium of the type [26], as shown in equation 1:

$$M + nL \leftrightharpoons ML_n \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

So the suggested tentative structure is shown in figure 7:

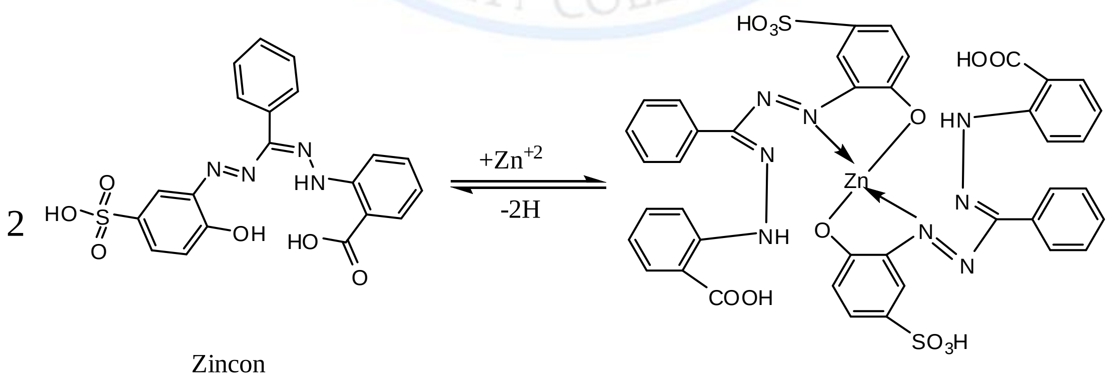

Figure 7: The tentative structure of (Zn^{2+}~zincon) complex

Applications: The proposed method was applied for the determinations zinc (II) in PVC system of drinking water in three sizes from different country samples. A known aliquot of the above sample solution is taken into a 20 mL standard flask and the zinc(II) content is determined as described is given in the general procedure. Of the 30 samples collected from three different PVC pipes, over different contact times with deionized water in PVC pipe (i.e., 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 days). The study identified the two -diameter pipes (i.e., 20 and 25 inches), at room temperature. Figure 8 presents the results from each pipe performed as well as details from these experiments.

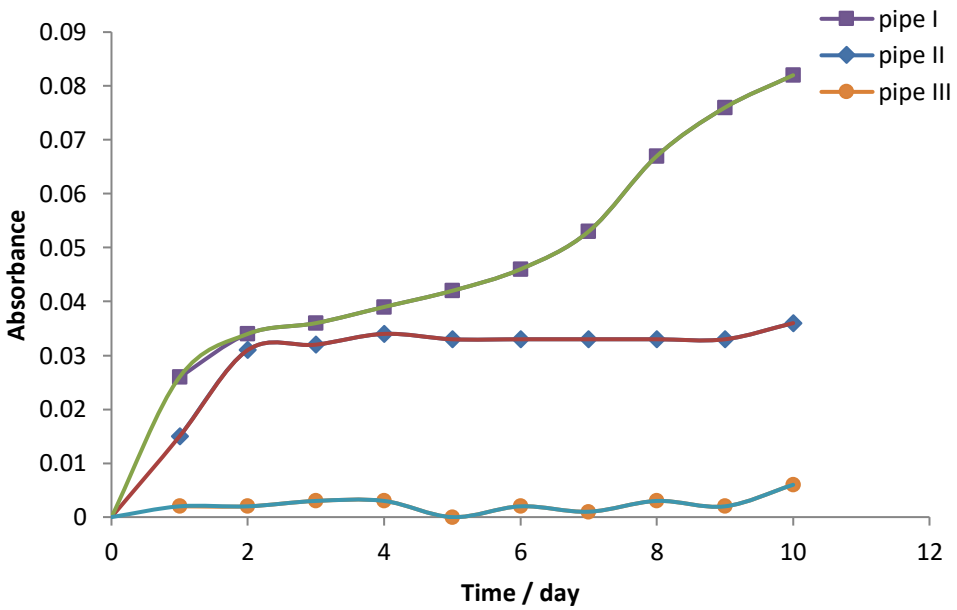

Figure 8: Plot of results of individual experiments performed in this study

The values of amount of complex precipitation calculated from three PVC pipe at different time was III << I < II. The true benefits are realized when the results are implemented at the utility level. The foundation's trustees are pleased to offer this publication as a contribution toward that end.

Conclusion

A method for the simultaneous determination of zinc(II) using spectrophotometric and complex method is proposed. A simple, sensitive, inexpensive, and non-polluting scheme for the simultaneous determination of zinc(II) was developed. No instances of complexion violations associated with leaching from PVC mains manufactured by three different

countries were cited in the literature. Additional research is required to estimate the quantity of PVC mains still in use. The method has good sensitivity, compared with other spectrophotometric determination methods. The selectivity of this method is enhanced by using masking agents for Zn (II). Finally, the developed method can be considerably declared for the determination of Zn (II) in water of PVC pipes.

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