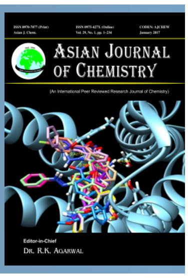
Asian Journal of Chemistry; Vol. 29, No. 5 (2017), 1065-1068

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20410



Analysis of Strontium(II) Ion by Turbidimetric Method Using Schiff Base Derivative

AHMED FADHIL KHUDHAIR*, SHAYMAA IBRAHIM SAEED, SAWSAN KHUDHAIR ABBAS and HUSSEIN MUBARAK MOHSIN

Department of Chemistry, College of Science, University of Kerbala, Kerbala, Iraq

*Corresponding author: E-mail: aliahmed79f@yahoo.com; ahmedfadhilkhudhair@gmail.com

Received: 14 November 2016; *Accepted*: 23 January 2017; *Published online*: 10 March 2017; AJC-18301

A sensitive and selective batching turbidity method was proposed for the quick determination of strontium(II) ion in analytical sample using Schiff base derivative. The proposed method was supported by the viscose cloud formation by reacting strontium(II) ion with Schiff base derivative and sodium dodecyl sulfate surfactant at pH 4.06. Linearity was observed from 0.5-3.0 μg mL^{-1} with detection point of accumulation of 0.057 μg mL^{-1}. Recovery and relative error values of precision and accuracy of the method were found to be RSD % 4.38 %. The proposed method was applied successfully in the determination of strontium(II) in different natural samples.

Keywords: Strontium, Schiff base derivative, Cloud point extraction, Turbidity.

INTRODUCTION

Strontium in its elemental form takes place naturally in many partitions of the environment, counting rocks, water and air. Its chemical substances traveled throughout the environment practically simply, due to a lot of the compounds are soluble in water [1]. The cloud point extraction (CPE) is a tool to pre-concentrate and separate most of the trace elements from many chemical and biological systems [2]. It is isolated into two layers: one phase containing a higher surfactant concentration in a little volume and an another phase with a surfactant near to the critical micelle concentration [3]. Cloud point extraction can be coupling with turbidity method to determine bismuth(III) ion, this process is based reaction between Bi(III) ion with fuchsine reagent and sodium dodecyl sulfate (SDS) as a micelle compound in aqueous solution to form red ion-pair complex as turbid phase [4]. Literature survey reveals those various analytical methods have been reported for determination of strontium ion in natural samples which include ICP-MS technique to determinate of strontium isotope ratio of brown rice [5] and in wine in orderliness to be used as a finger mark of its regional origin [6], Other methods reported in the literature for determination of strontium *e.g.*, flame photometric determination of strontium in sea water [7]. In the present study, an attempt has been made to establish a new method for the extraction of strontium ion by CPE and its detection by turbidity method. The method is based on the formation of an ion-association hydrophobic complex between strontium ion and Schiff base as a synthesized reagent in acidic medium and subsequently extracted into the surfactant SDS at optimum status. The proposed method was applied for the determination of strontium(II) ion in different environmental matrices.

EXPERIMENTAL

All reagents and solvents were procured commercially and utilized as received, toluidine 99 % (Fluka), vaniline 99 % (Fluka), absolute ethanol 100 % (GCC) and glacial acetic acid 98 % (GCC). The apparatus were used to prepare the organic reagent and determine the strontium ion as the IR spectra were recorded using KBr discs 4000-400 cm^{-1} on an FT-IR test scan Shimadzu model 8400 while the UV-visible spectra were recorded in DMSO on a Shimadzu 160A UV-Visible spectrophotometer using 1 cm quartz cells and the Gallen kamp capillary melting point apparatus was used to measure the melting point of the ligand. A Lovibond turbidimeter-Germany have 1 cm cells which are standardized with series concentration for formazine solutions from 10 to 1000 NTU while pH meter (a Bench Top) was used for pH measurements.

Preparation of Schiff base derivative: The *o*-toluidine (1.06 g, 0.005 mol) was dissolved in absolute ethanol (20 mL) containing two drops of glacial acetic acid, then equal amount to 0.010 mol of 4-hydroxy,5-methoxybenzaldehyde was added. The reaction mixture was refluxed with stirring on a water bath at 70 °C for 3-4 h. TLC (Et_2O:*n*-hexane, 2:1) showed that the reaction was completed. The mixture was then allowed to cool down to room temperature and yellow coloured precipitate was filtered then recrystallized from ethanol.

Cloud point extraction method: The viscosity cloud formation was obtained by 10 mL solutions contain 25 μg mL^{-1} Sr(II) ion added to 0.5 mL of 1 mmol L^{-1} for new synthesis Schiff base then mixed with 0.5 mL from 0.4 % w/v SDS was adjusted to related pH 4.0, the miscellanea mixture shaken for 1 min and left to stand in a thermostatic bath at 60 °C for 18 min, the precipitate was formed as Sr(II)-Schiff base-SDS system, the bulk aqueous phase was readily evaluated by turbidity meter to measure the attenuation of incident light.

RESULTS AND DISCUSSION

Characterization of ligand: The ligand was insoluble in water but soluble in DMF and DMSO solvents. The FT-IR spectra as shown in Fig. 1a and 1b of synthesized bisimine derivative [Schiff base] illustrated good evidence that the condensation reactions happened successfully by disappearing the sharp bands at (3468, 3410) cm^{-1} and (3373, 3338) cm^{-1} which attributed to the asymmetric and symmetric stretching vibrations of the two amino (-NH$_2$) groups in *o*-toluidine, also disappearing the sharp and strong band at 1624 cm^{-1} due to the scissoring bending vibration of (-NH$_2$) groups and appearing sharp and medium-strong band at lower frequencies at the general range (1626) cm^{-1} assigned to the stretching vibration of imine (C=N) group. Other data of functional groups and some physical properties for ligand was illustrated in Table-1.

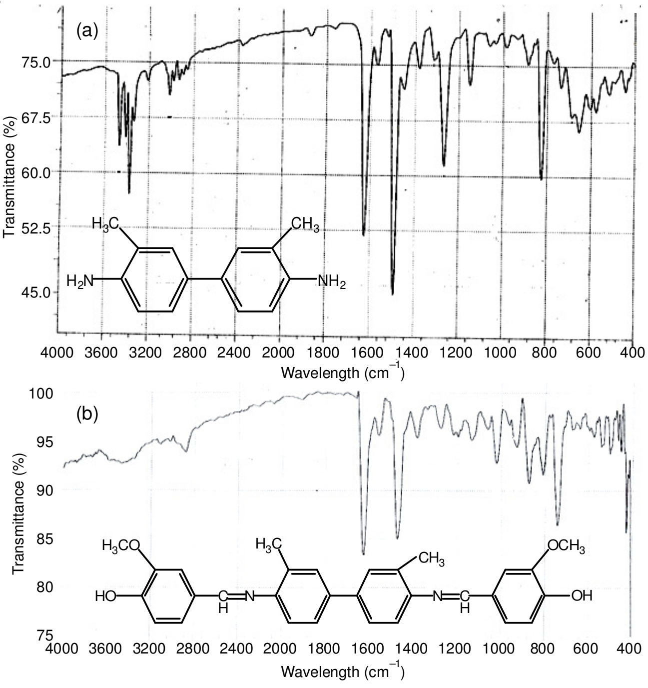
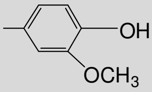


Fig. 1. FT-IR spectra of (a) the *o*-toluidine (b) the Schiff base

^{1}H NMR spectrum: Proton magnetic resonance spectra of Schiff base was showed the following signals at δ (ppm); the singlet signals at 2.302 ppm belongs to methyl groups proton, (6H, 2×CH$_3$) (Fig. 2). The singlet signal at 3.855 ppm attributed to methoxy groups, (6H, 2×H$_3$C-O). The signal at 2.423 ppm belongs to DMSO-d_6 solvent. The singlet signal at 3.345 ppm due to H$_2$O in DMSO solvent [8]. The signals at the range (6.904-7.563) ppm attributed to aromatic protons. The signals at the range (8.397-8.839) ppm belong to imine group while the signal at 12.171 due to (O-H) proton.

TABLE-1
PHYSICAL PROPERTIES AND OTHER CHARACTERISTICS FOR THE SYNTHESIZED BISIMINE AND FT-IR CHARACTERISTIC BANDS AND THEIR LOCATION OF THE BISIMINE COMPOUND

m.f.	$C_{30}H_{28}N_2O_4$
m.w. (g/mol)	480.2
Colour	Yellow
Yield (%)	79
m.p. (°C)	181-184
Ar	
ν(C–H) aromatic	3021
ν(C–H) aliphatic	2885
(C=N)	1628
ν(C=C) aromatic ring	1558
ν(C–N)	1276
ν(O–H)	3421

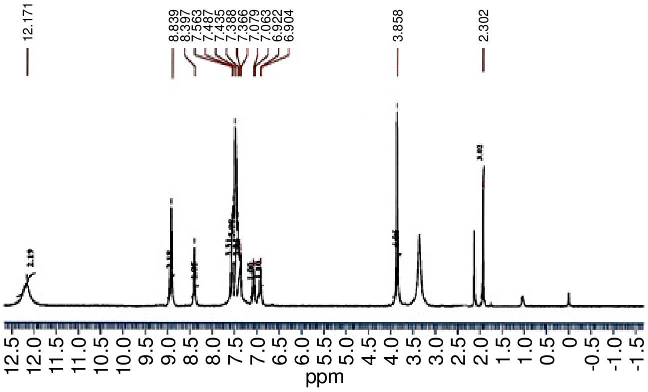


Fig. 2. ^{1}H NMR of Schiff base

Optimization of cloud point extraction procedure: With a specific end goal to accomplish most extreme extraction effectiveness by CPE, a few parameter lead a generous part in the extraction and gathering of the Sr(II) ion. The most critical are; order addition effect, pH effect, organic reagent concentration and the SDS amount and the time with the favourite temperature were fixed.

Effect of order addition: The orders of addition of solution are inspected and the outcomes appear in Table-2. From the results, the system (I) has been used for a subsequent experiment, because of the most significant affectability.

TABLE-2
ORDER ADDITION EFFECT [CONDITIONS: 25 mg L^{-1} Sr(II) ION; 0.05 mmol L^{-1} AQUEOUS SOLUTION ANALYTICAL REAGENT (A$_1$); 0.2 % (w/v) SDS]

Number of solution	Order addition	Turbidity (NTU)
I	M + A$_1$ + S	54.0
II	M + S + A$_1$	16.8
III	A$_1$ + M + S	52.5
IV	A$_1$ + S + M	20.0
V	S + M + A1	20.8
VI	S + A$_1$ + M	18.6

Strontium (M), SDS (S), Analytical reagent (A$_1$) – Schiff base

Effect of analytical reagent concentration: The effect of concentration of the Schiff base on the CPE in estimation the Sr(II) was used the various concentrations of (0.01-0.07 mmol L^{-1}. Table-3 tabulated the results which was demonstrated the optimum concentration at 0.05 mmol L^{-1} of the Schiff base. As it is seen for the turbidity of complex, the signal increases up to a known concentration of ligand, reach a plateau, which is considered as the top determination to strontium(II) ion.

TABLE-3
ANALYTICAL REAGENT (A_1) CONCENTRATION EFFECT ON THE TURBIDITY MEASUREMENT

[Schiff base] (mmol L^{-1})	Turbidity measurement (n = 3)	RSD (%)	Confidence interval at 95 % $\bar{y} \pm t_{0.05/2}\sigma_{n-1}/\sqrt{n}$ (n = 3) (NTU)
0.01	22.50	2.67	22.50 ± 1.49
0.02	26.53	1.52	26.53 ± 1.01
0.03	34.30	0.50	34.30 ± 0.43
0.04	38.40	0.90	38.40 ± 0.86
0.05	54.37	0.56	54.37 ± 0.76
0.06	48.57	1.13	48.57 ± 1.37
0.07	36.80	1.26	36.80 ± 1.14

Effect sodium dodecyl sulfate amount: The amount of surfactant was utilized in the CPE as an important factor. SDS was chosen because of its commercial availability in a high-purified homogeneous, low toxicological property and low-cost compound as well as the good density of the surfactant-rich phase. The influence of surfactant concentration on the determination of Sr(II) was examined within the SDS concentration range from 0.02 to 0.36 w/v %. Table-4 was illustrated that the measured turbidity increase with increasing concentration of the surfactant and after that decreases when the surfactant concentration is more than 0.04 % (w/v) SDS. Therefore was used achieve the highest determination efficiency.

TABLE-4
EFFECT OF SDS SURFACTANT AMOUNT ON THE TURBIDITY MEASUREMENT, [CONDITIONS: Sr(II) = 25 µg mL^{-1} of 0.5 mL OF LIGAND = 1 × 10^{-3} M]

Concentration of SDS (w/v %)	Turbidity measurement (n = 3)	RSD (%)	Confidence interval at 95 % $\bar{y} \pm t_{0.05/2}\sigma_{n-1}/\sqrt{n}$ (n = 3) (NTU)
0.02	49.80	0.60	49.80 ± 1.50
0.04	72.83	0.32	72.83 ± 0.79
0.12	66.53	0.38	66.53 ± 0.94
0.20	54.57	0.21	54.57 ± 0.53
0.28	42.27	1.12	42.27 ± 2.78
0.36	31.53	0.18	31.53 ± 0.46

Effect of pH: This factor played a critical role in the metal complex formation and subsequent extraction and has been a significant parameter for CPE. Thus, extraction yield depends on the pH of which complex formation is investigated. A set of similar experiment was carried out in the pH series of 2.0-12.0 by utilizing diverse pH solutions (0.1 M HCl and 0.1 M NaOH). As appeared in Fig. 3 that the turbidity first increased sharply with increasing pH and achieved a greatest at pH 4.06 demonstrating extraction effectiveness was accomplished. The turbidity was gradually decreased because of partial dissociation of the complexes at higher pH, which may product in an unfinished extraction of a complex. Therefore, pH 4 was selected as the optimum workings pH for a full formation of Sr(II)-Schiff base-SDS complex manipulation and hence an extraction.

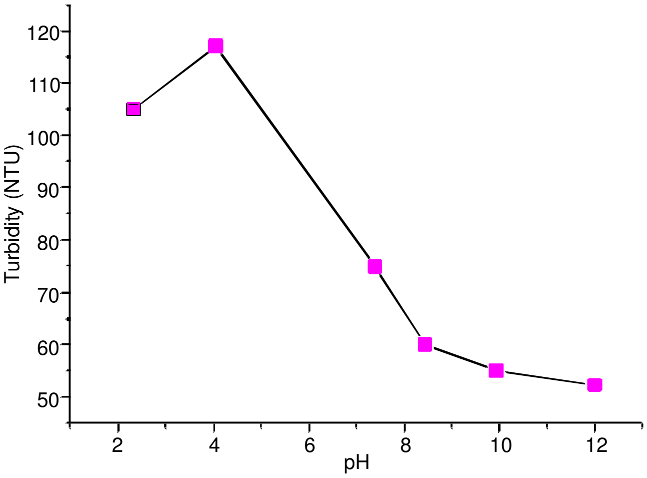


Fig. 3. Effect of pH on the formation of Schiff base-Sr(II) complex

Effects of equilibrium measure temperature and time: It was attractive to utilize the shortest equilibration time and the lowest probable equilibration temperature, as cooperation between finish point of extraction and efficient separation of phases. Therefore, the effect of equilibration temperature in the range of 30-90 °C was examined. It was found that 50 °C is satisfactory and enough to complete extraction and measure Sr(II) ion. The confidence of extraction productivity upon equilibration time was additionally examined for a time interval in a period 5-45 min. An equilibration time of 20 min was chosen as an optimum value. The temperature and time influence on the Sr(II) ion determination by turbidity signal were shown in Fig. 4a and 4b respectively. The stability of the complex that study by measuring with time leaving, it is illustrated the stability of the complex for a long time.

Scatter line characteristic method: A calibration curve of turbidness against the concentration of Sr(II) solutions was adjusted by pulling together the turbidity signals of different volumes of Sr(II) standard solutions submitted to the method proposed. Under the optimum trial conditions, the scatter line for Sr(II) ion is linear from 0.5 to 30.0 µg mL^{-1} with a correlation coefficient 0.9994. Table-5 gives the parameters of the calibration curve, the relative standard deviation obtained for 8 replicates subjected to the complete procedure and the detection limit. The limit of detection defined as $3S_b/m$ is 0.057 µg mL^{-1}.

TABLE-5
EFFECTIVE PARAMETERS OF THE CALIBRATION CURVE

Parameter	Value
RSD	0.043803
Accuracy	99.39112 ± 4.353593
Slope	9.7183
Intercept	1.6171
Correlation coefficient (R^2)	0.9994
Range	0.5-30 µg mL^{-1}
SE of intercept	1.405
SD of intercept	4.215
LOD (3.3 × SD of intercept/Slope)	1.4313
LOQ (10 × SD of intercept/Slope)	4.337178
t_{cal}	110.22 > t_{tab} at 95 % (2.447)

TABLE-7
STRONTIUM(II) ION ANALYSIS IN DIFFERENT NATURAL SAMPLES

Type of sample	Hosseinieh river	Indian river	Macon river	Hosseinieh soil	Indian soil	Macon soil
Concentration of Sr(II) (μg mL^{-1})	13.72	8.37	10.74	15.78	5.70	10.32

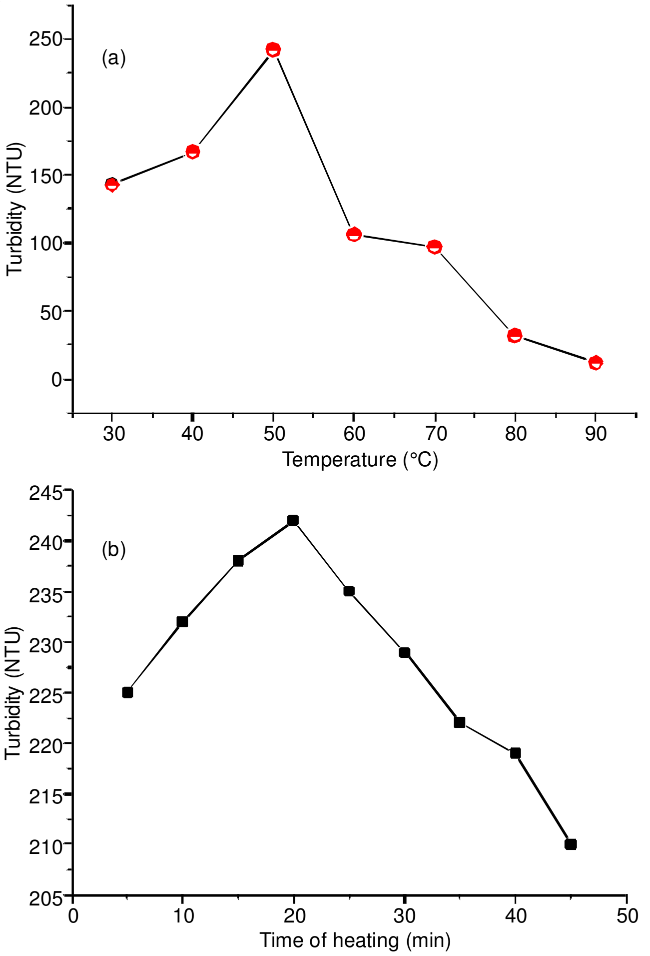


Fig. 4. Turbidity signals outcome effected by a variety of (a) temperature (b) time of heating. [The conditions : Sr(II) = 25 μg mL^{-1} of 0.5 mL of ligand = 1×10^{-3} M, 0.1 mL of 4 % (w/v) SDS at pH 4.06]

Repeatability: The estimation value of the relative standard deviation (RSD %) for Sr(II) 25mg.L^{-1} was demonstrated in Table-6. The percentage relative standard deviation under 1 % was obtained demonstrating a dependable estimation can be accomplished utilizing this method.

TABLE-6
REPEATABILITY OF Sr(II) AT OPTIMUM PARAMETERS

[Sr] (μg mL^{-1})	Average response (n* = 8)	RSD (%)	Confidence interval at 95 % $\bar{y}_i \pm t_{0.05/2,\, n-1}\sigma_{n-1}/\sqrt{n}$
25	242	0.52	242.00 ± 1.042

n* = Number of repeated measure, $t_{0.05/2,7}$ = 2.365

The new method was utilized to the assurance of strontium ion in different waters and soils sampling from Kerbala community. Table-7 is tabulated the summary of results from the six sampling.

Conclusion

The new, rapid, easy and low cost method was utilized to evaluated strontium ion in different environmental samples that based on pre-concentration metal ion by cloud point extraction method by forming a solid ion-association hydrophobic complex depending on the reaction between strontium ion with a Schiff base as a synthesized reagent in acidic medium and subsequently extracted into the surfactant SDS at the optimum conditions.

REFERENCES

1. G. Apaydin, V. Aylikci, E. Cengiz, M. Saydam, N. Kup and E. Tirasoglu, *Turk. J. Fish. Aquat. Sci.*, **10**, 215 (2010); https://doi.org/10.4194/trjfas.2010.0209.
2. C.K. Wei, *The Experiment*, **34**, 2122 (2015).
3. W.I. Mortada, M.M. Hassanien and A.A. El-Asmy, *Egypt. J. Basic Appl. Sci.*, **1**, 184 (2014); https://doi.org/10.1016/j.ejbas.2014.07.001.
4 A.F. Khudhair and S.I. Saeed, *Int. J. Sci. Res.*, **5**, 218 (2016).
5. A. Kawasaki, H. Oda and T. Hirata, *Soil Sci. Plant Nutr.*, **48**, 635 (2002); https://doi.org/10.1080/00380768.2002.10409251.
6. C.M. Almeida and M.T.S.D. Vasconcelos, *J. Anal. At. Spectrom.*, **16**, 607 (2001); https://doi.org/10.1039/b100307k.
7. T.J. Chow and T.G. Thompson, *Anal. Chem.*, **27**, 18 (1955); https://doi.org/10.1021/ac60097a006.
8. R.M. Silverstein, F.X. Webster and D.J. Kiemle, Spectrometric Identification of Organic Compounds, John Wiley & Sons, Inc., USA, edn 6 (2005).