Photoluminescence Property of 1-(2-Hydroxyphenyl)thiourea and its Quenching by Chromium(VI) Ions

A Sunil and S Jagadeeswara Rao
Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Prasanthi Nilayam, Puttaparthi-515134, Anantapur, Andhra Pradesh, India.
E-mail: asunil@sssihl.edu.in

Abstract. 1-(2-Hydroxyphenyl)thiourea is a fluorogenic compound and it undergoes a very slow autooxidation to form an yellow coloured disulphide, 1-hydroxy-2-[([N-(2-hydroxyphenyl) carbamimidoyl]disulfanyl carbamimidoyl) amino] benzene. In the presence of chromium(VI) ions, the rate of formation of the disulphide increases which results in the quenching of fluorescence. This analytical property has been utilized for chromium(VI) determination. The emission studies were recorded at $\lambda_{Ex}=416$nm and $\lambda_{Em}=520$nm respectively. The influence of analytical properties, role of surfactants and activators are reported. Fluorescence quenching studies have been experimentally verified using Stern-Volmer plots.

1. Introduction

There is an expeditious requisition for conscientious and reliable analytical methods for the determination of chemical forms of elements that are toxic and pose harm to the environment. Chromium is one such element that most frequently occurs as chromium(VI) or chromium(III) in aqueous solutions. Among these, chromium(VI) is known to be a strong oxidizing agent, posing a high risk to humans and animals due to its carcinogenic and mutagenic properties\[1\]. That is why the determination of chromium in environmental and biological samples is of great interest.

Chromium has versatile industrial applications and enters the environment as a result of effluent discharge from industries. The major industries that contribute to water pollution by chromium are mining, leather tanning, textile dyeing, electroplating, aluminum conversion coating operations, plants producing industrial inorganic chemicals and pigments, and wood preservatives. Therefore, the level of chromium in expelled industrial wastewater should be monitored\[2\].

Many sophisticated techniques such as electro-osmosis\[3\], flame atomic absorption spectrometry\[4\], electrothermal atomization\[5,6\], flow injection analysis\[7\], electro analytics\[8\] etc. have been utilized for determination in trace levels but they are tedious and require very expensive equipment. Fluorescence based analytical techniques are very attractive because fluorescence measurements are consistently very sensitive (parts per billion/trillion), relatively cheaper and easy to monitor\[9\]. Catalytic methods have proved to be more economical and impeccable alternative tool to the instrumental analyses for trace determinations\[10\]. Catalytic methods for chromium sensing are mostly developed based on its effect on the oxidation of organic compounds with appropriate oxidant, most frequently hydrogen peroxide\[11-13\]. The current method utilizes the auto-oxidation property of
1-(2-Hydroxyphenyl)thiourea (A) to form its disulphide (B). This special indicator reaction led to the ascendancy of the current proposed method.

2. Experimental

All the chemicals used in the investigation are of analytical grade with high purity (Sigma Aldrich Chemicals Ltd) and HPLC grade solvents (Merck). The buffer solutions for pH studies were prepared as prescribed by Vogel[14]. MICROPRO pH meter was used for all the pH adjustments. Quartz cells of 10mm path length (Hellma make) were used to record the emission and excitation intensities of the chromophore in Perkin Elmer LS-55 fluorospectrophotometer. Mettler Toledo: AB204-S was utilized for all the weight measurements.

Compound A was synthesized as per the standard procedure [15,16]. 1.0mL of potassium phosphate buffer solution (pH=8.0) and appropriate amount (0.3ng/mL-320ng/mL) of chromium(VI) solution were pipetted in to a 10.0mL volumetric flask, followed by 1.0mL of 1% 2,2'-bipyridyl and 1.0mL of 1% sodium dodecyl sulphate (SDS). The temperature was maintained at 25°C. 3.0 mL of 1-(2-Hydroxyphenyl)thiourea (1mg/mL) solution was then added and millipore water was added up to the mark. The resulting reaction mixture was transferred into 10mm quartz cuvettes of fluorospectrophotometer. The fluorescence emission measurements were recorded at $\lambda_{\text{Em}}=520\text{nm}$ upon excitation at $\lambda_{\text{Ex}}=416\text{nm}$ respectively at 20th minute. The blank experiments were repeated by following the same procedure to obtain relative fluorescence intensity $I_0$ and the value of $I_0-I$ was calculated. The calibration graph was plotted and the method was applied for the determination chromium in waste water samples. Water samples were boiled, treated with concentrated nitric acid and then filtered to remove organic particulate matter before using for the analysis.

3. Results and discussion

Compound A undergoes a very slow auto-oxidation to form B and based on its auto-oxidation property which was reported[17], determination of cadmium(II), copper(II) and mercury(II) was done[18, 19]. The excitation and emission studies of A were studied thoroughly, which reveals that A is fluorogenic in nature and the catalytic action of hexavalent chromium leads to the product formation B quickly with a visible colour change and a drop in fluorescence intensity. By monitoring both the colour and signal changes the quantification of chromium was done. Various analytical parameters were studied for reporting the ambient reaction conditions. Activators and surfactants were used to enhance the sensitivity to much lower limits of detection. The fluorescence emission studies were done by excitation of compound A at $\lambda_{\text{Ex}}=416\text{nm}$, which gave a good emission peak at $\lambda_{\text{Em}}=520\text{nm}$. At this emission wavelength, the intensity of the chromophore starts reducing upon addition of chromium(VI). The experimental observations show that fluorescence quenching of A is proportional the concentration of chromium(VI) added.

![Figure1. Chromium(VI) sensing based on photoluminescence property of ‘A’](image-url)
The investigation of analytical parameters such as pH, reaction time, temperature, concentration of the reagent and chromium(VI) ion were studied. It was evident from the recorded observations that the chromium(VI) catalysed transformation of A to B is more pronounced at pH~8. Hence, the same pH was maintained throughout the study. The rate of reaction showed no significant improvement upon altering temperature. Therefore, the investigation was carried out at normal laboratory temperature of 25°C±5°C. Optimum concentration of A was determined to be 3mg/mL and the same concentration was maintained throughout the investigation. By varying the concentration of chromium(VI) ion in the range 0.3ng/mL-320ng/mL, fluorescence emission study was done. The fluorescence spectrum [figure2(I)] shows that the intensity quenches linearly with the increase in concentration of chromium(VI) ions, which was supported and proved using the Stern-Volmer plot [figure2(II)]. The Stern-Volmer plot is obeyed in the range 10 ng/mL-250ng/mL of chromium(VI) with Stern-Volmer quenching constant, $K_{SV} = 0.929$ indicating a good linearity in the method.

![Figure2. (I) Fluorescence spectrum showing the quenching of 1-(2-Hydroxyphenyl)thiourea by chromium(VI) ions. (II) Stern-Volmer plot showing the efficiency of fluorescence quenching](image)

Activators and surfactants have been used to improve the sensitivity of the method. The activators such as 1,10-phenanthroline, bathophenenthroline, pyridine, 2-aminopyridine, quinoline, 2,2'-bipyridyl, nicotinic acid were used and the observations show that 1% 2,2'-bipyridyl enhanced the reaction rate in the formation of product B. One can achieve more stable reaction conditions using micellar medium and to observe the effect of surfactants on the reaction, surfactants such as cetyltrimethylammonium bromide(CTAB), Tween-80, Triton-X, sodium dodecyl sulphate(SDS) were used and 1% SDS has showed a promising effect on the reaction rate. In this current investigation, the synergy of 2,2'-bipyridyl and SDS in enhancing the sensitivity is a notable result. Without the activator and surfactant system, the determination was possible only till 30ng/mL but, by using the same, the sensitivity was enhanced up to 0.3ng/mL. In current range of determination many metal ions like manganese(II), cobalt(II), arsenic(V), lead(II), mercury(II), cadmium(II), zinc(II), rhodium(III), iridium(III), platinum(II), silver(I), molybdenum(IV) do not interfere at all. Iron(II) and copper(II) interfere very slightly but, can be eliminated by the addition of fluoride and thiosulphate respectively. The method is fairly sensitive and was applied to determine the chromium(VI) content in waste water.
samples using the calibration curve. Recovery test was done to validate the method with a satisfactory range of 98%-102%.

4. Conclusions

A simple and sensitive photoluminescence technique has been developed for determination of hexavalent chromium, exhibiting a good number of advantages compared to the various methods reported earlier. The reaction utilized in the investigation is an auto-oxidation reaction and hence, no need for any oxidizing agents unlike other methods. Reagent synthesis is very simple, cost effective and starting products required for synthesis are also inexpensive. The method is bench-stable with no inert conditions required and can be done at normal room temperature. No pre-concentration procedures are involved. The sensitivity levels are greater or equivalent to some of the earlier methods.

Acknowledgements

The authors sincerely acknowledge the inspiration and support rendered by the Founder Chancellor, Bhagawan Sri Sathya Sai Baba and authorities of Sri Sathya Sai Institute of Higher Learning.

References

[1] Barceloux DG 1999 Clin. Toxicol. 37(2) 173-194
[2] Dakiky M, Manassra A, Mereb M 2002 Adv. Environ. Res. 6(4) 533-540
[3] Gan W, Yang L, He Y, Zeng R, Cervera M L and De La Guardia M 2000 Talanta 51(4) 667-675
[4] Anthemidis A N, Zachariadis G A, Kougioulis J S and Stratis J A 2002 Talanta 57(1) 15-22
[5] Ezer M, Elwood S A and Simeonsson J B 2001 J. Anal. At. Spectrom. 16(10) 1126-1130
[6] Nise G and Vesterberg O 1979 Scand. J. Work Environ. Health. 5(4) 404-410
[7] Paleologos E K 1998 Analyst 123(5) 1005-1009
[8] Lin L, Lawrence N S, Thongngamdee S, Wang J and Lin Y 2005 Talanta 65(1) 144-148
[9] Quang D T and Kim J S 2010 Chem. Rev. 110(10) 6280
[10] Yatsimirskii K and Tikhonova L 1987 Talanta 34(1) 69-75
[11] Mohamed A A, Ahmed S A and El-Shahat M F 2001 J. Trace Microprobe Tech. 19(2) 297-311
[12] Stoyanova A M 2004 Turk. J Biochem. 29(2) 204-207
[13] Liu Z and Wang X 1996 Fenxi Huaxue (Analytical Chemistry) 24(2) 164-167
[14] Vogel A I and Jeffery G H. 1989 Vogel's Textbook of Quantitative Chemical Analysis (Longman Scientific &Technical) p 268
[15] Beilstein. 1943 Handbuch Der Organischen Chemie (Ann Arbor, Michigan) Band XIII 375 (Edwards Brothers Inc., Publishers)
[16] Sunil A and Jagadeeswara Rao S 2012 Res. J.Chem.Sc.i 2(3) 30-40
[17] Feigl F 1966 Spot tests in Organic Analysis (New York: Elsevier)
[18] Sunil A and Jagadeeswara Rao S 2012 Int. J. Curr. Res. 4(2) 210-215
[19] Sunil A and Jagadeeswara Rao S 2012 Int. J. Chem. Anal. Sci. 3(2) 1318- 1321