

TRANSITION METAL-OXO BASED SENSING OF CHROMIUM (III) USING 1, 2-HYDROXYPHENYLTHIOUREA IN ACTIVATOR AND SURFACTANT MEDIUM

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ABSTRACT

1,2-hydroxyphenylthiourea (HPTU) undergoes oxidative dimerisation to form a yellow coloured disulphide in the presence of chromium(III)-oxo species which acts as a catalyst. This catalytic process is enhanced to a great extent in the presence of 1,10-phenanthroline which played the role of an activator and sodium dodecylsulphate as a surfactant. The reaction was monitored at $\lambda_{ex} = 416 \text{ nm}$ and $\lambda_{em} = 520 \text{ nm}$. The studies reveal that the rate of reaction and the amount of chromium(III) are proportional. This sensing mechanism lead to the development of an analytical method for determination of chromium(III) using photometric and fluorometric techniques. The developed methods were applied for the determination of chromium (III) in plant and waste water samples.

Keywords: 1, 2-hydroxyphenylthiourea, Chromium(III), Photometric and fluorometric techniques, 1,10-phenanthroline, SDS.

Contribution/ Originality

This study contributes to the existing literature, a novel way to sense chromium(III) using HPTU for the first time. The methodology involved for determination is very simple and uses affordable instrumentation available in normal laboratories. The paper's primary contribution is the analytical investigation of the catalytic reaction of HPTU catalysed by chromium in the presence of activators and surfactants.

1. INTRODUCTION

Trivalent chromium is an important bio-element and plays an exceptional role in metabolic processes. It acts as a cofactor in the maintenance of both normal lipid and carbohydrate metabolism by assisting the action of insulin on a cell membrane. It also helps in lowering the levels of cholesterol and triglyceride. According to the National Research Council, the daily recommended intake of chromium (III) is 50.0 - 200.0 μg . It was reported that many organic

chromium(III) complexes have significantly higher tissue incorporation activity and absorption compared to inorganic salts such as chromium(III) chloride. Daily intake from food sources, excluding supplements is estimated to be 0.1 mg. Chromium deficiency causes impaired glucose tolerance and glucose utilisation, loss of weight, neuropathy, disturbed plasma fatty acid profile and nitrogen metabolism, and depressed respiratory quotient. Specific transport mechanisms are responsible for the transport of chromium(III) into the cells and several in-vitro studies indicated that high concentrations of chromium(III) in the cell can lead to DNA damage [1]. Moderate intake of chromium(III) through dietary supplements proves no risk.

In industry, chromium metal is used as an alloying element to harden steel and to manufacture stainless steel. Chromium compounds found their applications in chrome plating (e.g. protective coatings for automotive and equipment accessories) as dyes, inorganic paint pigments, fungicides, wood preservatives and catalysts. The large increase in the discharge of industrial effluents and sewage is the main cause of concern. The contamination of chromium in ground water makes it improper for drinking. In view of such alarming health and environmental problem, constant monitoring and analysis of chromium becomes a major necessity. In continuation of the development of suitable methods for the determination of metals, especially in natural samples, a sensitive and selective method was developed for the determination of chromium(III). Though a number of spectrophotometric methods have been reported for the determination of chromium [2], only a limited number of methods are available for chromium(III) [2-10].

Kinetic-catalytic methods for determination of metal ions have a special importance because of the levels of sensitivity that are achieved. In spite of this fact, there are less number of kinetic methods reported for chromium(III). Hence, it was proposed to contribute sensitive methods using 1,2-hydroxyphenylthiourea(HPTU) for determination of chromium(III).

2. EXPERIMENTAL SECTION

2.1. Chemicals and Instrumentation

All the chemicals used in the investigation are of analytical grade with high purity purchased from Sigma Aldrich Chemicals Ltd. The solvents used are HPLC graded purchased from Merck. The buffer solutions for pH studies were prepared as prescribed by Vogel, et al. [11]. 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 fluorescence meter. HITACHI-2001 spectrophotometer was utilized for photometric studies. Mettler Toledo: AB204-S was utilized for all the weight measurements.

2.2. Recommended Procedure

The reagent, HPTU was synthesized [12] and the analytical parameters and their influence was studied systematically. 1.0mL of acetate buffer solution of pH = 4.0 and appropriate amount (5 ng/mL - 300 ng/mL) of chromium(III) solution were pipetted in to a 10.0mL volumetric flask, followed by 1.0 mL of 1,10-phenanthroline and 1.0mL of 1% SDS. The temperature was

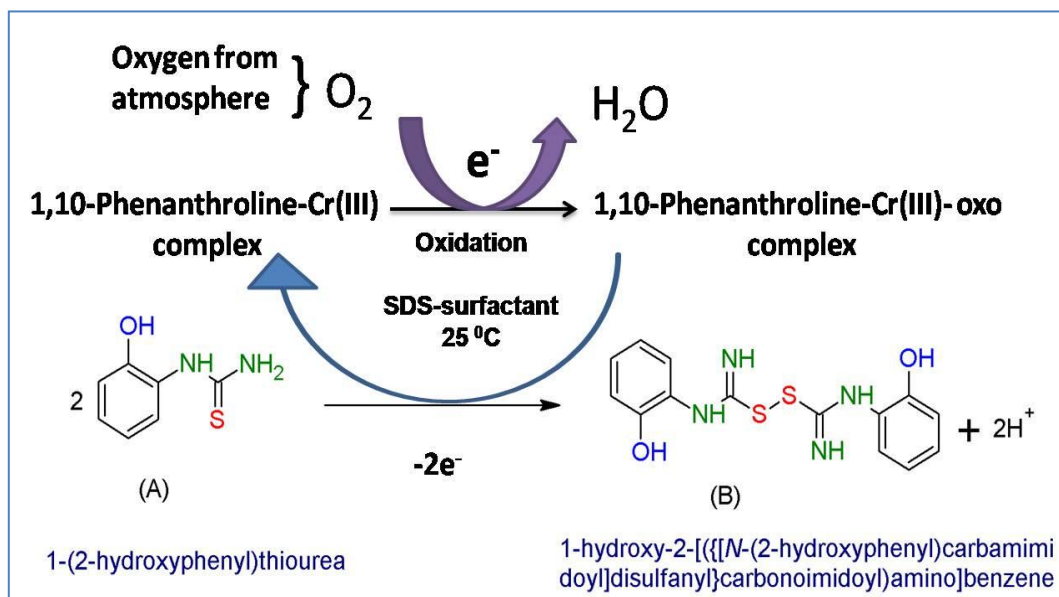
maintained at 25 °C. 2.0 mL of HPTU (1mg/mL) solution was then added and millipore water was added up to the mark. The resulting reaction mixture was transferred into 10 mm quartz cuvettes. The photometric measurements were recorded at $\lambda_{\text{Max}} = 416 \text{ nm}$. The fluorescence emission measurements were recorded at $\lambda_{\text{Em}} = 520 \text{ nm}$ upon excitation at $\lambda_{\text{Ex}} = 416 \text{ nm}$ respectively at 30th 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 of chromium in waste water and plant samples. Water samples were boiled, treated with concentrated nitric acid and then filtered to remove organic particulate matter before using for the analysis. The digestion for plant sample was done as mentioned [13].

3. RESULTS AND DISCUSSION

3.1. Proposed Mechanism

The proposed mechanism describes that chromium(III) complexes with 1,10-phenanthroline forming an organo-metallic complex. This complex reacts with atmospheric oxygen to form a highly reactive oxo-complex, which is also unstable and short lived. This reactive oxo species attains a higher oxidation state of (V) which is unstable and in order to get back to its stable state from the highly unstable one, it would accept the electrons from the HPTU. This process enables the conversion of HPTU to its disulphide. In this way the catalytic action of chromium(III) in presence of an activator and a surfactant was proposed.

Scheme-1. The proposed mechanism for the process of catalytic effect of chromium(III) on HPTU



3.2. Photometric Determination of Chromium (III)

The rate of reaction is influenced by pH of the solution, amount of the reagent, temperature of the system, the presence of certain activators, sensitizers and foreign ions associated with it. Hence the above factors were studied in detail to establish suitable conditions for higher sensitivity and simplicity in the determination. The catalysed oxidation reaction was studied in different buffers of varying pH. The reaction was sufficiently fast in acetate buffer compared to others like carbonate, borate, etc. Maximum absorbance values were recorded for chromium(III) catalysed reaction of HPTU in the pH range of 3.5 - 4.2 (Figure 1). Hence the pH was maintained at 4.0 in the investigation. The experiment was carried out by varying the amount of HPTU from 0.2 - 5.0 mg/mL and the absorbance values are recorded at 30th minute. The obtained data infers that the reaction was sufficiently fast when the concentration of HPTU is 2.0 mg/mL and above (Figure 2). Hence, 2.0 mg of HPTU was selected as the optimum amount of reagent required for the investigation. The catalysed oxidation reaction was studied by varying the temperature. Satisfactory results were recorded at room temperature itself and hence, the method was carried at normal laboratory temperature of 25 °C. Satisfactory results were obtained at 30th minute of the reaction and hence, various analytical parameters like pH, reagent concentration, etc., were studied at 30th minute. Activators like 2-aminopyridine, 2,2'-bipyridyl, quinoline, nicotinic acid, pentatic acid, etc., did not show any promoting effect compared to 1,10-phenanthroline in the determination of chromium(III) (Figure 3). Hence, 1,10-phenanthroline was selected as a suitable activator in the current investigation. CTAB, tween 80 and triton x-100 did not show any sensitizing effect in the enhancement of rate of catalysed oxidation. But the anionic surfactant, SDS showed a good enhancement in the sensitivity (Figure 4). Hence, 1% SDS was chosen as an appropriate surfactant in the investigation. The chromium(III) ion concentrations were varied in the range of 5 ng/mL - 300ng/mL and the investigation was carried out by following three approaches. The fixed time approach was followed by studying the behaviour of the reaction in the above mentioned range at 30th minute. A good linearity was observed in this particular range (Figure 5). In order to improve the accuracy of the method, the tangents' approach also was followed. A clear linearity was observed in this particular range inferring that the developed method is reliable (Figure 6 & 7). The study of kinetics of HPTU-Cr(III) reaction system infers that the order of reaction is pseudo-second order in nature.

3.3. Fluorometric Determination of Chromium (III)

HPTU undergoes a very slow auto-oxidation to form disulphide and based on its auto-oxidation property which was reported [14]. The excitation and emission studies were studied thoroughly, which reveals that HPTU is fluorogenic in nature and the catalytic action of chromium(III) enhances the product formation very quickly with a visible colour change and a drop in fluorescence intensity. By monitoring both the colour and signal changes the quantification of chromium(III) 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 HPTU 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 quenching upon addition of chromium(III). The experimental observations show that fluorescence quenching of HPTU is proportional the concentration of chromium(III) added. The influence of analytical parameters such as pH, reaction time, temperature, concentration of the reagent and chromium(III) ion were studied. It was evident from the recorded observations that the chromium(III) catalysed transformation of HPTU is more pronounced at pH range of 3.5 - 4.2 (Figure 8). Hence, the pH of 4.0 was maintained in the study. The rate of reaction showed no significant improvement upon varying temperature. Therefore, the investigation was carried out at normal laboratory temperature of 25 °C. Optimum concentration of HPTU was determined to be 2.0 mg/mL and the same concentration was maintained throughout the investigation. Activators and surfactants have been used to improve the sensitivity of the method. The activators such as 2,2'-bipyridyl, bathophenanthroline, pyridine, 2-aminopyridine, quinoline, nicotinic acid were used and the observations show that 1,10-phenanthroline enhanced the reaction rate in the formation of disulphide which is indicated by the quenching of the intensity(Figure 9). One can achieve more stable reaction conditions using micellar medium and to observe the effect of surfactants on the reaction. Surfactants such as CTAB, tween-80, triton-X, SDS were used and 1% SDS has showed a promising effect on the reaction rate (Figure 10). In this current investigation, the synergy of 1,10-phenanthroline and SDS in enhancing the sensitivity is a notable result. By varying the concentration of chromium(III) ion in the range 5 ng/mL – 300 ng/mL, fluorescence emission study was done. The fluorescence studies show that the intensity quenches linearly with the increase in concentration of chromium(III) ions, which was supported and proved using the Stern-Volmer plot (Figure 11). The Stern-Volmer plot is obeyed inferring a uniform quenching and indicating a good linearity in the method. The temperature studies also support the stern-Volmer plots, which is indicative of the collisional quenching mechanism.

3.4. Interference by Foreign Ions

The effect of various anions and cations on the determination of chromium(III) under the optimum conditions was studied in both the methods. It was clear from the interference studies that anions such as nitrate, sulphate, oxalate, phosphate, fluoride, citrate, bromide, chloride, and borate did not interfere even when present in more than 1000 fold excess. Cations such as sodium(I), potassium(I), barium(II), magnesium(II), aluminium(III), lead(II), arsenic(III), antimony(III), bismuth(III) did not interfere even above 1000 fold excess. Scandium(III), zirconium(IV) rhenium(II), zinc(II), cobalt(III), osmium(IV), tungsten(VI) can be tolerated up to 800 folds. Vanadium(V), manganese(II), chromium(VI), nickel(II), silver(I), gold(III), rhodium(III), ruthenium(III), cadmium(II), mercury(II), platinum(II), palladium(II), iron(III), can be tolerated up to 500 folds. Copper(II), iron(II), cobalt(II) can be tolerated up to 50 folds. Cobalt(II) showed no interference at pH of 4.0. A slight interference of copper(II) and Iron(II) was noted, which was masked by using thiosulphate and tartarate respectively.

3.5. Analytical Application of the Methods

The reliability of the two methods was tested by experimental determination of chromium(III) content in apple leaves and the results showed that the values obtained are in complete agreement with the certified value reported (Table 1). The developed methods are fairly sensitive and were applied to determine the chromium(III) content in waste water samples (Table 2). The obtained results of water sample analysis using absorbance and emission studies have been statistically treated using student's *t*-test and ANOVA (Table 3). The student's *t*-test shows that the statistical value is less than the one-sided critical value inferring concurrency between both the methods. A high degree of linear relationship between both the methods is very much evident from the Pearson Correlation value of 0.999. The F_{Ratio} value calculated from ANOVA: single factor is lesser than 1, again inferring no significant difference between the two pertained methods. Also, the analysis shows that the type of sample chosen has no significant effect on the developed methods.

4. CONCLUSION

Chromium(III) is thought to be necessary and important for a normal functioning of living organisms but, the excessive usage of this analyte in industries is giving way to serious health hazards. Some laboratory studies have also shown that the trivalent chromium can cause allergy and some of the Cr(III) compounds are toxic, even genotoxic for humans. Hence, simple, rapid and sensitive methods using photometry and fluorometry were proposed for the determination of chromium(III). The determination was carried out in the pH range of 3.5- 4.2. In the photometric method, fixed time and tangents' approaches were followed to determine chromium(III) in the range of 5.0 – 300.0 ng/mL. Stern-Volmer plots were used to interpret the quenching of fluorescence in fluorometric method. The plots infer that the quenching is uniform and the temperature studies reveal that the mechanism of quenching is collisional in nature. The study of kinetics for Cr(III)-HPTU reaction system shows that pseudo-second order rate equation is satisfied. The sensitivity in the determination was enhanced using 1,10-phenanthroline and SDS as activator and surfactant. The sensitivity range is comparable to other analytical methods allowing chromium determination at nanogram level. The method is fairly simple and sensitive and was applied for the determination of chromium(III) present in apple leaves and waste water samples.

5. ACKNOWLEDGEMENTS

Authors are thankful to the founder, chancellor, Bhagawan Sri Sathya Sai Baba, and authorities of Sri Sathya Sai Institute of Higher Learning for the support and guidance.

Tables and figures

Table-1. Application of developed methods to plant samples

Standard reference material	Quantity weighed (mg)	Reported amount (ng)	Determined chromium(III)(ng) of	
			Photometric absorption	fluorescence quenching
Apple leaves:1515	300.0	90.0	89.35 ± 0.38	89.75 ± 0.55

Table-2. Application of developed methods to waste water samples

Water sample taken	Spiked amount (ng)	Determined quantity of chromium(III)(ng)		
		Photometric absorption	fluorescence quenching	AAS method
WS 1	30	28.68 ± 0.13	28.84 ± 0.16	28.80 ± 0.15
WS 2	60	63.52 ± 0.12	64.98 ± 0.10	64.67 ± 0.14
WS 3	100	101.98 ± 0.21	101.96 ± 0.12	101.90 ± 0.18
WS 4	150	152.78 ± 0.12	152.84 ± 0.18	152.80 ± 0.16
WS 5	200	204.82 ± 0.19	205.74 ± 0.18	205.71 ± 0.15

Table-3. Statistical analysis of the obtained data

Statistical Parameter	Calculated Value
t_{Stat}	-1.93
t_{Crit}	2.77
Pearson Correlation	0.999
F_{Ratio}	0.0016
p -value	0.969

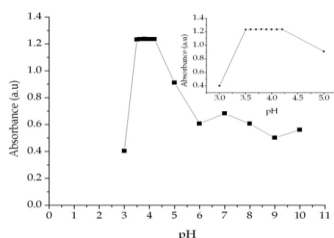


Figure 1: Study of effect of pH on chromium(III) catalysed oxidation

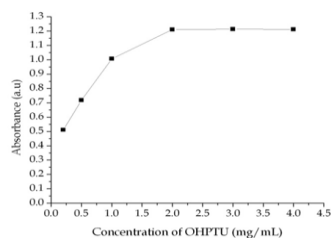


Figure 2: Effect of HPTU on HPTU-Cr(III) reaction system

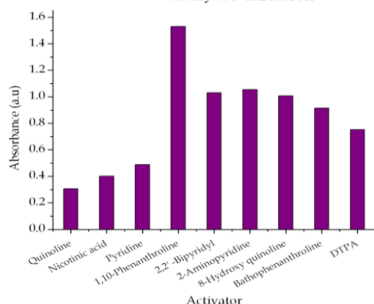


Figure 3: Effect of activators on HPTU-Cr(III) reaction system

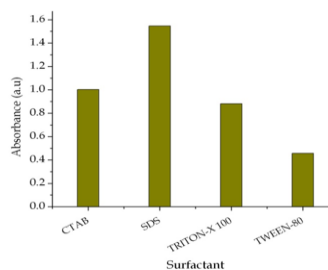


Figure 4: Effect of surfactants on HPTU-Cr(III) reaction system

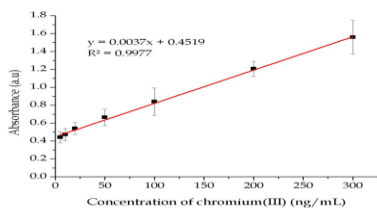


Figure 5: Study using fixed time approach for HPTU-Cr(III) reaction system

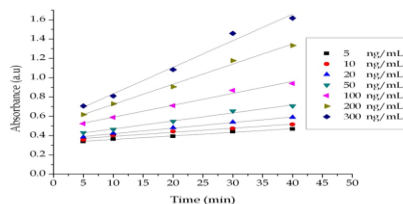


Figure 6: Study using variable time approach for HPTU-Cr(III) reaction system

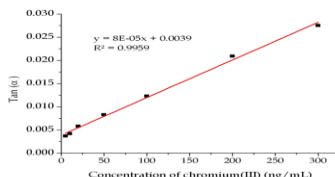


Figure 7: Study using tangents' approach for HPTU-Cr(III) reaction system

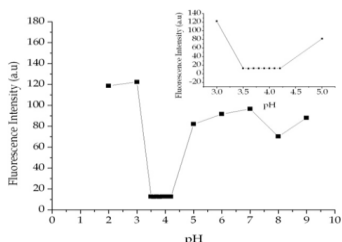


Figure 8: Study of emission intensity of HPTU-Cr(III) reaction system with varying pH

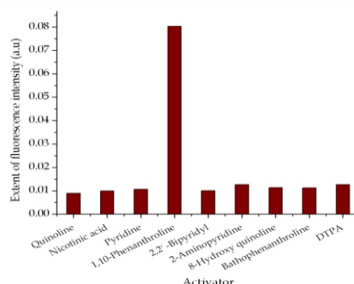


Figure 9: Study of emission intensity of HPTU-Cr(III) reaction system with activators

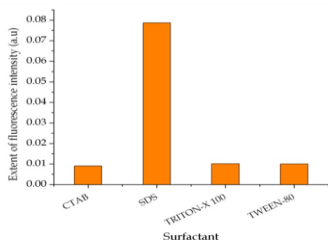


Figure 10: Study of emission intensity of HPTU-Cr(III) reaction system with surfactants

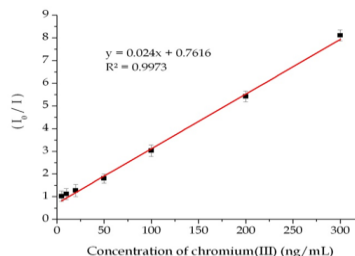


Figure 11: Study of emission intensity of HPTU-Cr(III) reaction system using Stern-Volmer plots

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