



SODIUM DODECYL SULPHATE AS A SURFACTANT MEDIUM FOR PHOTOMETRIC AND FLUOROMETRIC SENSING OF NICKEL (II) USING 1-(2-HYDROXYPHENYL) THIOUREA

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ABSTRACT

The determination of nickel (II) was achieved using 1-(2-hydroxyphenyl) thiourea (OHPTU) reaction system under neutral pH conditions at pH of 7.0 using phosphate buffer with spectrophotometry and spectrofluorimetry. The entire study was done at normal laboratory temperature, 25°C. The activator system that suited for the current study was 1% pyridine and the surfactant system was 1% SDS. The synergy of both pyridine and SDS led to the enhancement of sensitivity. Using the current methods, nickel (II) was determined in the range 0.6 ng/mL – 100 ng/mL. Stern-Volmer relation for fluorescence quenching was obeyed. The method was successfully applied to determination of nickel (II) in plant and waste water samples.

Key words: 1-(2-hydroxyphenyl) thiourea (OHPTU), Nickel (II), Spectrophotometry, Spectrofluorimetry, Stern-volmer, Fluorescence quenching.

INTRODUCTION

Nickel is one of the most substantial elements among the metals that play a vital role in industry as well as living systems. In industry, it is used as an alloying metal for steel and cast iron, as enamel for ceramics and as an electrode in batteries. It is present in the living systems as urease, a nickel metallo-enzyme that plays a vital role in pigmentation. The anthropogenic emission of this metal into environment is resulting in the increase of its concentration levels leading to serious health hazards. Hence, it is important to be aware of its levels and various analytical methods atomic absorption spectrophotometry, inductive coupled plasma emission spectrometry, X-Fluorescence spectrometry etc. have been developed for nickel (II) determination¹⁻⁸. Only few reagents are available for the

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spectrophotometric and spectrofluorometric determination of nickel (II)⁹. Therefore, a sensitive and simple analytical methods were developed for the determination of nickel (II) with OHPTU system using photometric absorption and fluorescence quenching techniques.

EXPERIMENTAL

Materials

AR grade chemicals were used in this study (Sigma-Aldrich Chemicals Ltd). HPLC graded solvents were procured from Merck Chemicals Ltd. Double distilled deionised water from Millipore Mill-Q plus System was used in the experiments. All the buffer solutions were prepared as per the standard method prescribed by Vogel¹⁰ and pH meter (Micropro) was used for pH adjustments. Weighing balance (Mettler Toledo: AB204-S) was used for all the weight measurements. A UV-Vis spectrophotometer (Hitachi U-2001) was used to record the absorbance measurements and fluorescencemeter (Perkin Elmer LS-55) was used to record fluorescence intensity measurements. For all the absorbance and fluorescence measurements, 10 mm path length quartz cuvettes (Hellma) were used.

Methods

1.0 mL of phosphate buffer solution (pH = 7.0) was taken along with suitable amounts (0.6 ng/mL – 100 ng/mL) of nickel (II) solution into a 10.0 mL volumetric flask, followed by 1.0 mL of 1% pyridine and 1.0 mL of 1% sodium dodecyl sulphate (SDS). The temperature was adjusted to laboratory temperature of 25°C. The OHPTU solution (1 mg/mL) was then added and flask was made up to the mark using deionised water. The resulting solution was properly mixed and left aside for 30 minutes. Then, appropriate amount of the resulting solution was transferred into the quartz cuvettes of spectrophotometer and fluorescencemeter. The absorbance and fluorescence emission measurements were recorded at $\lambda_{\text{max}} = 416 \text{ nm}$ and $\lambda_{\text{Em}} = 520 \text{ nm}$ respectively. 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 as described¹¹. The calibration graphs for both the studies were plotted and the method was applied to determine nickel present in water and plant samples. Water samples were boiled, treated with concentrated nitric acid and then filtered to separate any unwanted organic matter.

Digestion procedure for nickel determination in apple leaves: Appropriate amount of the standard reference material-1515 was weighed and placed in a 250 mL teflon beaker. The weighed material was digested using concentrated perchloric and nitric acids. The undigested residue of siliceous material was treated with small amounts of hydrofluoric acid

to obtain total dissolution. The resulting clear solution was transferred into a 50 mL volumetric flask and made upto the mark using deionised water.

RESULTS AND DISCUSSION

OHPTU was synthesized as per the standard procedure¹² and was confirmed by spectral evidence¹³. The analytical property of OHPTU was well conceived from Feigl¹⁴ and it was utilized in studies related to quantification of trace transition metals such as copper¹⁵, cadmium^{16, 17}, rhodium¹⁸, mercury^{13, 19}, manganese²⁰, cobalt²¹, etc. OHPTU undergoes a very slow auto-oxidation to form an yellow coloured disulphide 1,1'-dithio-bis-N-(o-hydroxyphenyl)formamide. The rate of formation of the disulphide increases tremendously in the presence of nickel (II) ions resulting in nickel catalysed transformation of OHPTU to its disulphide. The reaction is followed by recording the absorbance of the disulphide at $\lambda_{\text{max}} = 416 \text{ nm}$. The absorbance of the reaction mixture increased with increase in concentration of nickel (II) and this phenomenon was used as a parameter for nickel determination. The excited state behavior of OHPTU was studied upon excitation at $\lambda_{\text{Ex}} = 416 \text{ nm}$, which emits at $\lambda_{\text{Em}} = 520 \text{ nm}$ and the emission intensity quenches with the increase in concentration of nickel (II). This property also acts as a parameter to determine nickel.

Optimization of experimental parameters

The effect of pH on the absorbance of nickel (II) catalysed transformation of OHPTU was examined over a wide pH range from 2.0-10.0. The catalytic activity of nickel (II) was observed to be high at pH of 7.0 as evident from maximum absorbance and fluorescence quenching (Fig. 1). Hence, the pH was maintained at 7.0 in the study.

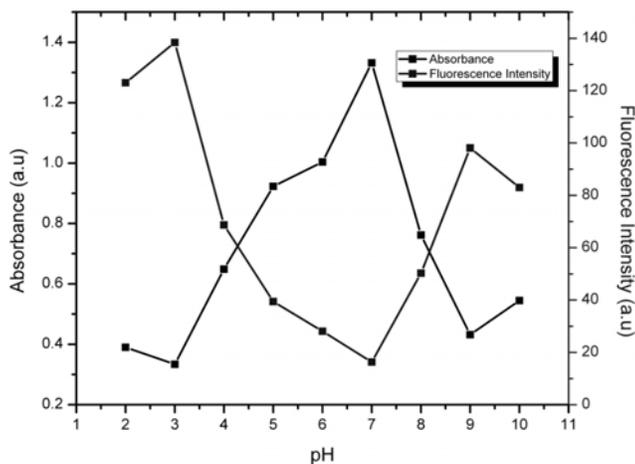


Fig. 1: Effect of pH on nickel (II) catalysed reaction of OHPTU

The amount of OHPTU was varied and 1.0 mg/mL was chosen as the desired amount. There is no influence of temperature on the catalytic reaction and therefore, the entire study was done at normal laboratory temperature of 25°C. The reaction was monitored for about 120 min. and the observations show that the reaction is stable after 30 min. So, all the measurements were recorded at 30th min. The sensitivity is enhanced by using activators like 1,10-phenanthroline, bathophenanthroline, quinoline, pyridine, 2-aminopyridine, diethylene triamine pentaacetic acid (DTPA), 2-hydroxyquinoline and nicotinic acid. Amongst these, 1% pyridine showed satisfactory results in both the absorbance and emission studies (Fig. 2). An increase in the absorbance and quenching effects due to availability of more static conditions in presence of micellar medium was observed. Surfactants like sodium dodecyl sulphate (SDS-anionic), tween-80 (non-ionic), triton X-100 (non-ionic), and cetyltrimethylammonium bromide (CTAB-cationic) were used in the investigation. 1% SDS showed a satisfactory effect in the rate enhancement of nickel (II) catalysed reaction (Fig. 3).

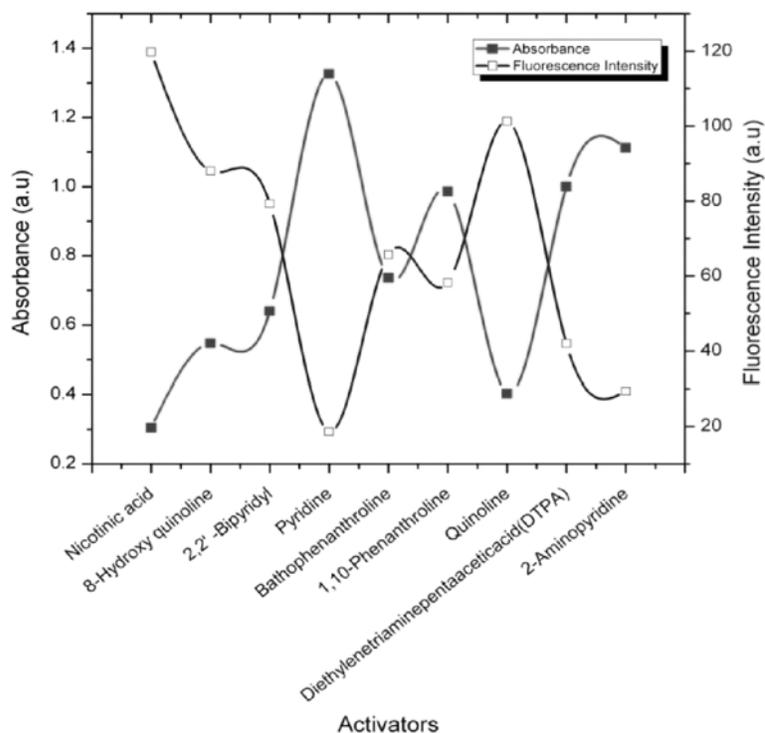


Fig. 2: Effect of activators on the nickel (II) catalysed reaction of OHPTU

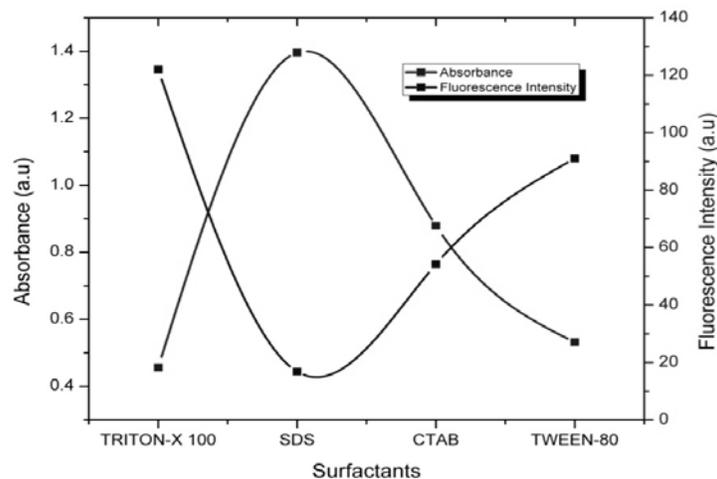


Fig. 3: Effect of surfactants on the nickel (II) catalysed reaction of OHPTU

The recorded UV-Vis spectrum shows an increase in absorbance at $\lambda_{\max} = 416 \text{ nm}$ as the nickel (II) ion concentration increases. By monitoring the amount of product formed, the nickel (II) concentration was quantified. Linearity was observed from the plotted graph between absorbance and concentration of nickel (II) in the range $0.6 \text{ ng/mL} - 100 \text{ ng/mL}$ [Fig. 4(I)]. The fluorescence spectrum showed a clear emission at $\lambda_{\text{Em}} = 520 \text{ nm}$ inferring the fluorogenic property of OHPTU. Addition of increased quantities of nickel (II) ions lead to quenching of intensity at 520 nm , which is attributed to the formation of the disulphide that is non-fluorogenic in nature. The rate of quenching is proportional to concentration of nickel (II) ions present in the sample. The efficiency of quenching for a fluorogenic species by a quencher follows the Stern-Volmer relationship¹¹. Stern-Volmer equation is given by $I_0/I_f = 1 + K_{\text{sv}}[Q]$ where I_0 and I_f are the fluorescence intensities in the absence and presence of the quencher respectively, if the fluorophore and quencher concentrations are in the appropriate range. The K_{sv} is the Stern-Volmer quenching constant and $[Q]$ is the concentration of the quencher. A straight line was obtained from the Stern-Volmer plot in the range $0.6 \text{ ng/mL} - 80 \text{ ng/mL}$ [Fig. 4(II)]. Therefore, the transformation of OHPTU to its disulphide is catalysed by nickel (II) and the two developed methods were utilized for nickel quantification in nanogram levels.

In the determination of nickel (II), there is no interference from anions such as nitrate, sulphate, oxalate, phosphate, fluoride, citrate, bromide, chloride, tartarate and borate. Cations such as cadmium (II), chromium (VI), chromium (III), arsenic (III), lead (II), cobalt (II), manganese (II), vanadium (V), silver (II), gold (III), zinc (II) do not interfere at pH of 7.0. A slight interference of copper (II) and iron (III) was noted.

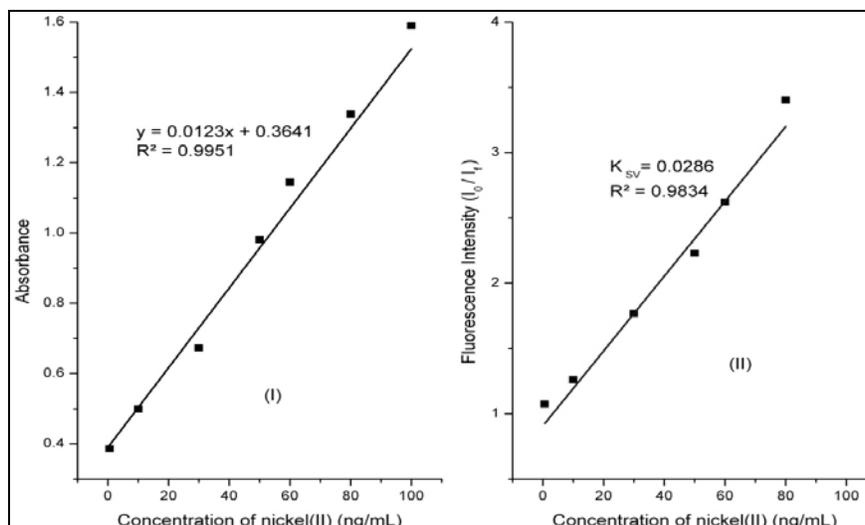


Fig. 4: Effect of nickel (II) concentration on absorbance and fluorescence intensity

Water samples were collected to determine the nickel (II) content. The samples were analysed using the two developed methods and the results are shown in Table 1.

Table 1: Analysis of water samples using the developed absorbance and emission methods

S. No.	Sample	Spiked (ng/mL)	Amount determined	
			Absorbance study* (ng/mL)	Emission study* (ng/mL)
1	Drainage water	5.00	22.10 ± 2.99	23.25 ± 2.21
2	Fountain water	10.00	19.65 ± 2.90	18.55 ± 1.32
3	Tap water	20.00	21.27 ± 1.25	21.60 ± 2.10

*Average of four determinations

The obtained results of water sample analysis using absorbance and emission studies have been statistically treated using student's *t*-test and ANOVA (Table 2). 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.

Table 2: Statistical data pertaining to the study of water sample analysis using the two developed analytical techniques

Statistical parameter	Calculated value
t_{Stat}	-0.190
t_{Crit}	2.919
Pearson correlation	0.999
F_{Ratio}	0.006
p -value	0.939

The reliability of the two developed methods was checked by the determination of nickel content in the standard reference material, apple leaves. The analysis (Table 3) shows that both the methods are in agreement.

Table 3: Determination of nickel in standard reference material

Sample	Certified amount of nickel in the sample ($\mu\text{g/g}$)	Amount determined	
		Photometric absorbance study* ($\mu\text{g/g}$)	Fluorescence emission study* ($\mu\text{g/g}$)
Standard reference material 1515: Apple Leaves	0.91 ± 0.12	0.862 ± 0.035	0.882 ± 0.045

*Average of four determinations

CONCLUSION

Simple, sensitive and affordable analytical methods were developed for the determination of nickel (II) in nanogram levels. The analytical range of the methods shows the sensitivity and the statistical analysis proves their reliability. The reaction utilized in this study is a unique reaction in itself because, the reagent synthesis is very simple and cost effective. Unlike the few methods reported, here, there is no need to add any oxidizing agent in the reaction system. There are no pre-concentration methods involved, entire study was done at normal laboratory temperature and free of inert conditions.

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