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ARTICLES

First Derivative Spectrophotometric Determination of Copper(II) and Nickel(II) Simultaneously Using 1-(2-Hydroxyphenyl)thiourea[1]

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Abstract—A sensitive simultaneous determination of copper(II) and nickel(II) was achieved using first derivative spectrophotometry based on zero-crossingover technique. In the current method, 1-(2-hydroxyphenyl)thiourea (**HPTU**) was used as a chromogenic reagent. To enhance the sensitivity in the method, pyridine was used as activator, cetyltrimethylammonium bromide (**CTAB**) and sodium dodecyl sulfate (**SDS**) were used as surfactants. Analytical parameters such as pH, reagent concentration, reaction time, etc., have been investigated. The ranges of determination for copper(II) and nickel(II) were 0.003–0.9 and 0.5–100 ng/mL, respectively. The proposed method was applied to plant samples for the determination of copper(II) and nickel(II) simultaneously.

Keywords: 1-(2-hydroxyphenyl)thiourea, copper(II), nickel(II), first derivative spectrophotometry, pyridine, CTAB, SDS

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The direct spectrophotometric determination of metal ions in multi component systems is often complicated because of the interferences from the sample matrix and spectral overlapping. The interferences can be treated in many ways, such as solving two simultaneous equations or using absorbance ratios at certain wavelengths. In any case, the interferences or overlap of spectra would certainly lead to results that cannot be reproducible. Other approaches like pH induced differential spectrophotometry, least squares and orthogonal function methods aimed at solving this problem. Scientists have realized that derivative spectrophotometry can be a useful means of resolving two overlapping spectra and eliminating matrix interferences in the assay of two-component mixtures using the zero-crossing technique. In the absence of a zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture. The latter method is based on criteria for selecting the optimum working wavelength. In addition, the component being determined should make a reasonable contribution to the total derivative reading of the mixture at the selected wavelength. Derivative spectrophotometric analysis of two-component mixtures can be carried out without solving simultaneous equations. The compensation method is also used for the purpose. This is a non-mathematical method for the detection and elimination of unwanted absorption during photometric analysis [1].

The differentiation of absorption spectra has many advantages for spectrophotometry in the UV and visible regions. It is the key for the potential enhancement of resolution of overlapping bands. It facilitates the detection of poorly resolved absorption peaks arising from admixtures or impurities in solution or due to structural reasons. It enables the exact determination of λ_{max} of the particular analyte species and increases the sensitivity of the spectrophotometric procedure. In addition, it is an excellent background elimination technique. The influence of Rayleigh scattering, constant background absorbance, nonselective absorption of the matrix or accompanying components is removed and the resolution of signal-to-noise ratios is improved [2]. However, the derivative technique offers greater selectivity than normal spectrophotometry in the simultaneous determination of two or more components without the requirement of prior separation. The principles, advantages and applications of this technique have been reviewed by Ojeda et al. [3].

Certain metals like copper and nickel are usually present and associated with most of the minerals and alloys. Hence, selective analytical techniques and methods have been put forward for simultaneous determination of both elements. Derivative spectroscopy is a very useful means for the determination of a single component in mixtures with overlapping spectra which may eliminate interferences. Hence, this technique was used for the determination of the individual analyte in complex matrices. Among the available

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methods for simultaneous determination, derivative spectrophotometry has advantages such as simplicity, fast reaction time, sensitivity and selectivity. This method is unaffected by various sources of error that affect the precision and accuracy of spectrophotometric measurements. Moreover, it reduces and eliminates base-line shifts, which advances the accuracy of quantification. The use of the derivative technique also reduces the effects of scattered light produced by the thickness of the solution [4].

Nickel and copper metals appear together, or alone, in many real samples such as Monel (68% Ni, 32% Cu, traces of Mn and Fe) and cupro-nickels (up to 80% Cu). The authors had reported the determination of copper(II) and nickel(II) using spectrophotometric and spectrofluorometric methods individually. But, it is a well known fact that these metals are associated together in many samples and this paper addresses the simultaneous determination of both the metal ions in a sample matrix. With respect to the importance of nickel and copper from biological and industrial viewpoints, it is useful to develop sensitive and selective analytical techniques that do not use expensive or complicated test equipment for the simultaneous determination of copper(II) and nickel(II) ions in different samples.

EXPERIMENTAL

Reagents. All the chemicals used in the investigation were of analytical grade with high purity purchased from Sigma Aldrich Chemicals Ltd. HPLC grade ethanol was purchased from Merck and used for preparation of various reagent solutions.

Instrumentation. Micropro pH meter was used for all the pH adjustments. Hitachi-2001 spectrophotometer and Quartz cells of 10 mm path length (Hellma) were utilized for photometric studies. Mettler Toledo AB204-S was used for weight measurements.

Preparation of solutions. The buffer solutions for pH studies were prepared as prescribed by Vogel [5]. 100.0127 mg of copper(II) chloride was weighed and dissolved in deionised water in an A graded 100-mL volumetric flask. The solution was standardised by titrating with EDTA solution in presence of monosodium salt of 4-(2-pyridylazo)resorcinol as indicator, to get a stock solution of 7.4 mM (1.0 mg/mL) of copper(II) [6]. 100.0370 mg of nickel(II) chloride was weighed and dissolved using deionised water. A stock solution of 7.7 mM (1.0 mg/mL) of nickel(II) was obtained by standardising complexometrically with EDTA using murexide as indicator [6]. Solution of HPTU (6 mM) was prepared by dissolving 25 mg in 25 mL of HPLC graded ethanol to give 1 mg/mL stock solution. Distilled pyridine (10.0 mL) was added to distilled ethanol in a 100-mL volumetric flask to get 12.38 mM concentration of pyridine. SDS (1.0 g) was dissolved in distilled water using a 100-mL volumetric flask to get a 1% SDS solution. In a 100-mL volumetric flask, 1.0 g of CTAB was dissolved in distilled water to get 1% CTAB solution.

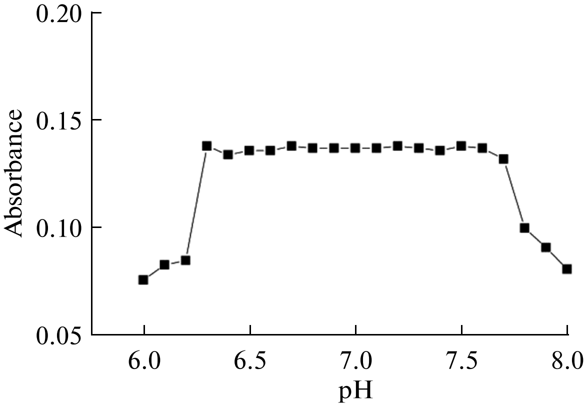

Fig. 1. Effect of pH on the reaction.

Recommended procedure. HPTU was synthesised using microwave assisted synthesis as reported [7]. Phosphate buffer solution of pH 7.0, 1.0 mL, and appropriate amounts of copper(II) and nickel(II) solutions were pipetted into a 10.0 mL volumetric flask followed by 1.0 mL of 12.38 mM pyridine. HPTU, 2.0 mL 1.0 mg/mL solution, was then added and Millipore water was added up to the mark. 1.0 mL of 1% CTAB in the case of copper(II) and 1% SDS in the case of nickel(II) was added. The resulting reaction mixture was transferred into 10-mm quartz cuvettes. Using spectrophotometer, the first derivative amplitudes were monitored for copper(II) and nickel(II) systems at 430 and 480 nm, respectively. The calibration graphs were plotted and the method was applied for the simultaneous determination of copper(II) and nickel(II) in plant samples.

RESULTS AND DISCUSSION

Copper(II) and nickel(II) were simultaneously determined using first derivative spectrophotometric method based on zero cross over technique. To carry out the method, it is required to study few analytical parameters like pH, reagent concentration, reaction time, temperature, etc., and fix the ambient analytical parameters so that the method is reproducible. The determination was carried out at different pH ranging from 2.0 to 11.0. It was evident from the observations that the reaction is more pronounced and stable with acetate buffer in the pH range of 6.3–7.3 (Fig. 1). Hence, the entire study was done by choosing the pH of 7.0 using acetate buffer. The amount of HPTU was varied from 0.5 to 4 mg/mL and the observations inferred that the optimum amount of the reagent is 2.0 mg/mL (Fig. 2). The variation in temperature from 20 to 60°C did not show any significant change in the determination and hence, all the experiments were carried out at normal laboratory temperature of 25 ± 5°C.

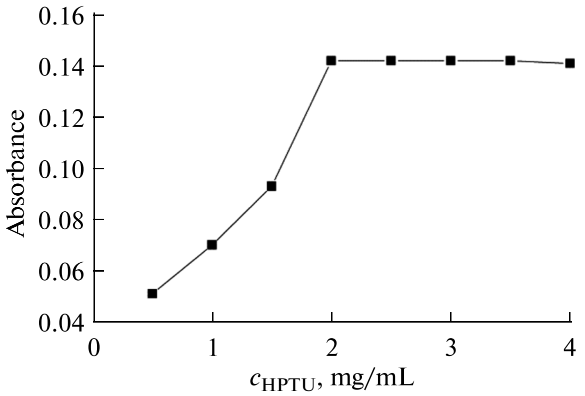

Fig. 2. Effect of HPTU concentration on the reaction.

The Fig. 3a shows the absorbance spectrum of Cu(II)–HPTU, Ni(II)–HPTU and Cu(II) + Ni(II)–HPTU systems using direct spectrophotometric method. It was very tough to identify and determine the concentration of respective metal ions because of overlapping spectra. This problem was addressed by first derivative spectrum using zero cross over technique. Though the formation of disulphide took place in presence of both copper and nickel, the derivative amplitude varied depending on the metal ion present. The first order derivative spectra for Cu(II)–HPTU system has showed a maximum derivative amplitude at 480 nm with a zero crossing at 430 nm and Ni(II)–HPTU system has showed a maximum derivative amplitude at 430 nm with a zero crossing at 480 nm (Fig. 3b). Hence, the first derivative amplitudes for the experimental solutions containing variable amounts of copper(II) and nickel(II) were recorded at 480 and 430 nm, respectively. It was observed that the first derivative amplitude is proportional to the amount of copper(II) and nickel(II) present at respective wavelengths. The variation in derivative amplitude for copper(II) and nickel(II) systems can be attributed to the catalytic effect of the respective metal ions. Copper(II) catalyses the dimerisation of HPTU at t = 20 min [8] and nickel(II) at 30 min [9]. Hence, a difference in the amplitude is seen in the recorded experiments because of the difference in catalytic rates. Thus, the simultaneous determination of copper(II) and nickel(II) was possible using first derivative method. Linearity in the recorded amplitudes for both copper(II) and nickel(II) was in the range of 0.003–0.9 and 0.5–100 ng/mL, respectively (Figs. 4, 5), which is indicated by the values of correlation coefficients.

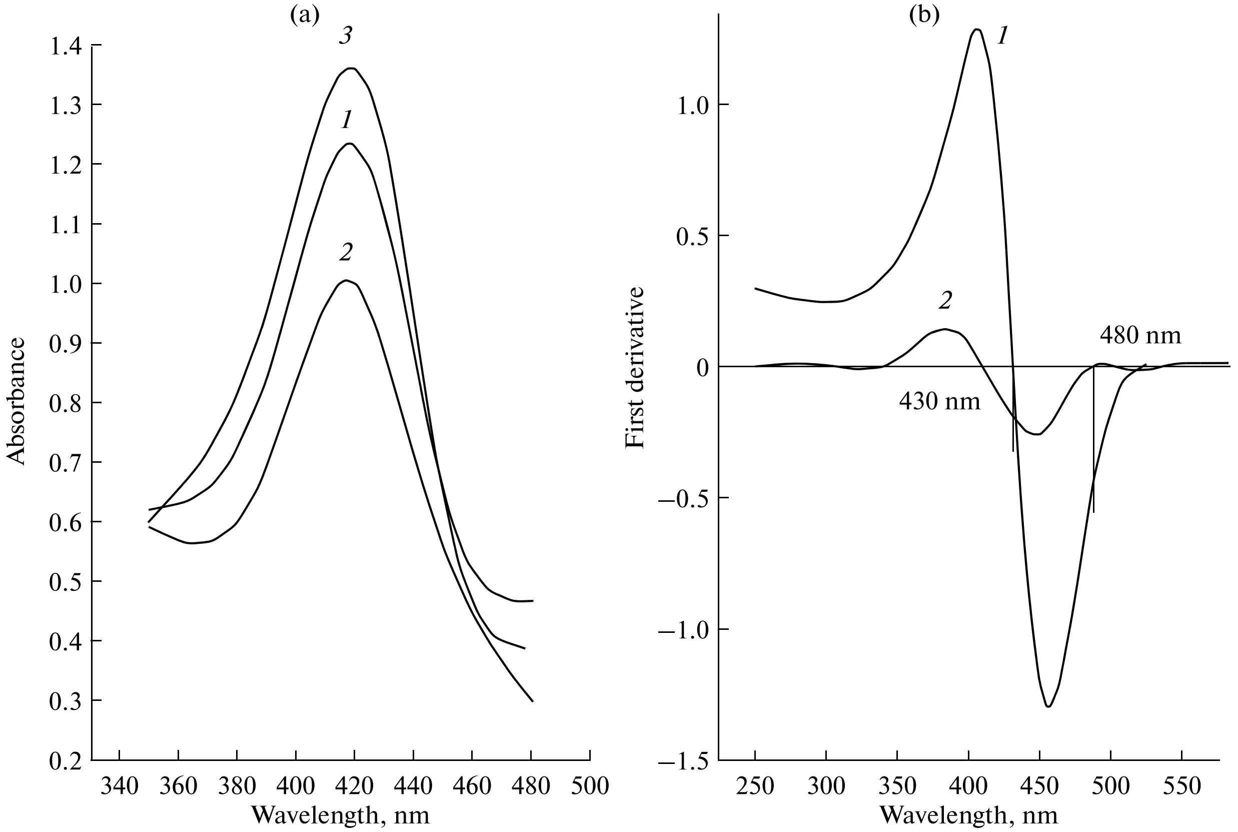

Fig. 3. UV–Vis spectrum of Cu(II)–HPTU (*1*), Ni(II)–HPTU (*2*) and Cu(II) + Ni(II)–HPTU (*3*) systems. (a)—direct method, (b)—first derivative method.

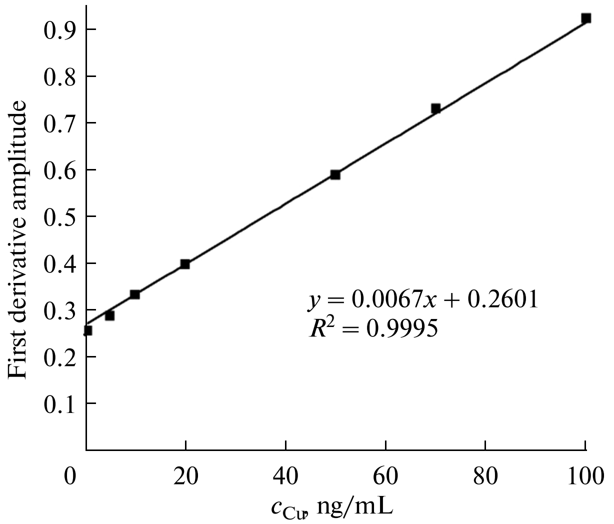

Fig. 4. Amplitude versus the concentration of copper(II) at 480 nm.

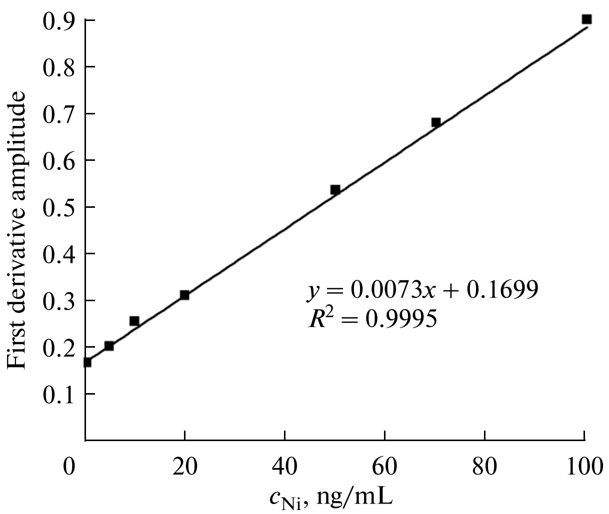

Fig. 5. Amplitude versus the concentration of nickel(II) at 430 nm.

In homogeneous catalysis, an activator has been defined as a chemical species that does not catalyse the reaction but whose presence results in a considerable increase in the reaction rate. Activation is a modification of the catalytic effect that, from an analytical point of view yields a better sensitivity and lower limit of detection in the catalytic determination. Complexing agents like pyridine, 2,2'-bipyridyl, etc., complexes with the metal ion forming catalyst-ligand π-bonds and as a result, the effective charge of the metal ion increases, resulting in increased catalytic activity. In the current determination, pyridine showed a good promoting effect in terms of increasing the sensitivity by lowering the limit of detection, and hence this was used as an activator [10].

Surfactants are surface active reagents which reduce the interfacial free energy of surfaces or interfaces. They stabilise the electrostatic attractions in a reaction system and increase the solubility resulting in good reactivity. At concentrations greater than CMC, formation of micelles leads to greater catalytic activity. They also act as phase transfer catalysts [11]. The selective use of surfactants also helps in enhancing the sensitivity of the determination. In the case of copper(II), 1% CTAB was used [7, 12] and in the case of nickel(II), 1% SDS was used [13]. Nickel(II) is attracted strongly to the oppositely charged SDS micelle surface and hence, the catalytic activity. In the case of copper(II), unlike the anionic SDS micelles, CTAB micelles have an electrostatic repulsion with the cationic copper(II)–pyridine complex. Therefore, interaction of this complex would involve the hydrophobic effect of the photosensitizer ligand like pyridine in the alkyl core of the micelles. The hydrophobic interactions are powerful enough to overcome a strong electrostatic repulsion of the cationic complex and bind to it as tightly as a strongly attracted, less hydrophobic, anionic species. Thus, CTAB acts as a promising surfactant in sensing copper(II).

The proposed method was applied to determine copper(II) and nickel(II) simultaneously in the standard reference material 1515: Apple leaves. The determined values (Tables 1, 2) using proposed method are concurrent with respect to the certified, reported values in the certificate.

Interference by foreign ions. In the current study, there is no interference from anions such as nitrate, suphate, oxalate, phosphate, fluoride, citrate, bromide, chloride, tartarate and borate even up to 1000 folds. Cations such as Ca(II), Mg(II), Al(III),

Table 1. The results (ng) of the determination of nickel in standard reference material (**SRM**)—Apple Leaves ($n = 5$)

Amount of SRM, mg	Certified	Found
1000.0	91.0	91.60 ± 0.08
800.0	72.8	72.00 ± 0.10
500.0	45.5	44.90 ± 0.03
300.0	27.3	27.13 ± 0.04
200.0	18.2	18.37 ± 0.05

Table 2. The results (ng) of the determination of copper in standard reference material ($n = 5$)

Amount of SRM, mg	Certified	Found
80.0	451.20	453.31 ± 0.08
50.0	282.00	281.00 ± 0.03
40.0	225.60	225.00 ± 0.06
20.0	112.80	111.73 ± 0.05
10.0	56.40	56.07 ± 0.06

Table 3. Analytical limits of detection (**LODs**) (ng/mL) of derivative spectrometric procedures for simultaneous determination of copper(II) and nickel(II)

Chromophore used for the study	Copper(II)	Nickel(II)	pH	Reference
3-Methoxy salcilaldehyde-4-hydroxybenzoyl hydrazone	4.6	5.5	5	[14]
H-point standard additions method	0.5	0.7	10	[15]
Methylthymol blue	500	500	6	[16]
6-(2-Naphthyl)-2, 3-dihydro-1,2,4-triazine-3-thione	260	130	10	[17]
Anthrone phenylhydrazone	1.9	4.2	9	[18]
6-(Anthracen-2-yl)-2, 3-dihydro-l,2,4-triazine-3-thione	500	500	10	[6]
Proposed method using HPTU	0.003	0.5	7	–

Na(I), K(I), Ba(II), Zr(IV), Mo(IV), Rh(III), Os(III), Pt(II), Pd(II), Au(III) do not interfere up to 1000 folds at pH 7.0, in which the entire study was done. Metal ions like Cd(II), Cr(VI), Cr(III), As(III), Pb(II), Mn(II), V(V), Ag(II), Zn(II) do not interfere up to 700 folds. Co(II) can be tolerated up to 50 folds. Iron(III) interferes at a very neglible extent and in any case, which can be eliminated by addition of sodium ascorbate.

* * *

A first derivative spectrophotometric method with zero crossing technique was proposed for the simultaneous determination of copper(II) and nickel(II) using HPTU at neutral pH. The proposed method utilizes the auto-oxidation reaction of HPTU. The determination was carried out at normal laboratory temperature. The sensitivity was enhanced using pyridine as activator. The selectivity was attained to an extent by using surfactants, CTAB in the case of copper(II) and SDS in the case of nickel(II). The range of determination for copper(II) and nickel(II) is 0.003–0.9 and 0.5–100 ng/mL respectively. The method is fairly sensitive and was applied to determine the copper(II) and nickel(II) content in apple leaves. The obtained experimental values are in accordance with the certified amounts. Hence, we can say that the method is reliable. The derivative methods reported for simultaneous determination of copper(II) and nickel(II) are given in Table 3. In comparison with those, the proposed method proved its sensitivity by lowering the limits of detection, even up to pico-gram level especially in the case of copper, is really striking. It is also evident that, the determination range is improved along with other analytical parameters like pH, reaction time, etc. The major contribution of this work to the existing methods is good sensitivity range, simple working conditions such as neutral pH, ambient temperature and simple synthesis of the chromophore (HPTU).

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