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ORIGINAL PAPER

Spectrofluorimetric Determination of Nickel (II) with Murexide

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Abstract A very sensitive and selective spectrofluorimetric method has been developed for nickel (II) determination in environmental samples. The method is based on measuring the decrease in fluorescence intensity of murexide after nickel (II) binding. The intensity of the fluorescence emission peak was measured at ex/em 345/431 nm in several solutions with pH interval 3.0–7.0. The fluorescence intensity decrease was found to be linear in the concentration range of 0.007 mg.L^{-1} to 0.1 mg.L^{-1} and 0.1 mg.L^{-1} to 20 mg.L^{-1} of nickel (II) by using 10^{-4} M murexide at pH 3. The detection limit was found 0.004 mg.L^{-1}. Relatively large excesses of over 20 cations and anions do not interfere. The method was successfully applied to the analysis of nickel (II) in sea, rain and ground water. This method is very precise and accurate (R.S.D.= 0.42 % for the determination of 0.05 mg.L^{-1} nickel in 10 replicates).

Keywords Nickel (II) · Spectrofluorimetry · Murexide · Quenchofluorimetric detection

Introduction

Nickel traces are industrially important, environmentally pollutant, occupationally hazardous and biologically toxic and micronutrient [1]. Nickel toxicity causes different diseases, including asthma and cancer of the nose, lung and intestine [1, 2]. Therefore, its trace and ultra-trace analysis is of acute importance. AAS [3–5], GF-AAS [6, 7] and even ICP-AES [8–10] methods require pre-separation steps (e.g. solvent extraction using suitable chelating agents or ion-exchanger) for removal of matrix interferences enrichment of the analyte concentration and for increasing the sensitivities, making the methods lengthy and expensive. chemiluminescence methods [11], based on the catalytic action of nickel (II) are subject to interference from various metal ions capable of activating (or inhibiting) the chemiluminescence reactions. Relatively high interferences and low sensitivity and precision are common disadvantages of chemiluminescence methods. spectrofluorimetry has been widely applied to determine heavy metals [12]. However, few spectrofluorimetric methods have been investigated for the determination of nickel. These methods have been mainly based on measuring the fluorescence intensity of complexing agents due to complexation with nickel [13–16]. However, the given methods, suffer from limitations, such as low sensitivity [14, 15], interference from some ions [16, 17] and long time consuming [13]. The fluorimetric method being presented here is simpler, more selective and more sensitive than these methods. Murexide is an indicator used in complexometric determination [18]. In this work for the first time we have used this indicator to determination Nickel by means of a quenchofluorimetric method. The method is sensitive, rarely affected by foreign ions and has been applied satisfactorily for the determination of nickel in complex mixture and environmental samples.

Experimental

Instrumentation

All fluorescence measurements were performed using a Varian spectrofluorometer equipped with a xenon lamp 15 W and 1-cm quartz cells. Throughout the experiments both

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Table 1 Optimum experimental conditions selected

pH	3
Murexide concentration	10^{-4} M
Cell temperature	25 °C
Reaction time	<40s
Wavelength (ex/em)	345/431
Slit (ex/em)	10/10 nm

the excitation and emission band widths were fixed at 10 nm. A digital Metrohm pH meter model 691 was used for pH measurements.

Reagents and Solutions

Ammonium purpurate (murexide) solution: A 5×10^{-4} M solution of ammonium purpurate (C8H4O6N5. NH4; molecular weight 284.19) under the trade name of murexide [Merck , 98 % purity (minimum)] was prepared by dissolving the requisite amount (0.0071 g) in deionized water followed by acidification with 0.5 mL of H_2SO_4 3 M in a 50 mL volumetric flask. It was diluted with deionized water up to the mark. The reagent was stored in a refrigerator (10 °C). However, a freshly prepared reagent solution was used whenever required. More dilute solutions were prepared from the 5×10^{-4} M stock solution. One Hundred mililitre of nickel stock solution (300 mg.L^{-1}) was prepared by dissolving 0.134 g nickel sulfate hexahydrate [$NiSO_4$ $(H_2O)_6$] in 100 ml of deionized water. This solution was standardized by EDTA titration [19]. More diluted solutions were prepared from the stock solution as required. Solutions of inorganic ions were prepared from their water soluble salts (or the oxides and carbonates in acids). Double distilled demineralized water was used throughout the study. All glass vessels were cleaned by soaking in acidified solutions of potassium permanganate or potassium dichromate, followed by washing first with concentrated nitric acid and then several times with water.

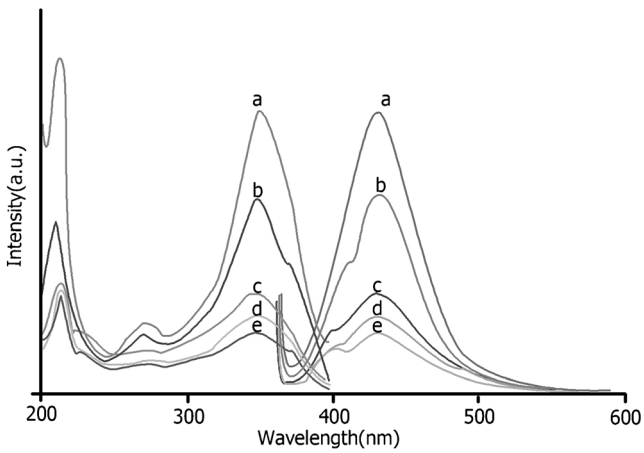

Fig. 1 Fluorescence excitation and emission spectra of murexide and its Ni (II) complexes .(a) 1×10^{-4} M murexide, (b) 0.5×10^{-4} M Ni (II), (c) 1×10^{-4} M Ni (II), (d) 3×10^{-4} M Ni (II), (e) 4×10^{-4} M Ni (II)

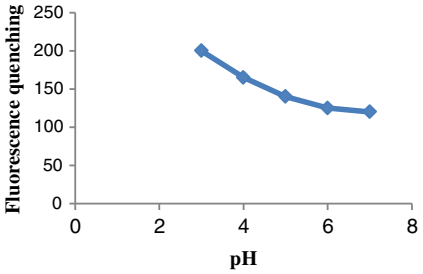

Fig. 2 Effect of pH on the fluorescence quenching intensity of Ni (II) - reagent system

Procedure

To a set of 10 ml flasks , appropriate volumes of the standard nickel solutions, 2.0 ml of 5×10^{-4} M murexide solution and 0.5 ml of H_2SO_4 3 M were added .Then it was made up to the mark with deionized water. The final concentration of nickel in the solutions was set to be 0.007–0.1 mg.L^{-1}. An aliquot of this solution was transferred to the 1-cm quartz cell and placed inside the spectrofluorometer. The highest decrease in the fluorescence intensity by the complexation between nickel and murexide was measured. The pH, murexide concentration, reaction time and cell temperature were examined to find the optimum complex formation of the nickel and fluorescent reagent. Eventually, the optimum experimental conditions were determined and are summarized in Table 1.

Results and Discussion

Spectral Characteristics

The uncorrected excitation and emission spectra of the murexide in presence and in absence of Ni, in acidic media were recorded with the spectrofluorimeter. The wavelength maxima of excitation and emission were found to occur at 345.0 and 431.0 nm respectively Nickel quenches the native fluorescence intensity of the reagent solution (Fig. 1).

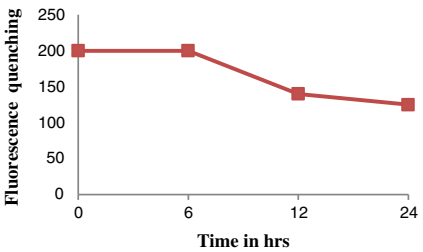

Fig. 3 Effect of time on the fluorescence quenching intensity of Ni (II) - reagent system

Table 2 The effect of foreign ions on the determination of 0.5 mg.L^{-1} nickel ion

Interfering ion	Tolerance [a]
NO_2^-,NO_3^-,CH_3COO^{2-}	1,000
Cl^-,I^-,SO_4^{2-},CO_3^{2-}	500
Na^+,K^+,Mg^{2+},CrO_4^{2-},$Cr_2O_7^{2-}$	100
Cr^{3+},Al^{3+},Co^{3+},Fe^{3+}	50
Mn^{2+},Fe^{2+}	5
Cu^{2+},Co^{2+}	1

[a] Maximum concentration ratio of foreign ions to nickel ion giving an error of <%5

Effect of pH

The effect of pH on fluorescence quenching for a sample containing 0.07 mg.L^{-1} of nickel

Was studied covering a wide range of sample pH values (3.0–7.0). The constant and maximum quenching of fluorescence was observed in the pH 3 (Fig. 2).

Effect of Time

The maximum quenching was observed immediately after making up the volume and remained constant for 6 h (Fig. 3).

Effect of Murexide Concentration

The murexide concentration was optimized for nickel-murexide complex formation. The effect of murexide concentration on the analytical signal was evaluated by using 0.01 mg.L^{-1} nickel and different concentrations of murexide. A linear relationship between the fluorescence intensity was observed with the concentration range of 1×10^{-5} to 1×10^{-4} M murexide for the Ni. Therefore a concentration of 10^{-4} M murexide was chosen as optimum for further experiments (Table 1).

Table. 3 Fluorescence intensity of Ni-Murexide at presence and absence of interfering ions

Interfering ion (2.5 mg.L^{-1})	Fluorescence Intensity of Ni-Murexide	
	at presence of interfering ions	at absence of interfering ions
Fe^{2+}	788	790
Cu^{2+}	790	791
Co^{2+}	791	792

Table. 4 Determination of Nickel in synthetic mixture

Sample	Composition of mixtures mg/L	Ni (II) taken mg/L	Ni (II) found[a] mg/L	Recovery % ± S.D mg/L
A	Ni^{2+} (0.05), Mn^{2+} (5) Co^{2+} (5), Cu^{2+} (5)	0.050	0.049	98±3.2
B	Ni^{2+} (0.05), Fe^{2+} (5) Co^{3+} (5), Cr^{+3} (5)	0.050	0.050	100±3.5
C	Ni^{2+} (0.05), Fe^{3+} (5) pb^{2+} (0.05), Cu^{2+} (5)	0.050	0.049	98±3.1

[a] Average of five determination

Interference Study

Using optimized conditions, the effect of twenty foreign ions on nickel ion determination was studied. The results are shown in Table 2.Tolerance is defined as the maximum concentration ratio of foreign ion to the nickel ion producing an error of <%5 in the determination of 0.5 mg.L^{-1} Ni^{2+}.

As can be seen from Table 2, all of the ions except Fe^{2+}, Mn^{2+}, Co^{2+} and Cu^{2+} do not interfere in the nickel determination at concentration ratios greater than 50.The interference effects of Fe^{2+}, $Cu^{2+}$and Co^{2+} were almost overcame by masking these interfering ions with KCN [20]. The results in Table 3 were obtained for sample solutions containing 0.5 mg.L^{-1} nickel and 2.5 mg.L^{-1} of each interfering cations after masking Fe^{2+}, Cu^{2+} and Co^{2+} by adding 10–15 ml of 5 % KCN solution. These results reveal the elimination of the interference effects of interfering cations.

Application

Determination of nickel in various synthetic mixtures and environment samples. The results are shown in Table 4 and Table 5. The usefulness of the developed method was evaluated by the determination of Ni in ground water, sea water and rain

Table 5 Nickel (II) determination in environmental waters

Samples[a]	Spiked mg/L	Nickel found[b] mg/L	Recovery % ± S.D
Ground water	0.04	0.040	100±3.1
	0.06	0.059	98.3±3.0
Sea water	0.040	0.039	97.5±3.4
	0.060	0.058	96.7±2.7
Rain water	0.040	0.050	97.5±2.8
	0.060	0.072	102±2.9

[a] Rain, Sea and Ground water were collected at Tehran, Iran

[b] Average of 5 replicate determinations

water samples. Ground water, sea water and rain water (in which Ni concentration was not detectable with the proposed method) were spiked with Ni at 0.05 mg.L^{-1} concentration level. The results of analysis in various types of samples in Table 5 show good agreement with expected and found values.

Conclusions

A new and versatile method has been developed for the quenchofluorimetric determination of nickel (II) with the help of an easy available, inexpensive reagent, murexide. The proposed method is more selective than previously mentioned methods for the spectrofluorimetric determination of trace amount of nickel. The advantage of the proposed method is that analysis can be done at room temperature in aqueous medium without an extraction procedure. The determination is reliable, reproducible the RSD value was lower than 0.5 for environmental samples and not time consuming.

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