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A Rapid Spectrophotometric Method For Determination Of Nickel In Industrial, Environmental, Biological And Soil Samples Using Bis(Salicylaldehyde)Orthophenylenediamine

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ABSTRACT

A very simple, ultra-sensitive and fairly selective spectrophotometric method is presented for the rapid determination of nickel at trace level using Bis(salicylaldehyde)orthophenylenediamine(BSOPD). The method is based on the reaction of non-absorbent BSOPD in a slightly acidic(5.0 $\times10^{-3}$- 1.5×10^{-2} M H_2SO_4) and 50 %(v/v) N,N-dimethylformamide (DMF) media with nickel(II) to produce a highly absorbent red-yellow chelate-product that has an absorption maximum at 466 nm. The reaction is instantaneous and the absorption remains stable for 24 h. The apparent molar absorption coefficient and Sandell's sensitivity were found to be 6.01×10^{4} L mol^{-1} cm^{-1} and 7ngcm^{-2} of nickel(II) respectively. Linear calibration graphs were obtained for 0.02 – 10.0 mgL^{-1} of Ni^{II}, the stoichiometric composition of the chelate is 1:1(BSOPD : Ni^{II}). A large excess of over 50 cations, anions and complexing agents(e.g. EDTA, tartrate, oxalate, citrate, phosphate, thiocyanate etc.) do not interfere in the determination. The method was successfully used for the determination of nickel in several standard reference materials(brass, steels and alloys) as well as in some environmental waters (portable and polluted) biological (human blood and urine) and soil samples and complex synthetic mixtures. The method has high precision and accuracy(s = ± 0.01 for 0.5 mg L^{-1}).

KEYWORDS

Non-extractive spectrophotometry;
Bis(salicylaldehyde)-orthophenylenediamine;
Nickel;
Environmental;
Biological;
Soil samples.

INTRODUCTION

Nickel traces are industrially important, environmentally pollutant, occupationally hazardous and biologically toxic and micronutrient[1]. Nickel toxicity causes different diseases, including asthma, eczema, dermatitis and cancer of the nose, lung and intestine[2]. Nickel carbonyl is the most toxic of nickel compounds. It has been established to be lethal in man at atmospheric exposures of 30 mgL^{-1} for 20 minutes[3]. On the other hand, micronutrient role of the metal ion is also well recognized[4]. Therefore, its accurate determination at trace and ultra-trace levels using simple and rapid methods is of paramount importance.

Spectrophotometry is essentially a trace analysis technique and is one of the most powerful tools in chemicalanalysis. Bis(salicylaldehyde) orthophenylene diamine (BSOPD) has been reported as a spectrophotometric reagent[5], but has not been used previously been used for the spectrophotometric determination of nickel. This paper reports in its use in a very sensitive, highly specific new spectrophotometric method for the trace determination of nickel. The method possesses distinct advantages over existing methods[6-18] with respect to sensitivity, selectivity, range of determination, simplicity, speed, pH / acidity range, thermal stability, accuracy, precision and ease of operation. The method is based on the reaction of non-absorbent BSOPD in a slightly acidic solution (0.005-0.015 M H_2SO_4) with nickel (II) to produce a highly absorbent red-yellow chelate product followed by a direct measurement of the absorbance in an aqueous solution. With a suitable masking, the reaction can be made highly selective and the reagent blank solutions do not show any appreciable absorbance.

EXPERIMENTAL

Apparatus

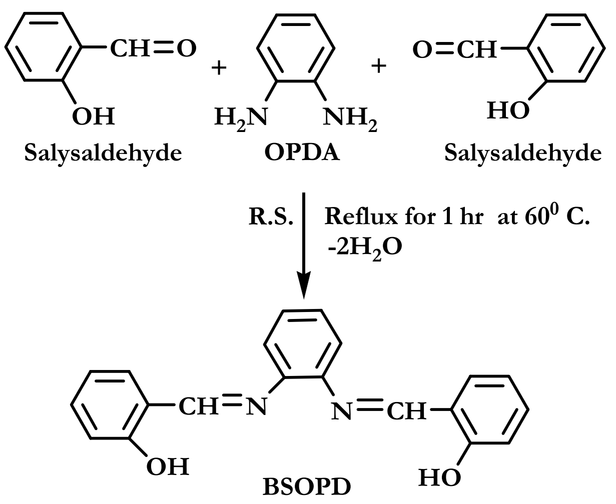
A Shimadzu (Kyoto, Japan) (Model-160) double beam UV-Visible recording spectrophotometer and Jenway (England, UK) (Model-3010) pH-meter with a combination of electrode were used for the measurements of absorbance and pH respectively. A Hitachi Ltd., Model 180-50, S.N. 5721-2 Atomic absorption spectrophotometer with a deuterium lamp background corrector, equipped with graphite furnace GA-3, with nickel hollow cathode lamps of Hitachi, and a Hitachi Model 056 recorder was used for comparing the results.

Reagents and the solutions

All the chemicals used were of analytical reagent grade or the highest purity available. Doubly distilled deionized water, which is non-absorbent under visible radiation, was used throughout. Glass vessels were cleaned by socking in acidic solutions of $KMnO_4$ or $K_2Cr_2O_7$, followed by washing with concentrated HNO_3 and rinsed several times with deionized water. Stock solutions and environmental water sample (1000 mL each) were kept in a polypropylene bottles containing 1 mL of concentrated HNO_3. More rigorously contamination control was applied when the nickel level in the specimen is low.

Synthesis and characterization of BSOPD

The reagent was synthesized according to the method of Salam et al[5]. The Schiff's base reagent bis(salicylaldehyde)orthophenylenediamine (BSOPD) was synthesized by refluxing a mixture of salicylaldehyde(700mmol) and orthophenylenedi amine(350 mmol) at 60°C for 1 hr. The yellow-brown



Bis(salicylaldehyde)orthophenylenediamine (BSOPD)

precipitate formed was filtered off on cooling, washed with ethanol and re-crystallized from ethanol and dried under vacuum over silica gel. Yield 80% and m.p. 152^0C [literature value 152.5^0C]. The prepared BSOPD was also characterized by IR spectra (νC = N at 1600 – 1640 cm^{-1}).

BSOPD solution, 7.9×10^{-3} M

The reagent solution was prepared by dissolving the requisite amount of bis(salicylaldehyde) orthophenylenediamine (BSOPD) in a known volume of N,N-Dimethylformamide(DMF). More dilute solution of the reagent was prepared as required.

Nickel(II) standard solution, 1.7×10^{-2} M

A 100 mL amount of stock solution (1 $mgmL^{-1}$) of nickel was prepared by dissolving 448.0 mg of nickel sulphate ($NiSO_4.6H_2O$) in doubly distilled deionized water. Aliquots of this solution was standardized by titrimetric analysis with EDTA[19]. More dilute standard solutions were prepared from this stock solution as and when required. Exact concentrations were also ascertained using the dimethylgly oxime method[19a].

Other solutions

Solutions of a large number of inorganic ions and complexing agents were prepared from their Analar grade or equivalent grade water soluble salts (or the oxides and carbonates in hydrochloric acid); those of niobium, tantalum, titanium, zirconium and hafnium were specially prepared from their corresponding oxides (Specpure, Johnson Matthey) according to the recommended procedure of Mukharjee[20]. In the case of insoluble substances, special dissolution methods were adopted[21,22].

Procedure

A volume of 0.1–1.0 mL of a neutral aqueous solution containing 0.1- 200 μg of nickel(II) in a 10 mL calibrated flask was mixed with a 1:90–1:200 foldmol arexcess of Bis(salicylaldehyde) ortho phenylenediamine(BSOPD) reagent solution(preferably 2 mL of 7.9×10^{-3} M) followed by the addition of 0.5–2.5 mL (preferably 1.0 mL) of 0.1M sulfuric acid and 3.0- 7.0 mL(preferably 5.0 mL) of N,N-dimethylformamide(DMF). The mixture was diluted to the mark with deionized water. The absorbance was measured at 466 nm against a corresponding reagent blank. The nickel content in an unknown sample was determined using a concurrently prepared calibration graph.

RESULT AND DISCUSSION

Absorption spectra

The absorption spectra of a nickel (II)-BSOPD system in a 0.1M sulfuric acid medium was recorded using the spectrophotometer. The absorption spectra of the nickel (II)-BSOPD is a symmetric curve with maximum absorbance at 466 nm and an average molar absorption coefficient of 6.01×10^4 $Lmol^{-1}$ cm^{-1} (Figure 1). The reagent blank did not show any absorbance in the range of determination. In all instances measurements were made at 466 nm against a reagent blank.

Effect of solvent

Because BSOPD is insoluble in water, an organic solvent was used for the system. Of the various solvents (benzene, chloroform, acetone, carbon tetrachloride, nitrobenzene, isobutyl alcohol, 1-butanol, isobutyl methyl ketone, ethanol, 1.4-dioxan and N, N-dimethylformamide DMF) studied, DMF was

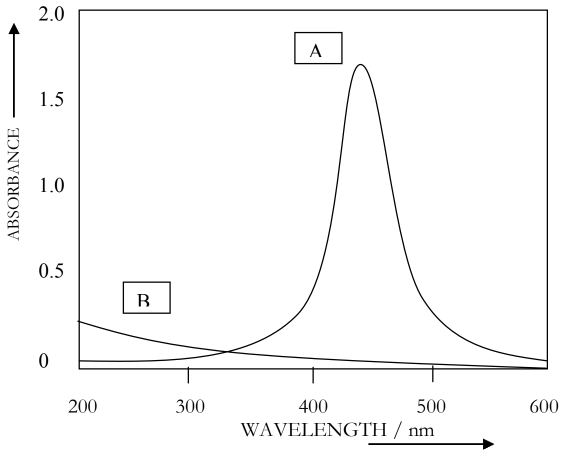


Figure 1: A and B absorption spectra of Nickel-BSOPD and the reagent blank (λ_{max}= 466 nm) in aqueous solution.

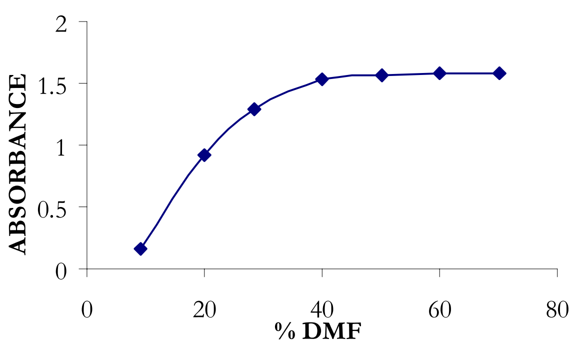


Figure 2: Effect of solvent (N,N-dimethyl formamide) on the absorbance of the Ni^{II}-BSOPD system

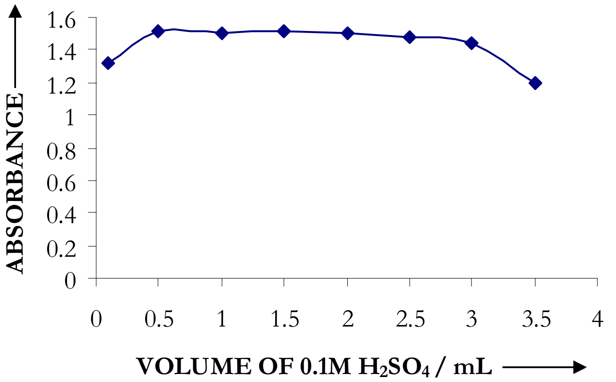


Figure 3: Effect of acidity on the absorbance of the Ni^{II}-BSOPD system.

found to be the best solvent for the system. No absorbance was found in the organic phase with exception of 1-butanol. In 50 ± 2 % (v/v) DMF medium, however the maximum absorbance was observed; hence, a 50% DMF solution was used in the determination procedure. It was observed that at 1 mgL^{-1} of Ni-chelate metal, 30-70% of DMF solution produced a constant absorbance of the Ni-chelate (Figure 2). A greater excess of DMF were not studied.

Effect of acidity

Of the various acids (nitric acid, sulfuric acid , hydrochloric acid and phosphoric acid) studied , sulfuric acid was found to be the best acid for the system. The variation of absorbance was noted after the addition of 0.1–3.5 mL of 0.1M sulfuric acid to every 10 mL of test solution. The maximum and constant absorbance was obtained in the presence of 0.5 – 3.0 mL of 0.1 M sulfuric acid at room temperature(25± 5)^{0}C. This corresponds to 0.005 – 0.03 molar acidity range (Figure 3) in the final dilution. For all subsequent measurements, 1 mL of 0.1M sulfuric acid (or pH 2.7) was added.

Effect of time

The reaction is very fast. A constant maximum absorbance was obtained just after dilution to volume and remained strictly unaltered for 24h(Figure 4).

Effect of reagent concentration

Different molar excess of BSOPD were added to a fixed metal ion concentration and the absorbance were measured according to the standard procedure. It was observed that at 1 mgL^{-1} of nickel metal, the reagent molar ratios of 1: 90 and 1:200 produce a constant absorbance of the Ni-chelate (Figure 5). For different nickel-concentration(0.5 and 1.0 mgL^{-1}) an identical effect of varying the reagent concentration was noticed. A greater excess of reagent were not studied. For all subsequent measurements, 2 mL of 7.9 ×10^{-3} M BSOPD reagent was added.

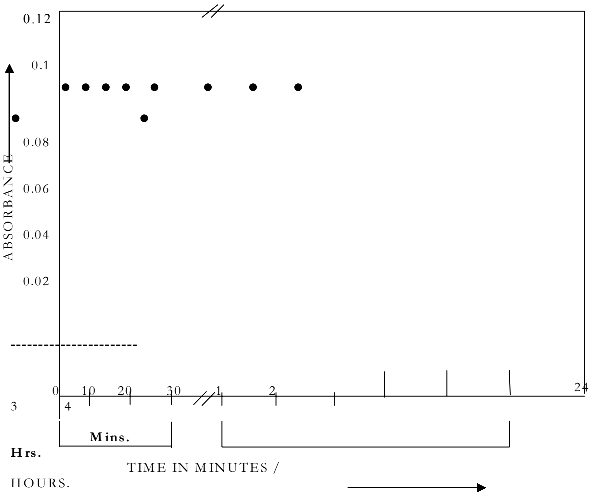


Figure 4: Effect of the time on the absorbance of Ni^{II}–BSOPD system

Calibration graph (Beer's law and sensitivity)

The well-known equation for spectrophotometric analysis in a very dilute solution was derived from

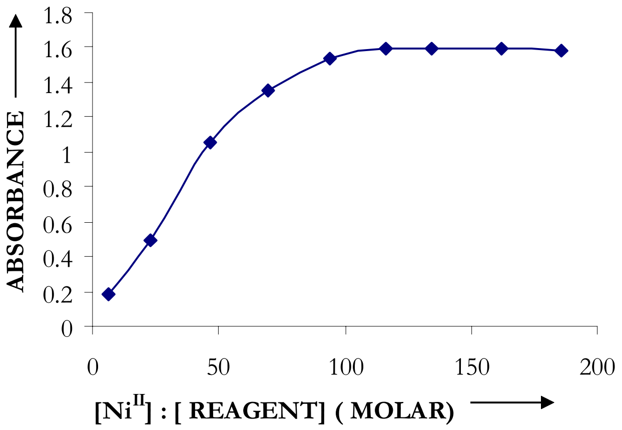


Figure 5: Effect of the reagent(BSOPD : Ni^{II} molar concentration ratio on the absorbance of the Ni^{II}-BSOPD system.

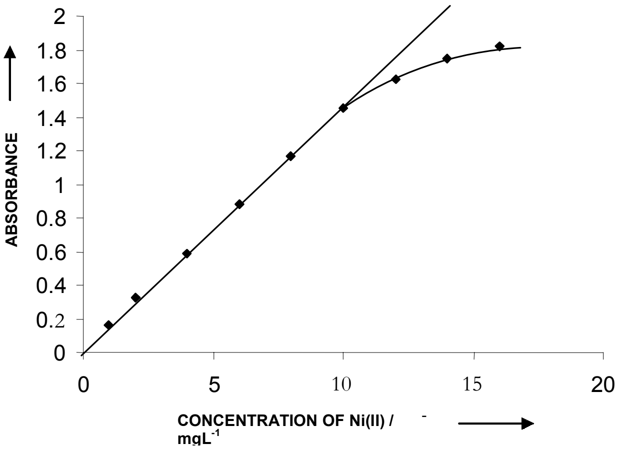


Figure 6: Calibration graph-C, 1.0-10.0 mgL^{-1} of nickel(II)

Beer's law. The effect of metal concentration was studied over 0.01 – 100 mgL^{-1} distributed in three different sets (0.01–0.1, 0.1–1.0, 1– 20 mgL^{-1}) for convenience of the measurements. The absorbance was linear for 0.02 – 10.0 mgL^{-1} of nickel at 466 nm. Of the three calibration graphs which shows the limit of linearity is shown in figure 6. Other two graphs were straight line passing through the origin. The molar absorption coefficient and the Sandell's sensitivity[23] were found to be 6.01×10^4 $Lmol^{-1}cm^{-1}$ and 7.0 $ngcm^{-2}$ of nickel (II) respectively. The selected analytical parameters obtained with the optimization experiments are summarized in TABLE-1.

Effect of foreign ions

The effect of over 50 cations and complexing agents on the determination of only 1mgL^{-1} of nickel(II) was studied(TABLE-2). The criterion for interference[24] was absorbance value varying ±5% from the expected value for nickel alone. The results are summarized in TABLE-2. As can be seen, a large number of ions have no significant effect on the determination of nickel. The most serious interference were from Cu(II) and Fe (III) ions. Interference from these ions are probably due to complex formation with BSOPD. The grater tolerance limits for these ions can be achieved by using several mask-

TABLE 1: Selected analytical parameters obtained with the optimization experiments

Parameters	Studied range	Selected value
Wavelength / λ_{max} (nm)	200 - 800	466
Acidity / M H_2SO_4	0.001 – 0.05	0.005 –0.015 (preferably, 0.01)
pH	4.5 – 2.0	1 min - 48h (preferably 5 min)
Time / h	0 - 72	48
Solvent / % DMF	0 - 100	40- 70 (preferably, 50)
Temperature / ^{0}C	25 ± 5	25 ± 5
Reagent (fold molar excess, M : R)	1 : 5 – 1 : 200	1 : 90 – 1 : 200 (preferably, 1 : 100)
Average Molar Absorption Co-efficient / L mol^{-1} cm^{-1}	$1.17\times10^4 – 7.52\times10^4$	6.01×10^4
Linear range / mgL^{-1}	0.01 - 100	0.02 – 10
Detection limit / μgL^{-1}	0.01 - 20	1.0
Sandell's Sensitivity / ng cm^{-2}	1-50	7.0
Reproducibility(% RSD)	0 - 2	0 -2
Regression Co-efficient	0.9985-0.9999	0.9998

TABLE 2: Table of tolerance limit of foreign ions

Species x	Tolerance ratio [Species (x) / Ni^{II} (w/w)	Species x	Tolerance ratio [Species (x) / Ni^{II} (w/w)]
Acetate	1000	Magnesium(II)	500
Arsenic(III)	100	Zinc(II)	500
Arsenic(V)	200	Manganese(II)	500
Azide	100	Mercury(II)	500
Barium	50[b]	Iron(II)	20[b]
Potassium	1000	Iron(III)	50[b]
Chloride	500	Silver	50[d]
Citrate	1000	Copper(II)	10[e]
Tartrate	1000	Phosphate	1000
EDTA	1000	Thiocyanide	1000
Bromide	1000	Sodium	1000
Fluoride	1000	Strontium	50[b]
Oxalate	500	Molybdenum(V)	50[b]
Iodide	1000	Cerium(III)	100
Aluminum	1000	Vanadium(V)	50[c]
Calcium (II)	1000	Tin(IV)	50[b]
Cadmium	100	Ammonium(I)	1000
Cobalt(II & III)[b]	50	Selenium(IV)	100
Nitrate	1000	Selenium(VI)	100
Chromium(III)	50[b]	Thallium(I)	100
Ascorbic acid	1000	Manganese(VII)	50
Chromium(VI)	50[b]	Beryllium(II)	50[c]
Lead(II)	50[b]	Sulphate	100

[a] Tolerance limit defined as ratio that causes less than 5 % interference.; [b] With 10 μg mL^{-1} EDTA; [c] With 10 μg mL^{-1} tartrate; [d] With 10 μg mL^{-1} chloride; [e] With 10 μg mL^{-1} hydrazine hydrate / Thiocyanide.

ing methods. In order to eliminate the interference of Cu(II), 10 mgL^{-1} hydrazine(aq.)) or thiocyanide was used. For Co(II), Co(III), Ba, Fe(II), Fe(II), Mo(V), Sn(IV), Cr(III) and Pb(II) 10 mgL^{-1} EDTA and for V(V) and Be(II) 10 mgL^{-1} tatrate and for Ag 10 mgL^{-1} chloride was added[25] and the precipitation formed in any case was filtered off(TABLE 2).

As stated above, the proper masking and precipitating agents may be added by while aiming at different interfering ions according to actual comparison of the sample. For this reason, the selectivity of the proposed method is greatly improved and practically is increased. Particularly, the nickel amounts in complex samples may be determined by using the proposed method. Moreover, the tolerance limits of NO_3^-, ClO_4^-, SO_4^{2-} are especially high which is advantageous with respect to the digestion of the samples.

Composition of the complex

Job's method[26] of continuous variation and the molar-ratio[27] method were applied to ascertain the stoichiometric composition of the complex. A Ni : BSOPD (1:1) complex was indicated by both methods.

Application

The present method was successfully applied to the determination of nickel (II) in a series of synthetic mixtures of various composition (TABLE 3), and also in a number of real samples, e.g., several certified reference materials (CRM) (TABLE 4). The

TABLE 3: Determination of nickel in some synthetic mixtures

Sample	Composition of mixtures / mgL^{-1}	Nickel(II)/mgL^{1}		
		Added	Found^{a}	Recovery ± s (%)
A	Ni^{2+}	0.50	0.49	98 ± 0.4
		1.00	1.00	100 ± 0.00
B	As in A + Cd^{2+} (25) + Mg^{2+} (25)	0.50	0.50	100 ± 0.00
		1.00	1.01	101 ± 0.5
C	As in B+ Ca^{2+} (25) + Ce^{2+} (25)	0.50	0.49	98 ± 0.5
		1.00	0.99	99 ± 0.3
D	As in C+ Na^{+} (25) + Mn^{2+} (25)	0.50	0.505	101 ± 0.8
		1.00	1.02	102 ± 0.6
E	As in D+ Zn^{2+} (25) + As^{3+} (25)	0.50	0.52	104 ± 1.0
		1.00	1.03	106 ± 1.2

^{a} **Average of five replicate determinations.**

TABLE 4: Determination of nickel in certified reference materials

Certified Reference Materials (Composition %)	Nickel		
	Certified Value(%)	Found (%)	RSD, %
BCS-261 Straight Nb 18/12 Stainless steel(C=0.083, Si= 0.39, Cr = 17.20, Ni = 13.08, Mn = 0.66, Nb+Ta= 0.71)	13.08	13.01	1.23
BAS-5g, Brass (Cu = 67.4, Sn = 1.09, Pb = 2.23, Zn= 28.6, Ni= 0.33, P= 0.01)	0.33	0.35	1.95
BAS-10g, High tensile brass (Cu = 60.8,Fe =1.56, Pb = 0.23, Ni = 0.16, Sn = 0.21, Al =3.34, Zn = 32.0, Mn = 0.12)	0.16	0.17	2.1
33b Alloy Cast Iron-(Mn = 0.64, Cr = 0.61,Ni = 2.24, Mo = 0.04)	2.24	2.25	1.32
BAS- 20b, Al-alloy, (Al = 90.5, Mg = 1.6, Cu = 4.1, Ni = 1.9, Fe= 0.43, Mn = 0.19, Si = 0.24)	1.90	1.85	1.52

method also extended to the determination of nickel in a number of environmental, biological and soil samples. In view of the unknown composition of environmental water samples, the same equivalent portions of each such sample were analyzed for nickel content; the recoveries in both the 'spiked' (added to the samples before the mineralization or dissolution) and the 'unspiked' samples are in good agreement (TABLE 5). The results of biological analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS (TABLE 6). The results of soil samples analyses by the spectrophotometric method are shown in (TABLE 7). The precision and accuracy of the method were excellent.

Determination of nickel in synthetic mixtures

Several synthetic mixtures of varying composition containing nickel(II) and diverse ions known concentrations were determined by the present method using tartrate or EDTA as a masking agent; and the results were found to be highly reproducible as shown in TABLE 3. Accurate recoveries were achieved in all solutions.

Determination of nickel in alloy, steel and brass (certified reference materials)

A 0.05 g amount of alloy or steel or brass sample containing 0.16-13.08 % of nickel was accurately weighed and placed in a 50 mL Erlenmeyer flask following a method recommended by Parker *et al*[28]. To it 10 mL of concentrated HNO_3 and 2 mL concentrated H_2SO_4 were carefully added and then covered with a watch-glass until the brisk reaction subsided. The solution was heated and simmered gently after the addition another 5 mL of concentrated HNO_3 until all carbides were decomposed. The solution was carefully evaporated to dense white fumes to drive off the oxides of nitrogen, and the cooled to the room temperature (25 ± 5)^{0}C. After suitable dilution with deionized water, the content of Erlenmeyer flask were warmed to dissolve the soluble salts.

TABLE 5: Determination of nickel in some environmental water samples

Sample		Nickel/ μgL^{-1}		Recovery ±s (%)	s_r[b] (%)
		Added	Found[a]		
Tap Water			32.0		
		100	132.0	100.0±0.0	0.00
		500	534.0	100.4±0.5	0.35
Well Water			35.6		
		100	136.0	100.3±0.0	0.25
		500	535.0	99.9±0.5	0.18
River Water	Karnaphuly (Upper)		17.24		
		100	118.0	100.6 ±0.8	0.27
		500	517.25	100±0.1	0.12
	Karnaphuly (Lower)		18.6		
		100	120.0	101.6 ±0.5	0.28
		500	518.0	99.9±0.2	0.15
Sea Water	Bay of Bengal (Upper)		27.7		
		100	128.0	100.2 ±0.6	0.35
		500	530.0	100.4±0.8	0.45
	Bay of Bengal (Upper)		27.7		
		100	128.0	100.2 ±0.6	0.35
		500	530.0	100.4±0.8	0.45
Drain Water	KAFCO[c]		75.2		
		100	176.0	100.4 ±0.5	0.29
		500	580.0	100.8±0.6	0.31
	Glass Factory[d]		153.5		
		100	255.0	100.6 ±0.4	0.25
		500	650.0	99.5±1.0	0.23
	Eastern Refinery[e]		46.0		
		100	147.5	101.6 ±0.3	0.32
		500	545.0	99.8±0.7	0.26
	KPM[f]		80.7		
		100	182.0	100.7 ±0.6	0.19
		500	585.0	100.8±0.8	0.26

[a]Average of five replicate determinations; [b]The measure of precision is the relative deviation(s_r); [c]Karnaphuly Fertiliser Company (KAFCO), Chittagong, Bangladesh; [d]Osmania Glass Factory, Kalurghat, Chittagong, Bangladesh; [e]Eastern Refinery, Chittagong, Bangladesh; [f]Karnaphuly Paper Mill, Chandraghona, Chittagong, Bangladesh.

The solution was cooled and neutralized with a dilute NH$_4$OH solution in the presence of a 0.1% (w/v) EDTA solution. The resulting solution was filtered, if necessary, through Whatman No. 40 filter paper into a 25 mL calibrated flask. The residue was washed with a small volume (5 mL) of hot (1: 99) H$_2$SO$_4$ followed by water ; the volume was made up to the mark with deionized water.

A suitable aliquot(1-2 mL) of the above mentioned solution was taken into a 10 mL calibrated flask and the nickel content was determined as described under procedure using EDTA as masking agent. Based on five replicate analyses, the average nickel concentration determined by spectrophotometric method was in close agreement with the certified values(TABLE 4).

Sample collection and preservation

Water: Water samples were collected in polythene bottles from shallow tube-wells, river, sea and drain of different places of Bangladesh. After collection, nitric acid (1 mLL^{-1}) was added as preservative.

Blood and urine: Blood and urine samples were collected in polypropylene bottles from affected persons of Chittagong Medical College Hospital, Bangladesh. Immediately after collection, they were stored in a salt-ice mixture and later, at the laboratory, were kept at 20^0C.

Soil: Soil (surface) samples were collected from different locations of Bangladesh. Samples were dried in air and homogenized with mortar.

Determination of nickel in environmental water

TABLE 6: Concentration of nickel in blood and urine samples

Sl. No.	Samples	Nickel/µgL^{-1}				Sample Source^a
		AAS (n=5)		Proposed method (n=5)		
		Found	RSD, %	Found	RSD, %	
1	Blood	21.1	1.5	21.5	1.2	Normal Adult(Male)
	Urine	5.3	1.0	5.5	0.8	
2	Blood	58.6	1.6	60.5	1.5	Angeoedema Patient (Male)
	Urine	21.5	1.2	22.3	1.3	
3	Blood	125.0	2.5	122.5	1.7	Nasal Cancer (Male)
	Urine	34.4	1.8	32.8	1.2	
4	Blood	168.8	2.3	170.6	2.0	Lung Cancer Patient (Male)
	Urine	42.2	1.5	45.0	1.5	

^{a}Samples were collected from Chittagong Medical College Hospital, Bangladesh.

samples

Each filtered samples(1000 mL) was evaporated nearly to dryness with a mixture of 5 mL of concentrated H_2SO_4 and 10 mL of concentrated HNO_3 in a fume cupboard, following a method recommended by Greenberg et al.[29] and was then cooled to room temperature. The residue was then heated with 10 mL of deionized water in order to dissolve the salts. The solution was then cooled and neutralized with dilute NH_4OH in the presence of a 1-2 mL of 0.1% (w/v) EDTA solution. The resulting neutral solution was then filtered and quantitatively transferred into a 25 mL calibrated flask and made up to the mark with deionized water.

An aliquot (1-2 mL) of this preconcentrated water sample was pipetted into a 10 mL calibrated flask and then nickel content was determined as described under the procedure using EDTA as a masking agent. The result of analysis of environmental water samples from various sources for nickel given in TABLE 5.

Determination of nickel in biological samples.

Human blood (2-5 mL) or urine (20-50 mL) sample was taken into a 100 mL micro-Kjeldah flask. A glass bed and 10 mL of concentrated nitric acid were added, and the flask was placed on a digester under gentle heating. When the initial brisk reaction was completed, the solution was removed and cooled, and digested following a method recommended by Stahr[30]. A 1 mL of volume of concentrated sulfuric acid was carefully added followed by the addition of 1 mL of 70% perchloric acid; and heating was continued to dense white fumes, while repeating nitric acid addition if necessary. Heating was continued for at least 0.5 h and then cooling was applied. The content of the flask was filtered and neutralized with NH_4OH in the presence of 1-2 mL of a 0.01% (w/v) EDTA solution. The resultant solution was then filtered and transferred quantitatively into a 25 mL calibrated flask and made up to the mark with deionized water.

A suitable aliquot (1- 2 mL) of the final solution was pipetted out into a 10 mL calibrated flask , and the nickel content was determined as described under procedure using EDTA as masking agent. The results of biological analyses by the spectrophotometric method were found to be in excellent agreement with those obtained by AAS. The results are given in TABLE 6.

Determination of nickel in soil samples

An air-dried homogenized soil sample (100 g) was accurately weighed and placed in a 500 mL beaker. The sample was digested in the presence of an oxidizing agent following a method recommended by Jackson[31]. The content of the beaker was filtered through Whatman No. 40 filter paper into a 25 mL calibrated flask, and neutralized with dilute ammonia solution in the presence of 1-2 mL of a 0.01% (w/v) EDTA solution. It was then diluted up to the mark with deionized water.

A suitable aliquot (1-2 mL) of the final solution was pipetted out into a 10 mL calibrated flask and a calculated amount of 0.1 molL^{-1} H_2SO_4 to give the final acidity 0.001-0.035 molL^{-1} was added followed

TABLE 7: Determination of nickel in some surface soil.[a,b]

Sl. No.	Nickel//μgL^{-1}	Sample source
S_1^C	13.3 ±1.0	Agricultural soil (Chittagong University Campus, Chittagong, Bangladesh).
S_2	27.2 ±1.2	Marine soil (Bay of Bengal, Chittagong, Bangladesh).
S_3	15.8 ±1.3	Industrial soil (Eastern Refinery, Chittagong, Bangladesh).
S_4	21.4±1.5	Industrial soil (Karnaphuly Paper Mill, Chandraghona, Chittagong, Bangladesh).
S_5	17.5 ±1.8	Road side soil (Chittagong- Rangamati Highway, Bangladesh)

[a]Average of five analyses of each sample; [b]The measure of precision is the standard deviation; [c]Composition of the soil samples: C, N, P, K, Na, Ca, Mg, Cu, Fe, Pb, NO_3, NO_2, Zn, SO_4, Mn, Mo, Co, etc.

by 1-2 mL of a 0.01% fluoride or thiocyanide solution as a masking agent. The nickel content was determined by the above-mentioned procedure and quantified from a calibration graph prepared concurrently. The results are given in TABLE 7.

Precision and accuracy

The precision of the present method was evaluated by determining different concentrations of nickel (each analyzed at least five times). The relative standard deviation (n=5) was 2 – 0% for 1 – 500 µg of nickel in 10 mL, indicating that this method is highly precise and reproducible(TABLE 1). The detection limit(3s of the blank) and Sandell's sensitivity (concentration for 0.001 absorbance unit) for nickel(II) were found to be 1.0 ngmL^{-1} and 7.0 ngcm^{-2} respectively. The results for total nickel were in good agreement with the certified values (TABLE 4). The reliability of our nickel-chelate procedure was tested by recovery studies. The average percentage recovery obtained for the addition of nickel(II) spike to some environmental water samples was quantitative, as shown in TABLE 5. The method was also tested by analyzing several synthetic mixtures containing nickel(II) and divers ions(TABLE 3). The results of biological analyses by the spectrophotometric method were in excellent agreement with those obtained by AAS(TABLE 6). Hence the precision and accuracy of the method were found to be excellent.

CONCLUSIONS

The proposed method possesses distinct advantages over the existing methods[7,11,12-14,19,19a] and recently published[6,8-10,15-18] spectrophotometric methods concerning nickel. First, the determination of nickel with the proposed color system can be directly conducted in an aqueous (50% DMF) solution without need for any separations or cleanup step. Second, the reaction is instantaneous and the absorbance remains stable for over 24 h. Third, the useful concentration range (0.02-10.0 mgL^{-1}) for Beer's law is widened. Fourth, with suitable masking, the reaction can be made highly selective and the reagent blank solution do not show any absorbance. Finally, the results obtained in this work show that the proposed method is applicable to a variety of nickel containing samples, and that the method is simple, selective and accurate. Therefore, this method will be successfully applied to the monitoring of small amounts of nickel in industrial, environmental, and biological and soil samples.

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