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Simultaneous determination of Nickel (II) and Aluminium (III) using Diacetyl monoxime Isonicotinoyl Hydrazone second order derivative spectrophotometric technique

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ABSTRACT

The analytical properties of DiacetylmonoximeIsonicotinoylHydrazone for the simultaneous determination of nickel(II) and Aluminium(III) are described for the first time the reagent gives intense yellow color in sodium acetate-acetic acid buffer medium. The maximum absorbance at 387 nm and 370 nm for nickel(II) and Aluminium(III) respectively. A second order derivative spectrophotometric technique has been used for the simultaneous determination of Ni(II) and Al(III) in alloys and synthetic mixtures.

Key words: Nickel (II), Aluminium (III) DiacetylmonoximeIsonicotinoylHydrazone (DAMINH), simultaneous, second order derivative spectrophotometric.

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INTRODUCTION

Azomethines are very good analytical reagents used for the determination of metal ions by spectrophotometric method in microgram quantities. Hydrazones act as chelating agents by forming colored complexes with metal ions. The potential applications of hydrazones derivatives for the spectrophotometric determination of metal ions have been reviewed by Singh et.al [1]. The great interest towards derivative spectrophotometry is due to the increased resolution of spectral bands that means it is resolving two overlapping spectra and eliminating matrix interferences in the assay of two component mixtures using zero-crossing technique [2-3]. In the absence of zero-crossing point, two simultaneous equations can be solved to determine the components in such a mixture [4-5]. Derivative spectrophotometric analysis of two-component mixtures is also carried out without need to solve simultaneous equations [6-7]. Hydrazones reagents are widely used in our laboratories for the derivative spectrophotometric determination of metal ions [5-8]. In the

Here in we report the simultaneous second order derivative spectrophotometric determination of nickel (II) and aluminium(III) using Diacetyl monoxime Isonicotinoyl Hydrazone (DAMINH). The proposed simultaneous method involves the use of peak-to-base line measurement technique.

MATERIALS AND METHODS

Apparatus

Shimadzu 160A microcomputer based U.V - Visible spectrophotometer equipped with 1.0 cm quartz cells used for all absorbance studies and amplitude measurements in derivative spectrophotometery. An ELICO LI-120 digital pH mater was used in pH adjustments.

Reagents

All the reagents used were A.R grade unless and otherwise stated. All the solutions were prepared with doubly distilled water. Stock solutions (0.01 M) of nickel(II) and aluminium(III) were prepared by dissolving requisite quantity of $NiCl_2.6H_2O$ (AR GSC) and $Al_2(SO_4)_3$ (AR GSC) in 250 mL doubly distilled water respectively. The stock solutions were standardized [9] and suitably diluted to obtain working solutions of metal ions.

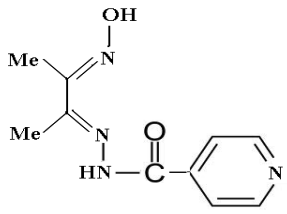

Figure 1:- Structure of Diacetyl monoxime Isonicotinoyl Hydrazone (DAMINH)

The reagent was prepared by simple condensation of Diacetylmonoxime with IsonicotinoylHydrazide in 1:1 mole ratio and its structure is given above in figure 1.The reagent solution (0.01 M) was prepared by dissolving 0.22 mg of compound in 100 mL of dimethylformamide (DMF) and the solution was found to be stable for 48 hours.

Triton X-100 solution

A 5% solution was prepared by diluting 5.0 mL of Triton X-100 (AR Merk) to 100 mL with doubly distilled water.

Buffer solutions

Buffer solutions prepared by Hydrochloric acid (1.0 M) – Sodium acetate (1.0 M) (pH 0.5 - 3.5); Acetic acid (0.2 M) - Sodium acetate (0.2 M) (pH 4.0 - 6.5); Acetic acid (0.2 M) - Sodium acetate (1.0 M) (pH 7.0); Sodium tetraborate decahydrate (0.25 M) - Hydrochloric acid (0.1 M) (pH 8.0 – 9.1); Sodium tetraborate decahydrate (0.2 5 M) - sodium hydroxide (0.1 M) (pH 9.2 - 10.8) were used in the present study.

Reaction with metal ions

At different PH values some important metal ions were tested with DAMINH reagent. The samples were prepared in 25 ml volumetric flasks by adding 10ml of buffer, 1 ml of metal ion, 1 ml of 0.01 M DAMINH, 3 ml of DMF. The reaction mixture was diluted to the mark with distilled water. The absorbance was measured in 250 - 600 nm range against reagent blank. The results are summarized in table 1 which indicates that the reagent is potential for the spectrophotometric determination of various metal ions.

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Table 1: Analytical characteristics of diacetyl monoxime Isonicotinoyl Hydrazone

Metal ion	pH	λ max	Color	Molar absorptivity (L mol^{-1} cm^{-1})
Ga(III)	3 - 6	362 nm	Green	3.17×10^4
V(V)	4 - 7	360 nm	Green	2.9×10^4
Fe(II)	5 - 10	355 nm	Yellow	3.83×10^4
Ru(III)	5 - 11	363 nm	Yellow	1.45×10^4
Hg(II)	3 - 7	364.5 nm	Orange	4.2×10^4

Recommended procedures

(a). Determination of aluminium

An aliquot of the solution containing 0.48 - 4.56 µg / mL (ppm) of Al(III), 10 ml of NH_4cl-NH_4OH buffer solution (pH 8.0), 3 ml of DMF and 1 ml o f 0.01 M DAMINH were combined in a 25 ml volumetric flasks and the resulting solution was diluted to the mark with distilled water. The absorbance of the solution was read at 355 nm against reagent blank. The measured absorbance is used to compute the amount of aluminium from predetermined calibration curve.

(b). Determination of nickel

An aliquot of the solution containing 0.39 – 5.6 µg / mL (ppm) of Ni(II), 10 ml of NH_4cl-NH_4OH buffer solution (pH 9.0), 3 ml of DMF and 1 ml of 0.01 M DAMINH were combined in a 25 ml volumetric flasks and the resulting solution was diluted to the mark with distilled water. The absorbance of the solution was read at 365 nm against reagent blank. The measured absorbance is used to compute the amount of aluminium from predetermined calibration curve.

(c). Simultaneous determination of Aluminium and Nickel

A known aliquot of a synthetic mixture containing 0.632 – 5.85 µg / mL Al(III) and 0.495 – 4.75 µg / mL of Ni(II), 3 ml of DMF and 1 ml of 0.01 M DAMINH were combined in a 25 volumetric flask and the resulting solution was diluted to the mark with distilled water. The absorbance was measured at 355 nm and 365 nm against reagent blank and the amounts of

Aluminium(III) and Nickel (II) were respectively determined by solving the simultaneous equations.

Analysis of Alloys:

2 gm of alloy sample was digested in 50 mL of aqua-regia by worming and the solution was evaporated to dryness. The residue was dissolved in 20 mL of diluted HCl and resulting solution concentrated to 10.0 mL, diluted to 100 mL with doubly distilled water, filtered and made up to the mark in a 250-mL volumetric flask.

RESULTS AND DISCUSSION

DiacetylmonoximeIsonicotinoylHydrazone is a new chomogenic reagent was not used for spectrophotometric simultaneous determination of Ni and Al so far. DAMINH reagent can easily prepared like any other Schiff base reagent. The reactions of some important metal ions with DAMINH are summarized in table1. The color reactions are mainly due to the complex formation of DAMINH with certain metal ions like Ni(II), Al(III), Ru(III), Fe(II), V(V), Hg(II), Ga(III) to give intense color complexes

Simultaneous determination of Ni(II) and Al(III) in synthetic mixture

The simultaneous spectrophotometric determination of aluminium(III) and nickel(II) in synthetic mixture was carried out by employing the recommended procedure and the results are presented in the table

Determination of aluminium (III) and nickel(II)

Aluminium(III) and Nickel(II) reacts with DAMINH in slightly alkaline medium to give yellow colored complex. The color reactions are instantaneous even at room temperature at pH 8 -9 range. The absorbents of yellow colored complexes remains stable for more than 10 hours in both cases. The maximum color intensity is observed at in the pH 8 – 9 and 7-8 range for Ni-DAMINH and Al-DAMINH complexes respectively. A 10 fold molar excess of reagent is sufficient for full color development in both systems. Addition of excess reagent has no adverse effect on the absorbance. The order of addition of metal ions, buffer, reagent and triton X-100 solutions has no adverse effect on the absorbance of complexes. Important analytical characteristics of Al-DAMINH and Ni-DAMINH complexes are summarized in table2.

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Table 2: Important analytical characteristics of Al-DAMINH and Ni-DAMINH complexes

Characteristics	Results	
	Al(III)-DAMINH	Ni(II)- DAMINH
λ_{max} (nm) Mole of reagent required per mole of metal ion for full colour development	355 5 - folds	365 10 - folds
Detection limit (µg/mL)	0.0735	0.0545
Limit of Quantization (µg/mL)	0.1454	0.1850
Molar absorptivity ($L.mol^{-1}.cm^{-1}$)	2.69×10^{4}	2.08×10^{4}
Sandell's sensitivity ($\mu g.cm^{-2}$)	0.00745	0.00282
Beer's law validity range (µg/mL)	0.828 – 8.0	0 .188 – 1.886
Optimum concentration range (µg/mL)	0.392 – 2.452	0.495 - 3.09
Slope (b)	0.224	0.174
Intercept (a)	0.045	0.03999
Correlation coefficient	0.9891	0.8998
Specific absorptivity ($ml.g^{-1}.cm^{-1}$)	2.08	1.76
Relative standard deviation (%)	0.346	0.477
Composition of complex (M:L) obtained in Job's and mole ratio method	1: 1	1: 1
Stability constant of the complex	1.011×10^{6}	3.815×10^{6}

The direct and first order spectra of solutions of Al(III)-DAMINH and Ni(II)-DAMINH complexes in an aqueous basic buffer medium (pH = 8.5) are shown in Figure 2. The absorption spectra overlap considerably and therefore direct and first order spectrophotometeric determination of one metal in the presence of the other is not possible.

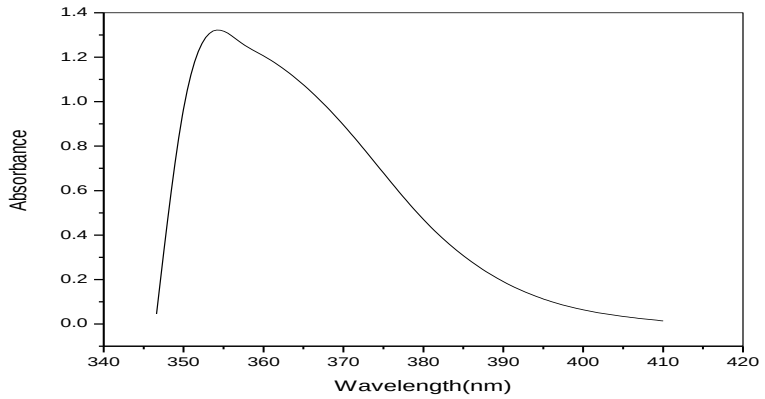

Figure1 Zero order spectrum of Al(III) + Ni(II) in the presence of DAMINH

[Al(III)] = 4×10^{-5} M [Ni(II)] = 1.6×10^{-5}M;
[DAMINH] = 5.6×10^{-4}M ; pH = 8.5

Derivative spectrophotometric determination of aluminium(III) and nickel(II)

Second order derivative spectrophotometric is useful technique for simultaneous aluminium(III) and nickel(II) because it decreases the interference of adverse ions i.e., increase the tolerance limit value of foreign ions and may be advantageously used for the determination

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of metal ins having overlapping spectra. The main reason why the interest in derivative spectra is due to simplicity, relatively quick, easy realization and increased analysis of minor components. The recommended derivative processor was employed for the simultaneous determination of aluminium(III) and nickel(II).

The typical second order derivative spectra of Al(III)-DAMINH and Ni(II)-DAMINH shown in figure 2

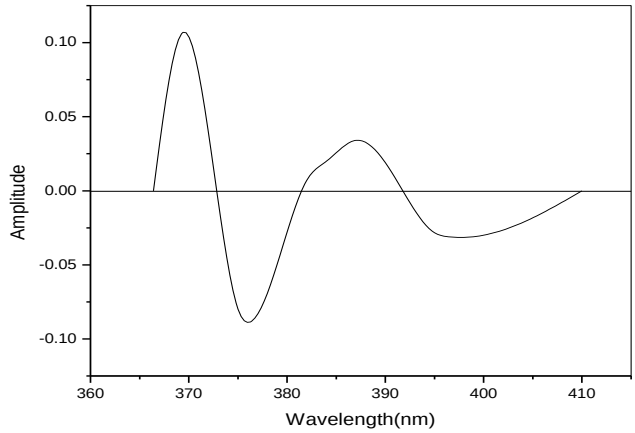

Figure2 Typical second order spectrum of Al(III) + Ni(II) in the presence of DAMINH

[Al (III)] = 4 x 10^{-5} M [Ni (II)] = 1.6 x 10^{-5}M; pH = 8.5

[DAMINH] = 5.6 x 10^{-4}M;

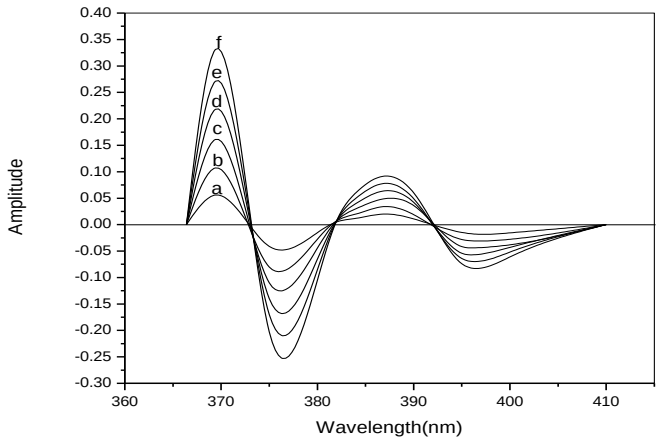

Figure 3. Second order spectrum of Al(III) + Ni(II) in the presence of DAMINH

[Al(III)] = 4.0 x 10^{-5} M; [Ni(II)] = 1.6 x 10^{-5} M

[DAMINH] = 5.6 x 10^{-4}M; pH = 8.5

a) 0.5 ml of Al(III) and Ni(II) each
b) 1.0 ml of Al(III) and Ni(II) each
c) 1.5 ml of Al(III) and Ni(II) each
d) 2.0 ml of Al(III) and Ni(II) each
e) 2.5 ml of Al(III) and Ni(II) each
f) 3.0 ml of Al(III) and Ni(II) each

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Interference

The selectivity of the derivative methods was tested by studying the effect of foreign ions which brings about change the amplitude by ± 2 % was taken as the tolerance limit. Interference of diverse ions which often accompany with Al(III) and Ni(II) has been studied in the determination of 1.38 µg/mL of Al(III) and 1.45 µg/mL of NI(II). The results are given in table3.

Table 3. Tolerance limit of foreign ions in the determination of 1.45 µg/mL Ni(II) and 1.38 µg/mL of Al(III).

Ni(II)-DAMINH			
Foreign ion	**Tolerance limit (µg/ml)**	**Foreign ion**	**Tolerance limit (µg/ml)**
Fluoride	16.52	Mo (VI)	15.35
Chloride	24.70	Mg (II)	6.27
iodide	483.40	W (VI)	35.87
nitrate	37.86	Zr (III)	36.49
acetate	41.40	Se (IV)	7.35
oxalate	30.61	Mn (II)	19.98
EDTA	326.50	Y (III)	35.56
thiosulphate	128.30	Cu (II)	0.781
		Fe (II)	0.61
		Ni (II)	1.43
		Hg (II)	1.64
		Pd (II)	1.08
		Cd (II)	1.38
		Zn (II)	0.76
		U (VI)	44
		Ru (III)	4.68

Al(III)-DAMINH			
Foreign ion	**Tolerance limit (µg/ml)**	**Foreign ion**	**Tolerance limit (µg/ml)**
Fluoride	20.54	U (VI)	82.80
Chloride	54.62	Ru (III)	13.26
iodide	253.8	W (VI)	63.95
nitrate	130.53	Co (II)	0.31
acetate	43.7	Mo (VI)	19.2
oxalate	8.85	Se (IV)	5.45
EDTA	1667	Pd (II)	0.12
thiosulphate	15.5	Mg (II)	32.41
		Cu (II)	0.45
		Sn (II)	14.84
		Ni (II)	0.612
		Zr (IV)	10.73
		Sr (II)	12.75
		La (III)	52.91
		Ti (IV)	6.96

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		Al (III)	13.49
		Th (IV)	64.01
		Cd (II)	0.804
		Cr (VI)	5.19

Applications

The simultaneous second order derivative spectrophotometric determination of Al(III) and Ni(II) in the synthetic mixtures, alloy samples were carried out by employing the recommended procedure. A known aliquot of the sample solution was taken in a 25-mL volumetric flask containing 10 mL buffer (pH = 8.5), 1.0 ml of Triton X-100 (5%) solution and 1.0 mL of DAMINH reagent (0.01 M) solutions. The contents in the flask were made up to the mark with doubly distilled water. The second derivative amplitudes of the reaction mixture were measured at 370 nm and 387 nm. The amount of aluminium(III) was computed from the pre-determined calibration plot at 370 nm. Similarly, the amount of nickel(II) was deduced from the pre-determined calibration plot at 387 nm. The results are presented in Table 4 and Table 5 respectively.

Table 4: Simultaneous determination of Al(III) and Ni(II) in synthetic pictures Al (III) and Ni (II)

Amount taken (µg mL^{-1})		Amount found* (µg mL^{-1}) (Recovery %)		Relative error (%)	
Al(III)	**Ni(II)**	**Al(III)**	**Ni(II)**	**Al(III)**	**Ni(II)**
0.419	0.505	0.418 (99.7)	0.507 (100.4)	-0.24	+0.40
0.558	0.505	0.557 (99.8)	0.501 (99.2)	-0.18	-0.79
0.698	0.505	0.705 (101)	0.503 (99.6)	+1.00	-0.39
0.838	0.505	0.831 (99.2)	0.499 (98.8)	-0.83	-1.18
0.977	0.505	0.985 (100.8)	0.509 (100.8)	+0.82	+0.79
1.117	0.505	1.109 (99.3)	0.511 (101.2)	-0.72	+1.19
0.558	0.252	0.558 (100)	0.249 (98.8)	0.00	-1.19
0.558	0.505	0.561 (100.5)	0.508 (100.6)	+0.54	+0.59
0.558	0.757	0.555 (99.5)	0.762 (100.6)	-0.53	+0.66
0.558	1.010	0.552 (98.9)	0.994 (98.4)	-1.07	-1.58
0.558	1.260	0.554 (99.3)	1.240 (98.4)	-0.72	-1.58
0.558	1.515	0.563 (100.9)	1.509 (99.6)	+0.89	-0.40

Table 5: Determination of aluminium(III) and nickel(II) in alloy samples

Sample	Certified (%)		Amount found (%)		Error (%)	
	Al(III)	**Ni(II)**	**Al(III)**	**Ni(II)**	**Al(III)**	**Ni(II)**
AL-NI-01-P.21AL	21	79	20.78	78.86	+1.04	+0.18
AL-NI-01-P.41AL	41	59	40.28	59.10	+1.756	-0.17
AL-NI-01-P.50NI	50	50	49.56	49.75	+0.88	+0.5
AL-NI-01-P.20NI	80	20	79.67	19.36	+0.41	+3.2

*average of three determinations

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CONCLUSIONS

Simultaneous spectrophotometric determination of Ni(II) and Al(III) using DAMINH in the presence of Triton X-100 is simple sensitive, simple and rapid triton X-100 increases the stability of the complex. The present method do not involve heating or filtration or separation, large amount of anions and citations do not interfere in the present method. Hence simultaneous determination of Ni(II) and Al(III) can be carried out by using DAMINH

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