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RESEARCH ARTICLE

Spectrophotometric Determination of Trace Amount of Nickel(II) in Tea Leaves Sample by Using Antipyriyl azo-2,7-naphthalendiol as New Reagent

MASAR A. AWAD and HUSSAIN.J.MOHAMMED*

Chemistry Department, Faculty of Science, Kufa University, Iraq
ibrahiem_af@yahoo.com

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Abstract: A new, simple, sensitive and rapid spectrophotometric method is proposed for the determination of trace amount of nickel(II). The method is based on the formation of a 1:2 complex with 1-(4′- pyrazolon azo) 2,7-naphthalendiol (1-APANDOL) as a new reagent is developed . The complex has a maximum absorption at 514 nm and ε_{max} of 2.0×10^4 L mol^{-1} cm^{-1}. A linear correlation (0.1-2.0 µg mL^{-1}) was found between absorbance at λ_{max} and concentration. The accuracy and reproducibility of the determination method for various known amounts of nickel(II) were tested. The results obtained are both precise (RSD was better than 0.63%) and accurate (relative error was better than 0.2%). The effect of diverse ions on the determination of nickel(II) to investigate the selectivity of the method were also studied. The stability constant of the product was 0.13×10^8 L mol^{-1}. The proposed method was successfully applied to the analysis of synthetic mixtures and tea sample without any preliminary concentration or separation.

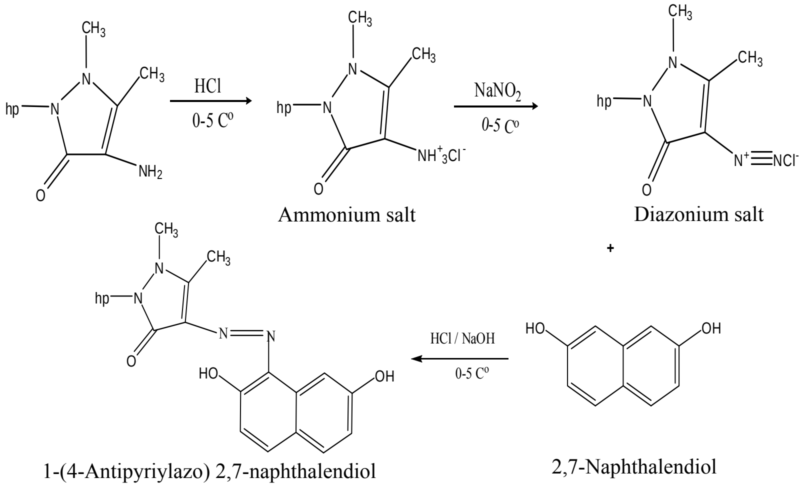
Keyword: Nickel(II) determination, Spectrophotometry, Antipyriyl azo 2,7-naphthalendiol, Tea leaves

Introduction

Azo compounds have a great industrial importance[1] as well as biological activity[2-4]. They can also be used in subtractive photographic process and color pictures[5] nickel is a nutritionally essential metal and widely distributed in nature[6]. In chemical analysis, metal chelation followed by solvent extraction and spectrophotometric detection is the preferred mode of analysis for a number of metal ions[7-9]. Due to its rapidity, simplicity and wide applications, pyrazolon azo forms colored water insoluble complexes with a large number of metal ions[10] At present, a lot of analytical methods have been proposed for the determination of nickel(II), including, inductively coupled plasma mass spectrometry (ICP - MS)[11], atomic absorption spectrometry (AAS)[12], solid–phase extraction[13] and X-ray fluorescence spectrometry[14] show good sensitivity but is limited because of expensive instrumentation and high cost for routine analysis. According to the best of our knowledge, this reagent has not been reported in the literature as being used for any cation determination. In this study, we wish to report this reagent as a selective reagent in spectrophotometric determination of trace amounts of nickel(II).

Experimental

The reagent was prepared by coupling 2,7-naphthalendiol with diazotate 4-amino antipyrine in alkaline alcoholic solution. A diazonium solution was prepared by taking 1 g 4-amino antipyrine in 25 mL of ethanol and concentrated hydrochloric acid with 5 mL of distilled water and adding sodium nitrite solution drop wise at 0-5 ^{0}C. 2,7- Naphthalendiol 1.1 g was dissolved in 20 mL of ethanol and 30 mL of 0.1 M sodium hydroxide were added at 0-5 ^{0}C. The mixture was left to stand over night. The precipitate was filtered off and recrystallized from ethanol[15] (Scheme 1).



Scheme 1. Preparation of reagent (1-APANDOL)

Preparation of nickel(II)complex

The complex was prepared by direct reaction between nickel chloride hexahydrate and the appropriate ligand (1-APANDOL) in 1:2 mole ratio, using aqueous ethanol as solvent. The formed precipitate was filtered off, washed with warm ethanol, then dried in a vacuum desiccator.

Apparatus

Spectrophotometric measurement was made with Shimadzu UV-Visible - 1700 double beam spectrophotometer using 1.00 cm glass cells. Vibrational spectra were recorded on test scan Shimadzu FT.IR 8000 series. Measurements of pH were made using Hanna**,** HI9811-5 pH-meter equipped with a glass - saturated calomel combined electrode. Melting points of both ligand and complex were obtained with an electrothermal melting point apparatus. Conductivity was measured in DMSO (1×10^{-3}) solution with an Alpha digital conductivity model-800. Elemental analysis (C.H.N) were carried out with a EuroEA Elemental Analyser.

Reagents

All chemicals used were of analytical grades

Nickel(II) stock solution (100 µg mL^{-1})

This solution was prepared by dissolving 0.081 g of nickel chloride hexahydrate in 200 mL of distilled water, working standard of Ni(II) solutions were prepared by simple dilution of the appropriate volume of the standard Ni(II) solution (100 µg mL^{-1}) with distilled water.

1-(4- Antipyriyl azo) 2,7-naphthalendiol (1 mM)

0.0476 g of Reagent was dissolved in 250 mL of ethanol.

Foreign ion solutions (10 µg mL^{-1})

All the solutions were prepared by dissolving an appropriate amount of the compound in distilled water in a volumetric flask.

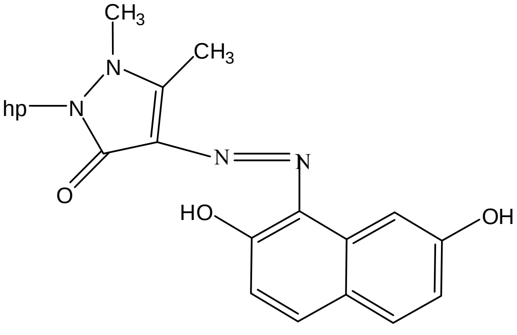
General procedure

An aliquot of sample containing 1-20 µg of Ni(II) was transfer into a series of 10 mL standard flask. 2 mL of 1 Mm of 1-APANDOL was added and pH was adjusted to 9. The complexes formed were solubilized in water and diluted up to 10 mL in a standard flask. The absorbance of the resulting solution was measured at the respective absorption maxima against a reagent blank prepared under similar condition.

Results and Discussion

Properties of (1-APANDOL) and its metal chelate

1-APANDOL is a tridentate with coordination of azo group nitrogen, hydroxyl group and carbonyl group; it has the following structure.



1-(4-antipyriylazo) 2,7-naphthalendiol

Structure of 1-APANDOL

Owing to the large conjugated system, the compound showed excellent chelating ability to form inner metal chelates. 1-APANDOL and its metal chelates can be easily solubilized in an aqueous solution. Elemental analyses were carried out on the resulting compound (C% calc. 67.37; found 68.16, H% calc.4.85; found 5.75, N% calc.14.96; found 15.34). m.p. 234 °C.

Spectra

The result of this investigation indicated that the reaction between Ni(II) and 1-APANDOL at pH 9 yield highly soluble coloured product which can be utilized as a suitable assay procedure for Ni(II). This coloured product has a maximum absorption at 514 nm , the blank at this wave length shows zero absorbance (Figure 1), was adopted in all subsequent experiments. The effect of various parameters on the absorbance intensity of the formed products was studied and the reaction conditions were optimized.

Effect of pH

The electronic absorption of 1- APANDOL and its complex in ethanol have been recorded in the wavelength range 190-800 nm (Figure 1). The electronic absorption of complex showed a red shift for (π - π^*) electronic transition band. [Ni (L)$_2$] shows one broad in visible region at (16000-21000) cm^{-1} refer to (${}^3A_{2g}(F)\rightarrow T_{2g}(F)[\nu_1]$, ${}^3A_{2g}(F)\rightarrow {}^3T_{1g}(F)[\nu_2]$, ${}^3A_{2g}(F)\rightarrow T_{1g}(P)[\nu_3]$) that is in accordance with octahedral geometry of nickel metal ion[16,17]. The pH of metal complex solutions was adjusted using dilute solutions of (0.05 M) NaOH and (0.05 M) HCl and the effect on absorbance was studied (Figure 2). The absorbance of the complex was maximum and constant in the pH range given in Table 1.

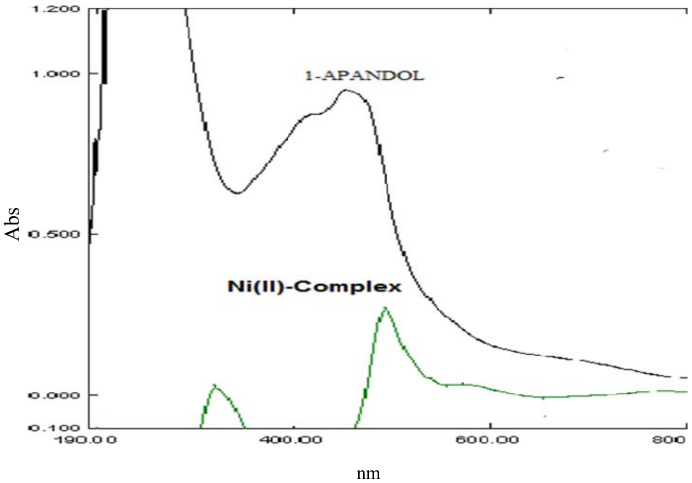


Figure 1. Absorption spectra of 20µg Ni(II) treated as described under procedure and measured against reagent blank and 1-APANDOL the reagent blank measured against ethanol.

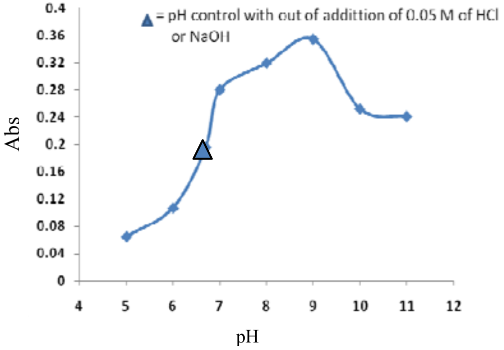


Figure 2. Effect of pH

Table 1. Analytical characteristics of Ni(II) - complex

Characteristic	Ni(II) -complex
Absorption maximum, nm	514
Beer's law range, ppm	0.1-2.0
pH range	7-9
Sandell's sensitivity µg. cm^{-2}	0.0029
Molar absorptivity (L. mol^{-1}. cm^{-1})	2.0x10^4
Stability constant (L. mol^{-1})	0.13x10^8
Melting point for reagent	232-234 ^{0}C
Melting point for Ni(II) - complex	288-290 ^{0}C

Effect of 1-APANDOL concentration

When various concentrations of of 1-(4'- antipyriylazo) 2,7-naphthalendiol was added to a fixed concentration of Ni(II), 2 mL of 1 mM 1-APANDOL solution was sufficient to develop the colour to its full intensity and gave minimum blank value, above 2 mL, the absorbance of the blank value was increased causing a decrease in the absorbance of the sample. Therefore, 2 mL of 1 mM of 1-(4'- antipyriylazo) 2,7-naphthalendiol was used in all subsequent experiments (Figure 3).

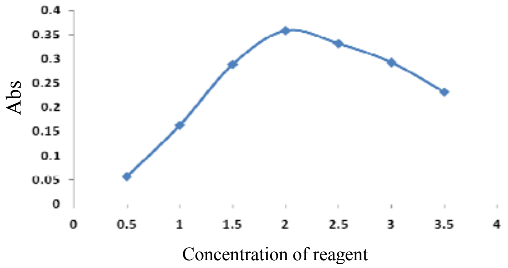


Figure 3. Effect of 1-APANDOL concentration

Effect of reaction time

The colour intensity reached a maximum after the Ni(II) has been reacted immediately with 1-APANDOL and became stable after one minute, therefore one minute development time was selected as optimum in the general procedure. The colour obtained was stable for at least 24 h (Figure 4).

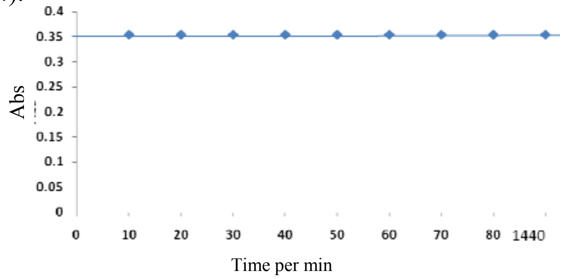


Figure 4. Effect of time on complex of Ni[1-APANDOL]$_2$

Effect of temperature

The effect of temperature on the colour intensity of the product was studied. In practice, the same absorbance was obtained when the colour was developed at room temperature (20-40 ^{o}C), but when the volumetric flask were placed in a water-bath at 50-70 ^{o}C a loss in colour intensity and stability were observed, therefore it is recommended that the colour reaction should be carried out at room temperature for complex (Figure 5).

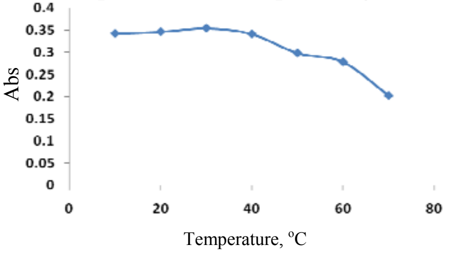


Figure 5. Effect of temperatures on complex Ni[1-APANDOL]$_2$

Calibration graph

The calibration equation for (0.1-2.0 µg per mL) Ni(II) is Y = 0. 347x + 0.0009 (R^2 = 0.9962). Since the coloured complex is stable for 24 h, the method can be applied to large series of samples. The molar absorptivity and Sandell' sensitivity are given in Table 1.

Composition of the complex

The composition of complex was studied in the excess of reagent solution by the mole-ratio and Job s methods (Figure 6,7). A break at a 1:2 (M:L) mole ratio suggested the formation of complex where M= Ni(II) and L=(1- APANDOL).

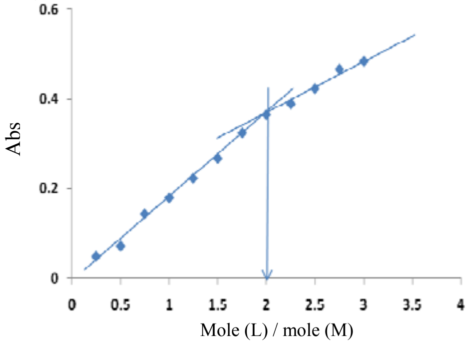


Figure 6. Mole-ratio method for Ni[1-APANDOL]$_2$ complex

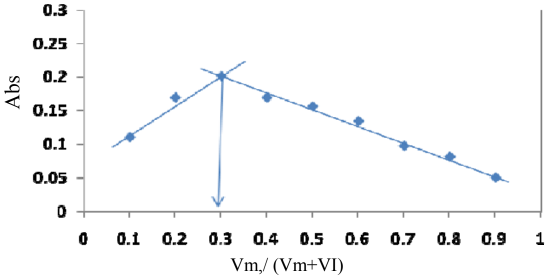


Figure 7. Job s method for Ni[1-APANDOl]$_2$ complex

Conductivity measurements

The solubility of the complexes in dimethy sulfoxide and ethanol permitted of the molar conductivity of 1x10^{-3} M solution at 25 °C and by comparison, the electrolytic nature for complexes. The low values of the molar conductance data listed in Table 2 indicate that the complexes are non electrolytes.

Table 2. Conductivity values of complex

Complex	Molar conductivity, S $mole^{-1}$ cm^2 (DMSO)	Molar conductivity, S $mole^{-1}$ cm^2 , (Methanol)
Ni(1-APANDOL)$_2$	9.7	12.4

Interferences

The effect of diverse ions in the determination metal ion was studied. The metal ion can be determined in the presence of a 5 or more fold excess of cation and anion (Table 3). In the experiment, a certain amount of standard Ni(II) solution, coexisting ion solution and masking agent (or absence of masking agent) were added. It is found that all the studied ions interfere seriously. However, their interferences are masked efficiently by addition 1.0 mL of 0.1 M of ($NaNO_2$).

Table 3. Effect of foreign ions

Foreign ion	M. F. of ion	Conc., ppm	Abs	Error %
Zn^{2+}	$ZnCl_2$	10	0.610	+41.96
Mn^{2+}	$MnCl_2$	10	0.505	+29.9
Co^{2+}	$CoCl_2.\ 6H_2O$	10	0.411	+16.1
Pb^{2+}	$pbCl_2$	10	0.401	+11.72
Cu^{2+}	$CuCl_2.\ 2H_2O$	10	0.543	+34.8
Fe^{3+}	$FeCl_3$	10	0.487	+27.31
Hg^{2+}	$HgCl_2$	10	0.441	+19.72
Pd^{2+}	$PdCl_2$	10	0.566	+37.45
$S_2O_8^{2-}$	NaS_2O_8	10	0.357	+0.84
I^{-1}	KI	10	0.437	+18.99
Br^-	NaBr	10	0.383	+7.57
SO_4^{2-}	Na_2SO_4	10	0.345	-2.6
Cl^-	KCl	10	0.425	+16.7
CO_3^{2-}	Na_2CO_3	10	0.420	+15.71
F^-	NaF	10	0.343	-3.2

FT IR of reagent and its complex

The FT IR of the free ligand and its metal chelate were carried out in the 400-4000 cm^{-1} Range. The IR bands of the 1-APANDOL and its Ni(II) complex with their probable assignment are given in Table 4. The IR spectrum of ligand shows a broad band at 3414 cm^{-1}, which can be attributed to the phenolic OH group. However, the υ(N=N) stretching band in the free ligand is observed at 1494 cm^{-1}. This band is shifted to lower with low intensity at 1454 cm^{-1} frequency value upon complexation suggesting chelation via the (M-N)[18]. The IR spectrum of the ligand revealed a sharp band at 1637cm^{-1} due to υ(C=O) of pyrazole azo. This band is shifted to lower with low intensity upon complexation[19]. The bonding of oxygen to the metal ion is provided by the occurrence of band at 509 cm^{-1} as the result of υ(M-O)[20,21].

Table 4. Selected FT IR data of 1-APANDOL and its complex with Ni(II)

Compound	υ (OH)	υ (C-H) arom.	υ (N=N)	υ (C=O)	υ (M-O)	υ (M-N)
HL	3494 m	3069 w	1494 m	1637 s	_	_
[Ni (L)]	3383b	3068 w	1454 m	1612m	509 w	455 w

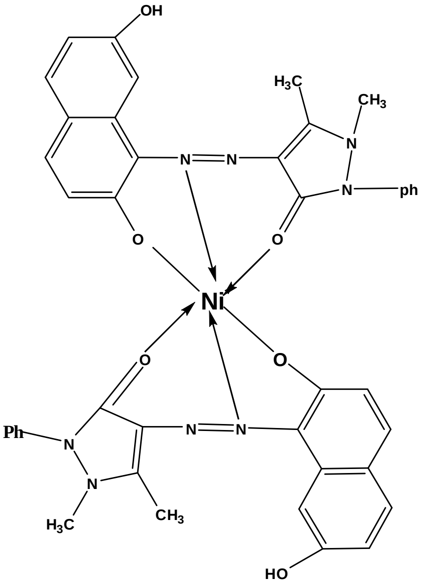
S: sharp; m: medium; w: weak; b: broad

On the basis of the FT IR, stoichiometric and elemental analysis molar conductivity data the structure of complex can be suggested as the following:-.

Applications

Determination of nickel(II) in practical samples

To determine the accuracy and precision of the method, nickel(II) was determined at two different concentrations with different interferences ions and masked these ions by using masking reagent. The results are shown in Table 5, indicate that satisfactory precision and accuracy could be attained with proposed method.



Structure of complex Ni(1-APANDOL)$_2$

Table 5. Determination of Ni(II) in synthetic samples

Amount taken of Ni(II) ppm	Recovery%	RSD%
0.5	99.8	0.63
1	99.9	4.0

Determination of nickel(II) in tea leaves samples

1 g of the powder of the tea leaves sample was taken in the crucible and heated on a hot plate about 30 min. to near dryness in 250 °C, it without frothing then heated strongly to 800-850 °C in furnace for 1 h after the moisture has been removed. We took utmost care avoid loss by sputtering. The ash was dissolved in the 2 mL of distilled water then added 10 mL of hydrochloric acid 1:1, after that heated the solution slowly until boiling, cooling to room temperature. After filtering the ash and transferred the filtrate volume into 25 mL volumetric flask and diluted with the same solvent, the solution becomes clear and transparent or a little green, the solution was left for 60 min and then ready for UV-Visible spectrophotometric analysis and atomic absorption[22] (Table 6).

Table 6. Ni(II) levels (μg.g^{-1}) in tea leaves sample

Ion in tea leave sample	Amount found by our Spectrophotometric method, μg.g^{-1}	Amount found by atomic absorption method, μg.g^{-1}
Liption yellow label tea	1.34	1.16
Liption clear green tea	4.51	4.7

References

1. Guha S, Lohar S, Hauli I, Mukhopadhyay S K and Das D, *Talanta*, 2011, **85** 1658-1664.
2. Patal S, “The Chemistry of Hydrazo, Azo and Azoxy Group” Part I, Wiley, New York, 1975.

3. Awad I M, *J Chem Technol Biotechnol*., 1992, **53(3)**, 227-236; DOI:10.1002/jctb.280530303
4. Zidan A S, El-Said A I, El-Meligy M S, Aly A A M and Mohammed O F, *J Therm Anal Calorim*., 2000, **62**, 665.
5. Awad I M A, *Phosphorus Sulfur Silicon*, 1996, **114**, 17-28; DOI:10.1080/10426509608046407
6. Nielsen G D, Soderberg U, Jorgensen P J, Templeton D M, Rasmussen S N, Andersen K E and Grandjean P, *Toxicol Appl Pharmacol*., 1999, **154(1)**, 67-75; DOI:10.1006/taap.1998.8577
7. Anithe C, Sheela C D, Tharmaraj P and Raja S J, *Spectrochim Acta Part A: Mole Biomole Spectro.*, 2012, **98**, 35-42; DOI:10.1016/j.saa.2012.08.022
8. Aritake Y and Akitsu T, *Polyhedron*, 2012, **31(1)**, 278-284; DOI:10.1016/j.poly.2011.09.025
9. Gaber M, El-Hefnawy G B, El-Borai M A and Mohamed N F, *J Therm Anal Calorim*., 2012, **109**, 1397-1405.
10. Abo El-Ghar M F, Abdel-Ghani N T, Badr Y and El-Borady O M, *ISESCO Sci Tech Vision*, 2007, **3(3)**, 58.
11. Santos V E O, Celante V G, Lelis M F F and Freitas M B J G, *J Power Sources*, 2012, **218**, 435-444; DOI:10.1016/j.jpowsour.2012.07.024
12. Khazaeli S, Nezamabadi N, Rabani M and Panahi H A, *Microchem J.*, 2013, **106**, 147-153; DOI:10.1016/j.microc.2012.06.002
13. Turan S, Tokalioglu S, Şahan A and Soykan C, *React Funct Polym.*, 2012, **72(10)**, 722-728; DOI:10.1016/j.reactfunctpolym.2012.07.002
14. Luo L, Chu B, Li Y, Xu T, Wang X, Yuan J, Sun J, Liu Y, Bo Y, Zhan X, Wang X, and Tang L, X-*Ray Spectrom*., 2012, **41(3)**, 133-143; DOI:10.1002/xrs.2364
15. Farukawa M and Shibata S, *Anal Chim Acta*, 1982, **140(1)**, 301-307; DOI:10.1016/S0003-2670(01)95476-5
16. Greenword N N and Earnshaw A, "Chemistry of the Elements" 2nd Edition, Butterworth Heinemann, 1997.
17. Sheelam C D, Anitha C, Tharmaraj P and Kodimunthiri D, *J Coord Chem*., 2010, **63**, 884-893; DOI:10.1080/00958971003660416
18. Li X, Wu Y, Gu D and Gan F, *Dyes and Pigments*, 2010, **86**,182-189.
19. Pandey G and Narng K K, *Synt Reas Inorg Metrog Chem*., 2004, **34**, 291.
20. Zaki Z M, *Spectrochim Acta*, 2000, **56(10)**, 1917-1923; DOI:10.1016/S1386-1425(00)00249-3
21. Boryana D, Karima B, Elisaventa I and Freddy A, *Canadian J Anal Sci*., 2004, **49(6),** 346-352.
22. Stasys T, Roland K and Aivaras K, *CHEMIJA*, 2004, **15(4),** 49-52.