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Liquid Chromatographic Determination of Cobalt(II), Nickel(II) and Silver(I) using 6-Methyl-2-pyridine Carboxaldehyde Isonicotinoyl Hydrazone as Derivatizing Reagent

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The reagent 6-methyl-2-pyridine carboxaldehyde isonicotinoyl hydrazone reacts with copper(II), nickel(II), cobalt(II), iron(II), zinc(II), mercury(II) and silver(I) to develop color in aqueous methanolic media with maximum in pH range 4-5. The molar absorptivity was observed within 6.2×10^3 to 3.9×10^4 $L \cdot mol^{-1} cm^{-1}$ within 335-372 nm. Cobalt(II), nickel(II) and silver(I) chelates separated from Kromasil 100, C-18, 10 µm (250 × 4.6 mm id) column, when eluted with methanol: water : acetonitrile : tetrabutyl ammonium bromide (1 mM) (53 : 25 : 20 : 2 v/v/v/v) with a flow rate 1 mL/min and UV detection at 256 nm. Linear calibration range for cobalt(II) and nickel(II) was 1-5 µg/mL, but for silver (I) it was (5-25) µg/mL. The detection limits for cobalt, nickel and silver were observed 80, 110, 400 ng/mL, respectively. The method was applied for the determination of cobalt and nickel from tea and tobacco leaves and silver from photographic film.

Key Words: Liquid chromotography, Co(II), Ni(II), Ag(I), 6-Methyl-2-pyridine carboxaldehyde isonicotinoyl hydrazone.

INTRODUCTION

The high performance liquid chromatography (HPLC) for the separation of metal chelates and the determination of these species at trace level is of considerable interest. The HPLC determination of metal ions has been reviewed[1]. A number of chelating reagents have been used for HPLC determination of cobalt(II), nickel(II) and silver(I). Some of the reagents used include 4(2-pyridylazo) resocinol[2], tetra (4-methoxyphenyl)porphyrine[3], tetra(*m*-aminophenyl)porphyrine[4], 2-(2'-quinolinylazo)-5-diethylaminophenol[5,6], diethyldithiocarbamate[7], 2-(4-methyl-2-quinolylazo-5-diethylaminophenol[8] and hexamethylenedithiocar-bamte[9].

Isoniazid (isonicotinyl hydrazine) commonly known as antibiotic anti-tuberculosis agent reacts with 6-methyl-2-pyridine carboxaldehyde to form a hydrazone derivative (Fig. 1)[10]. The present work reports the reactions of the hydrazone towards metal ions spectrophotometrically and for the HPLC separation and determination of cobalt, nickel and silver.

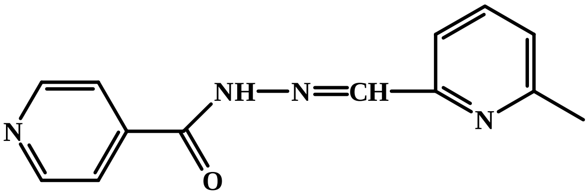

Fig. 1. 6-Methyl-pyridine isonicotinoyl hydrazone (MPA-INH)

EXPERIMENTAL

GR grade chemicals: sodium acetate, acetic acid, sodium bicarbonate, sodium carbonate, boric acid, borax, ammonium chloride, ammonia (23%), chloroform, acetonitrile, hydrochloric acid (37%) and nitric acid (65%) (E-Merck, Germany) were used. Freshly prepared doubly distilled water from all glass was used for HPLC studies. The buffer solutions in the pH range 1-10 at unit interval were prepared from the following: hydrochloric acid (0.1 M)-potassium chloride (1 M) pH 1-2; sodium acetate (1 M)-acetic acid (1 M) pH 3-6; ammonium acetate (1 M)-ammonia pH 7; boric acid (1 M)-borax (1 M) pH 8-9 and ammonium chloride (1 M)-ammonia (1 M) pH 10.

HPLC studies were carried out on Hitachi 655A liquid chromatograph connected with Rheodyne 7125 injector and variable wavelength UV monitor. The HPLC signals were measured with computer with CSW-32 (Data Apex Ltd ©, 2001 www.dataapex.com) software and HP Laser jet 1000. A Kromasil 100 C-18, 10 µm (250 × 4.6 mm id) (Teknokroma, S. Coop. C. Ltda Barcelone) column was used throughout the study. Spectrophotometric studies were carried using Hitachi 220 (Hitachi Pvt. Ltd. Tokyo) spectrophotometer. pH measurements were made with Orion 420A pH meter combined with glass electrode with internal reference electrode. Atomic absorption studies of nickel and cobalt were carried out on Varian Spectr AA 20 atomic absorption spectrophotometer using air-acetylene flame atomization at the conditions recommended by the manufacturer. The determination of nickel and cobalt contents was at 240.7 and 232 nm, respectively with delay time 3 s and integration time 3 s.

The reagent 6-methyl-2-pyridine carboxaldehyde isonicotinoyl hydrazone (MPA- INH) was prepared as reported[10]. Isoniazid (0.274 g) dissolved in ethanol: water (3:2 v/v) (10 mL) was added 6-methyl-2-pyridinecarboxaldehyde (0.242 g) and acetic acid (0.2 mL). The mixture was refluxed for 30 min and allowed to cool. The product was filtered and re-crystallized from ethanol, m.p 142ºC (Lit. 142.4ºC.

Analytical procedure

Spectrophotometric determinatioin: The solution (0.2-1.0 mL) containing copper(II) (2.5-12.5 µg), nickel(II) (2-10 µg), cobalt(II) (2-10 µg), iron(II) (2.5-20 µg), zinc(II) (1.5-12.0 µg), mercury(II) (5-25 µg) or silver(I) (25-125 µg) was transferred to 10 mL volumetric flask separately. The solution was added sodium acetate-acetic acid buffer pH 4, but for silver pH 5 was maintained. The reagent MPA-INH solution (2 mL) (0.02% w/v in methanol) was added and volume was adjusted to the mark. The absorption spectra were recorded against reagent blank within 250-500 nm.

HPLC procedure: Solution (1-2 mL) containing nickel(II) (1-5 µg), cobalt(II) (1-5 µg), and silver (I) (5-25 µg) was transferred to separating funnel and were added sodium acetate buffer pH 4 (1 mL), reagent solution (2 mL, 0.02 % w/v in methanol) and chloroform (2 mL). The contents were mixed well and layers were allowed to separate. The organic layer was collected in screw capped sample vial and aqueous layer was added sodium acetate buffer pH 5. The extraction was repeated with chloroform (1 mL). The combined extract was evaporated under nitrogen atmosphere and residue was dissolved in methanol (1 mL). The solution (20 µL) was injected on Kromasil 100 C-18, 10 µm (250 × 4.6 mm id) column and eluted with methanol: water: acetonitrile: tetrabutylammonium bromide (1 mM) (53 : 25 : 20 : 2 v/v/v/v) with a flow rate 1 mL/min and UV detection was at 256 nm.

Determination of cobalt and nickel from tobacco and tea leaves: Seven cigarette tobacco samples of (1) Capston (2) Boss (3) Gold leaf (4) Diplomat (5) Gold flake (6) K-2 and (7) Dunhill and eight tea samples from (1) Lipton (2)Tazedam (3) Danidar (4) Supreme (5) Dewan tea (6) Tapal danidar (7) Kenya and (8) Keenia* were collected from local market (Hyderabad). Sample (5 g each) for both tobacco and tea samples except Dunhill (8 g) was digested gently in aqua regia (20 mL), till the solution became clear. More acid was added if required. The solution was concentrated to 1-2 mL, residue was dissolved in water and volume was adjusted to 50 mL. In case of Keenia (sample 8) the Tea leaves remaining after aqueous extraction with 400 mL water at 100ºC for 5 min were treated as above. Solution (1 mL) was taken and HPLC analytical procedure was followed with a single extraction at pH 4. The quantization was carried out from external calibration curve.

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* = was extracted in aqueous phase in tea solution.

Determination of silver from photographic film: FUJI color film (FUJI Film Proplus II 100-36) (5.278 g) was transferred to crucible and heated on flame till most of carbon smoke evaporated. The residue was digested with nitric acid (65 %). The solution was concentrated to 1-2 mL and dissolved in water. The final volume was adjusted to 25 mL. The solution (1 mL) was taken and HPLC procedure was followed with single extraction at pH 5. The quantization was carried out from standard calibration curve.

RESULTS AND DISCUSSION

The reaction of the reagent MPA-INH towards a number of metal ions were examined, but copper(II), nickel(II), cobalt(II), iron(II), zinc(II), mercury(II) and silver(I) reacted to form colored complex in slightly acidic solution (pH 4 and 5) (Fig. 2) and absorbed maximally within 335-370 nm. The composition of the metal chelates was examined by variation of the metal:ligand mole ratio and it was observed that copper(II), nickel(II), iron(II) formed 1:2 and cobalt (II), zinc(II) mercury (II) and silver(I) with 1:3 metal-ligand ratio (Fig. 3). The complexes were soluble in aqueous methanolic solution and indicated high values of molar absorpitivity within 1.6 to 3.9×10^4 L mol^{-1} cm^{-1}, except silver(I) which indicated molar absorpitivity of 6.2×10^3 L mol^{-1} cm^{-1}. Highest molar absorpitivity of 3.9×10^4 L mol^{-1} cm^{-1} was indicated by iron(II).The linear calibration curves were observed with 0.2 to 2.5 µg/mL except silver(I) which was with 2.5 - 12.5 µg/mL and obeyed the Beer's law with coefficient of determination (r^2) with 0.9987 to 0.9903 (Table-1).

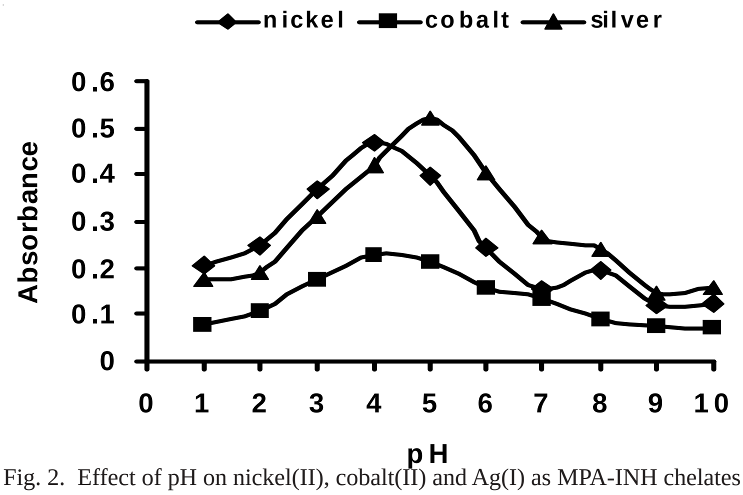


Fig. 2. Effect of pH on nickel(II), cobalt(II) and Ag(I) as MPA-INH chelates

For the selective determination of metal ions HPLC combined with UV detector was examined. The elution was initially carried out from Kromasil C-18, (250 × 4.6 mm id) column with methanol-water and acetonitrile-water. Symmetrical peaks for derivatizing reagent and metal chelates were obtained. However complete separation between nickel(II), cobalt(II), silver(I) and complexing reagent was obtained when eluted with methanol : water: acetonitrile: tetrabutyl ammonium bromide (1 mM) (53 : 25: 20 : 2 v/v/v/v) with a flow rate of 1mL/min. UV detection was at 256 nm. The resolution factor (Rs) between two adjacent peaks was >1.5. The capacity factor k' for nickel 0.105 increased to 1.42 for silver (Fig. 4). For quantitative determination, the effect of pH and reagent concentration on the extraction of metal ion was examined. pH was examined from 1-10 at unit interval and nickel(II) and cobalt(II) indicated maximum response at pH 4, but silver(I) indicated at pH 5 (Fig. 2). The variation in reagent solution (0.02% w/v) added was examined between 1-4 mL at an interval of 1 mL. A similar response was obtained from 1 mL, but 2 mL were selected to convert the metal ion into metal chelates quantitatively. Under the conditions, reproducibility of the elution in terms of peak height and retention time was examined for nickel, cobalt and silver chelates (n = 6) and relative standard deviations (RSD) were obtained within 0.6-3.4% and 1.2-4.1%, respectively. The linear calibration curves were obtained by measuring average peak height (n = 3) against concentration and were obtained with 1-5 µg/mL for cobalt and nickel, and 5-25µg/mL for silver with coefficient of determination (r^2) 0.9968, 0.9974 and 0.998 for nickel, cobalt and silver, respectively. The detection limits measured as three times the background noise were observed 80, 110 and 400 ng/mL for nickel, cobalt and silver, respectively.

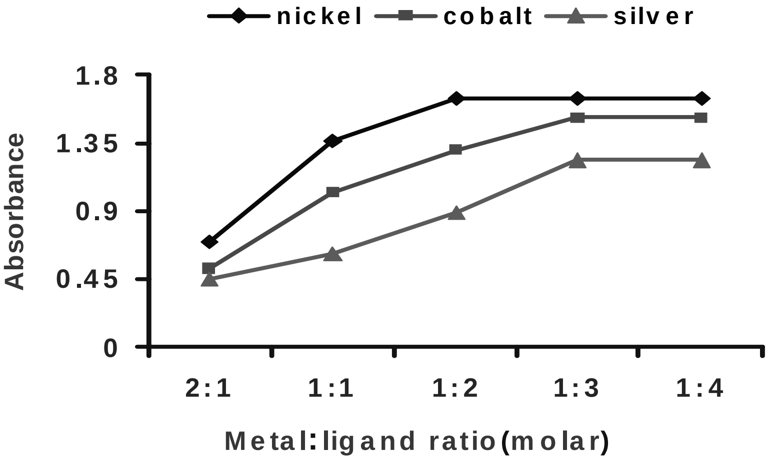


Fig. 3. Variation in metal: ligand ratio of nickel(II), cobalt(II) and Ag(I) as MPA-INH chelate

The method was applied for the determination of cobalt and nickel from tobacco and tea samples and silver from photographic film. Seven tobacco samples and eight tea samples collected from local market were analyzed after acid digestion. The quantitation was carried out by external calibration curve and spiking with metal ion (Fig. 5). The results of the analysis are summarized in Tables 2 and 3 and nickel was observed within 9.20-13.33 µg/g from tea samples and 2.50-6.00 µg/g of tobacco samples with RSD within 0.8-4.0 and 1.3-4.1 %, respectively. The results obtained were compared with air-acetylene flame atomic absorption spectrophotometer and good correlation was obtained. The cobalt was observed within 6.55-8.41 µg/g from tea samples and 3.07-5.04 µg/g of tobacco samples with RSD within 0.7-2.6 and 0.6-4.3 %, respectively (Fig. 6). The results obtained were compared with air-acetylene flame atomic absorption spectrophotometer and good correlation was obtained with RSD 1.4-9.1 %. The results obtained by standard addition (spiking) also correlated positively for both cobalt and nickel obtained by external calibration (Tables 2 and 3).

TABLE-1
QUANTITATIVE SPECTROPHOTOMETRIC DATA OF METAL CHELATES OF MPA-INH

Metal ions	λ_{max} (nm)	Composition of chelate Metal:ligand	pH of max: derivatization	Calibration range(µg/mL)	∑L (mol $^{-1}$ cm^{-1})	r^2
Cu(II)	370	1:2	4	0.25-1.25	3.2×10^4	0.9987
Ni(II)	370	1:2	4	0.20-1.00	3.3×10^4	0.9981
Co(II)	360	1:3	4	0.20-1.00	3×10^4	0.9914
Fe(II)	340	1:2	4	0.25-2.00	3.9×10^4	0.9921
Zn(II)	367	1:3	4	0.15-1.20	1.6×10^4	0.9903
Hg(II)	372	1:3	4	0.50-2.50	3.5×10^4	0.9945
Ag(II)	335	1:3	5	2.50-12.50	6.2×10^3	0.9932

TABLE-2
HPLC DETERMINATION OF COBALT AND NICKEL FROM TOBACCO SAMPLES

Sample	Amount of nickel found by HPLC µg/ g (RSD %) (n=3)	Amount of nickel found by AAS µg/ g (RSD %) (n=3)	Amount of cobalt found by HPLC µg/ g (RSD %) (n=3)	Amount of cobalt found by AAS µg/ g (RSD %) (n=3)
Capstan	6.00 (1.3)	6.21 (6.4)	5.04 (1.2)	5.17 (9.1)
Boss	4.15 (3.3)	4.05 (4.7)	4.17 (1.1)	4.28 (4.9)
Gold leaf	4.22 (4.1)	4.10 (8.3)	4.33 (2.7)	4.27 (6.4)
Diplomat	5.21 (2.0)	4.92 (5.6)	3.66 (0.6)	3.89 (4.0)
Gold flake	3.88 (1.7)	4.02 (7.3)	4.71 (3.4)	4.56 (5.7)
K-2	5.10 (2.2)	5.26 (9.2)	4.28 (4.3)	4.30 (9.7)
Dun-Hill	2.50 (3.8)	2.62 (4.8)	3.07 (3.0)	2.89 (8.7)
By standard addition				
BOSS	4.18 (2.4)	–	4.20 (1.4)	–
Diplomat	5.19 (1.8)	–	3.71 (2.3)	–
Dun-Hill	2.60 (3.7)	–	3.11 (4.1)	–

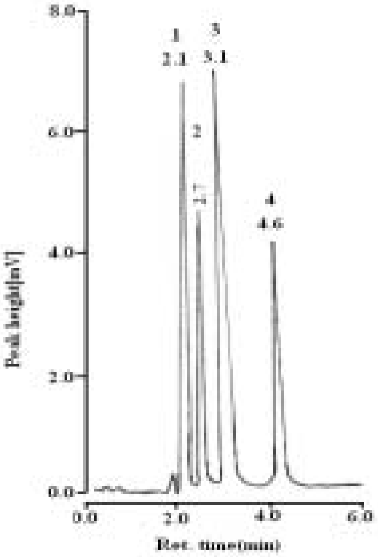
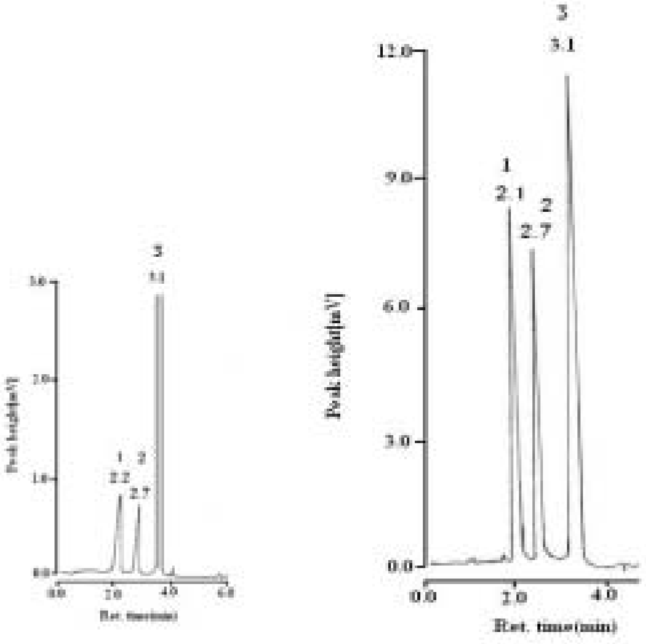


Fig. 4. HPLC separation of (1) nickel(II), (2) cobalt(II), (3) MPA-INH (4) silver(I) complexes of INH-MPA. Column Kromasil 100, C-18 (250×4.6 mm id). Elution with methanol: water: acetonitrile: tetrabutylammonium bromide (53: 25: 20:2 v/v/v), with flow rate 1 mL/min and UV detection at 256 nm



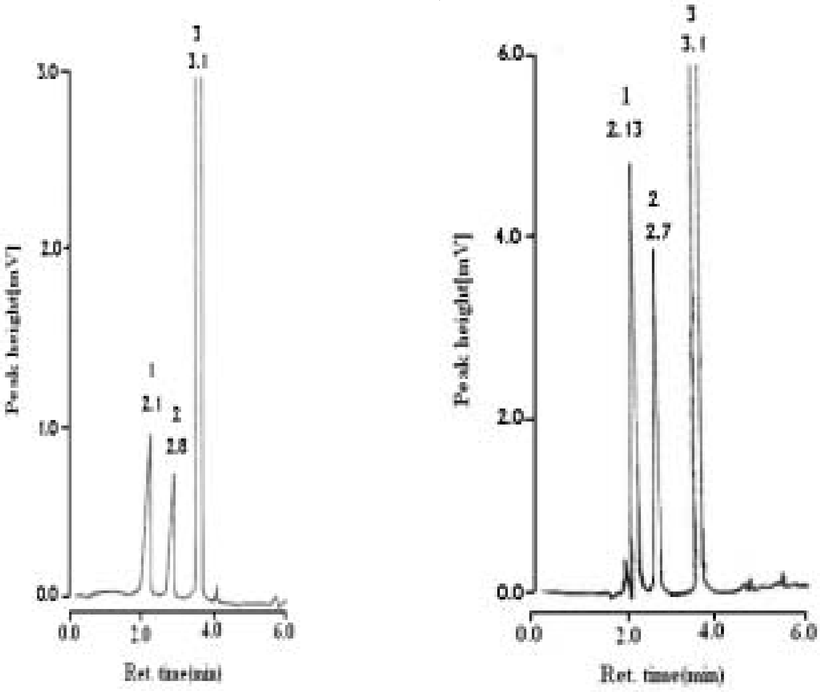
(a) (b)

Fig. 5. (a) HPLC response of nickel and cobalt from tobacco samples (b) HPLC response of nickel and cobalt from tobacco sample after spiking with 4 μg nickel and cobalt. Conditions as Fig. 4.

TABLE-3
HPLC DETERMINATION OF COBALT AND NICKEL FROM TEA SAMPLES

Sample	Amount of nickel found by HPLC µg/g (RSD %) (n=3)	Amount of nickel found by AAS µg/g (RSD %) (n=3)	Amount of cobalt found by HPLC µg/g (RSD %) (n=3)	Amount of cobalt found by AAS µg/g (RSD %) (n=3)
Lipton	11.40 (0.8)	12.31 (6.7)	7.32 (0.9)	7.58 (1.4)
Tazedam	9.21 (1.5)	9.04 (8.4)	6.55(2.1)	6.75 (2.8)
Danidar	12.83 (2.6)	12.30 (6.5)	8.02 (1.3)	8.25 (7.8)
Supreme	13.33 (1.7)	12.82 (7.9)	6.71 (1.7)	6.68 (2.5)
Dewan tea	11.14 (2.3)	12.02 (4.4)	7.32 (2.2)	7.10 (4.6)
Tapal danidar	12.94 (2.5)	12.55 (8.5)	7.05 (2.6)	6.93 (3.6)
Kenya	13.02 (4.0)	12.32 (3.6)	8.41 (1.8)	8.25 (8.5)
Keenia	11.42 (1.6)	10.80 (6.1)	7.20 (0.7)	7.03 (6.8)
By standard addition				
Lipton	11.51 (3.6)	–	7.12 (2.1)	–
Davidar	12.80 (1.7)	–	8.11 (2.6)	–
Dewam Tea	11.23 (2.5)	–	7.41 (1.6)	–
Kenya*	11.50 (1.2)	–	7.16 (3.4)	–

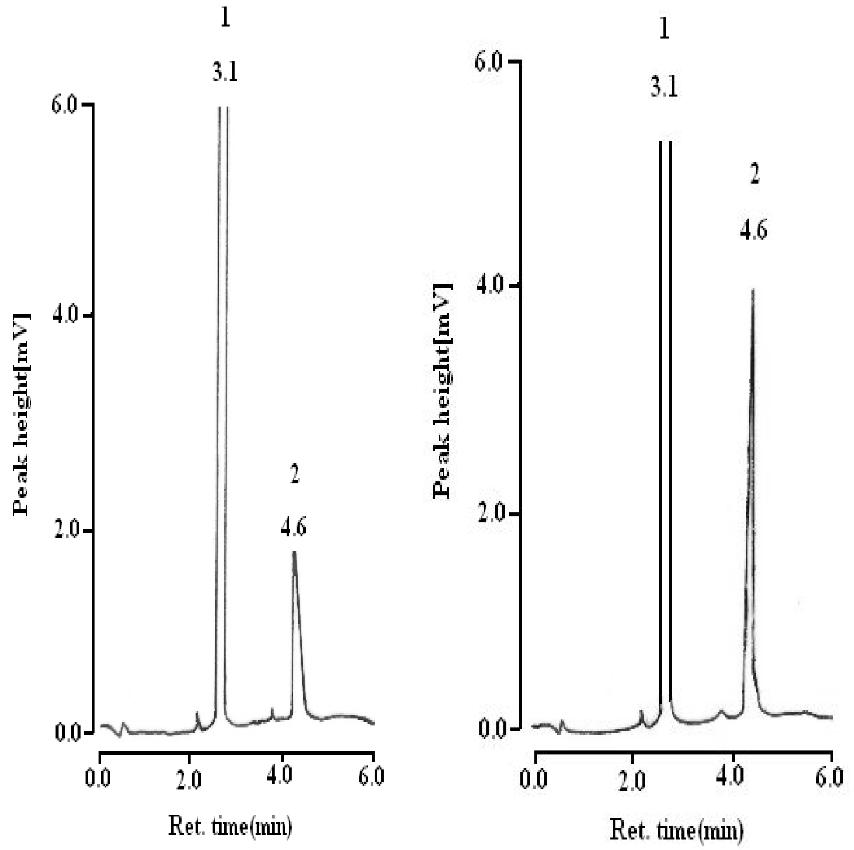
*Tea leaves after aqueous extractions.



(a) (b)

Fig. 6. (a) HPLC response of nickel and cobalt from tea sample (b) spiking with 3µg nickel and cobalt. Conditions as Fig. 4

The silver from a photographic film was obtained 80.26 µg/g with RSD 4.3 % (Fig. 7). The results obtained were compared with titrimetry and silver was found 83.8 µg/g with RSD 5.4% (n = 3). The results also corelated with analysis by stanard additions [80.34 µg/g (RSD 2.4 %)].



(a) (b)

Fig. 7. (a) HPLC response of silver from photographic film (b) spiking with 5 µg Ag(I) conditions as Fig. 4

Conclusion

Analytical procedure has been developed for the determination of cobalt, nickel and silver using new derivatizing reagent 6-methyl-2-pyridine carboxaldehyde isonicotinoyl hydrazone as chelating reagent. The optimum conditions of chelation including pH at 4 to 5 and nature of complex 1:2 or 1:3 molar ratios have been formed. The limit of detection has been observed at 80-400 ng/mL and method has been applied for the determination of cobalt and nickel from tobacco and tea leaves and silver from photographic film with RSD 0.8-4.3%.

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