

Full Length Research Paper

A study on the solid phase extraction of Co(II)-IIDE chelate with C₁₈ disk and its application to the determination of trace cobalt

Ali Moghimi^{1*}, Shahriar Ghammamy², Reza Ghiasi³

¹Department of Chemistry, Varamin (Pishva) Branch Islamic Azad University, Varamin, Iran.

²Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran.

³Department of Chemistry, East Tehran (Ghiam Dasht) Branch Islamic Azad University, Tehran, Iran.

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A sensitive, selective and rapid method has been developed for the determination of $\mu\text{g l}^{-1}$ level of cobalt based on the rapid reaction of cobalt(II) with isopropyl 2-[(isopropoxy carbothioyl) disulfanyl] ethanethioate chelate (IIDE) and the solid phase extraction (SPE) of the colored chelate with Waters Porapak Sep-Park C₁₈ disk. The isopropyl 2-[(isopropoxy carbothioyl) disulfanyl]ethanethioate chelate can react with Co(II) in the presence of pH 4.2 acetic acid /sodium acetate buffer solution and cetyl trimethylammonium bromide (CTMAB) medium to form a violet chelate of a molar ratio of 1:2 (cobalt to Isopropyl 2-[(isopropoxy carbothioyl) disulfanyl]ethanethioate chelate. This chelate can be retained on Waters Porapak Sep-Park C₁₈ disk quantitatively when they passed the disk as aqueous solution. At the end of the enrichment, the retained chelate can be eluted from the disk by 2.5 ml of ethanol (contain 5% acetic acid). In the measured solution, the molar absorptivity of the chelate was $1.58 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 635 nm, and Beer's law was obeyed in the range of 0.01-0.4 $\mu\text{g ml}^{-1}$. The relative standard deviation for 11 replicate sample of 0.01 $\mu\text{g.ml}^{-1}$ level was 2.54%. The detection limit was 0.01 $\mu\text{g ml}^{-1}$ (in original samples). This method can be applied for the determination of $\mu\text{g ml}^{-1}$ level of cobalt in drinking water with satisfactory results.

Key words: Cobalt, solid phase extraction spectrophotometry, isopropyl 2-[(isopropoxy carbothioyl) disulfanyl] ethanethioate chelate (IIDE).

INTRODUCTION

Cobalt is an important element, not only for industry but for biological systems as well. In rapidly expanding the analytical fields such as environmental, biological and material monitoring of trace metals, there is an increasing need to develop simple, sensitive and selective analytical

techniques that do not use expensive or complicated test equipment. For this reason, a wide variety of spectrophotometric methods for the determination of cobalt have been reported. The main chromogenic reagents are pyridylazo reagents, thiazolylazo reagents, benzothiazolylazo reagents, 8-aminoquinoline derivatives, nitroso dyes among others (Watanabe, 1974; Siroki et al., 1975; Khan et al., 1998; Ferrira et al., 1996; Busev et al., 1969; Shen et al., 1988; Carvalho, et al., 1996; San Andres et al., 1994; Singh et al., 1999; Park and Cha, 1998; Eskandari et al., 2001; Amin et al., 2001; Zhao et al., 1992; Tehrani et al., 2005; Carvalho et al., 1996; Park et al., 1998; San Andres et al., 1994; Moghimi et al., 2006; Hu et al., 2001; Nayebi and Moghimi, 2006; Moghimi, 2006; Watanabe, 1974). But the study of 2-quinolylazo derivatives such as chromogenic reagents for the determination of cobalt has received little attention. In previous work, some 2-quinolylazo derivatives were synthesized

*Corresponding author. E-mail: alimoghimi@iauvaramin.ac.ir.

Abbreviations: IIDE, Isopropyl 2-[(isopropoxy carbothioyl) disulfanyl] ethanethioate chelate; SPE, solid phase extraction; CTMAB, cetyl trimethylammonium bromide; NMR, nuclear magnetic resonance; IR, infrared; EDTA, ethylenediaminetetraacetic acid; CTMAB, cetyl trimethyl ammonium bromide; EGTA, glycoetherdiamine tetraacetic acid zinc salt; SDS, sodium dodecyl sulfate; ICP-MS, inductively coupled plasma mass spectrometry; EGTA, ethylene glycol tetraacetic acid.

and applied to the determination of metal ion (Chen et al., 2001; Hu et al., 2001; Moghimi, 2007a; Moghimi, 2007b; Hu et al., 2002; Zhao et al., 1992; Singh et al., 1999; San Andres et al., 1994; Poursharifi and Moghimi, 2009; Moghimi et al., 2009). In this paper, we thoroughly studied the colour reaction of isopropyl 2-[(isopropoxy carbothioly) disulfanyl] Ghasvand et al, 2006 ethanethioate chelate (IIDE) with cobalt (II), and the solid phase extraction (SPE) of the coloured chelate with Waters Porapak Sep-Park C₁₈ disk. A high sensitive, selective and rapid method for the determination of cobalt was developed.

MATERIALS AND METHODS

Apparatus

A spectrophotometer (Model 722, Third Analytical Instrument Factory, China) equipped with 1 cm cells was used for all absorbance measurements. Waters SPE device, which can prepare 20 samples simultaneously, Waters Porapak Sep- Park C₁₈ disk (1 cc per 30 mg, 30 mm) (Waters Corporation). The pH measurements were made with a Model pH S-2 C pH meter.

Reagents

Synthesis of sodium Isopropyl 2-[(isopropoxy carbothioly) disulfanyl] ethanethioate reagent (IIDE)

Iodine (1 mM) in CH₂Cl₂ (10 ml) was added to a stirred solution of potassium *o*-isopropyl(dithiocarbamate) (1 mmol) in CH₂Cl₂ (10 ml) and stirred for 1 h. The reaction mixture was washed with 10% of aqueous Na₂S₂O₃ (2×10 ml) and H₂O (2×10 ml). The organic layer was dried over MgSO₄ and evaporated under reduced pressure. More purification was carried out with the re-crystallization in hexane, so that the pale yellow crystals of L were obtained in 90% yield (0.24 g). The structure and purity of L was confirmed by elements analysis, Nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy. ¹H NMR (CCl₄). δ (ppm): 1.43 (t, 12H, CH₃), 5.63 (m, 2H, CH). IR (KBr). ν_{max} (cm⁻¹): 2979.8 (s), 2869.9 (w), 1463.9 (s), 1442.7 (s), 1373.0 (s), 1271.1 (s, b), 1145.6 (s), 1082.2 (s), 1048.0 (s, b), 898.8 (s), 796.5 (s), 690.5 (m). a 2.5×10⁻⁴ mol l⁻¹ of solution was prepared by dissolving (IIDE) with ethanol. All of the solutions were prepared with ultrapure water obtained by a Milli-Q50 SP reagent water system (Millipore Corporation). A stock standard solution of Co(II) (1.0 mg ml⁻¹) was prepared by dissolving appropriate amount of Co(NO₃)₂·6H₂O with water and adjusting the volume to 500 ml in a 500 ml calibrated flask, then standardized by ethylenediaminetetraacetic acid (EDTA) titration, a working solution of 0.2 mg ml⁻¹ was prepared by diluting this solution with acetic acid/sodium acetate buffer solution of pH 3.8, cetyl trimethyl ammonium bromide (CTMAB) solution 2.0%, dissolving with 10% of ethanol, glycoetherdiamine tetraacetic acid zinc salt (Zn-EGTA) solution, 5%. NaF solution: 10%. All chemical used were of analytical grade unless otherwise stated.

Procedure

To a standard or sample solution containing no more than 1.0 mg of Co(II) in a 250 ml of flask, 10 ml of acetic acid sodium acetate buffer solution, with a pH of 3.8, 5.0 ml of Zn EGTA solution, 5.0 ml of NaF solution, 5.0 ml of IIDE solution and 5.0 ml of CTMAB

solution were added. The mixture was diluted to a volume of 250 ml and mixed well. After 10 min, the solution was then passed to the Waters Porapak Sep-Park C₁₈ disk at a flow rate of 50 ml.min⁻¹. The coloured chelate would be retained on the disk. At the end of the enrichment, the retained chelates from the disk were eluted with 2.5 ml of ethanol (contain 5% acetic acid) at a flow rate 5 ml.min⁻¹ in reverse direction. The absorbance of this solution was measured at 635 nm in 1 cm cell against a reagent blank prepared in a similar way without cobalt.

RESULTS AND DISCUSSION

Absorption spectra

In the measured solution, the absorption spectra of IIDE and its Co(II) chelate are shown in Figure 1. The absorption peaks of IIDE and its complex are located at 478 and 635 nm.

Effect of acidity

Results showed that the optimal pH for the reaction of Co (II) with (IIDE) was 2.5-/5.2. A pH of 4.2 was recommended as the addition of 5-15 ml of the acetic acid-/sodium acetate buffer solution (pH 4.2) per 250 ml of final solution was found to give a maximum and constant absorbance. The use of 10 ml of buffer was recommended.

Effects of surfactants

Both the IIDE and the Co(II)-IIDE chelate had poor solubility in water solution. There was need to add surfactants to enhance the solubility of Co(II)-IIDE system. Experiment shows that all the anionic surfactants, nonionic surfactants or cationic surfactants have good effect to enhance the solubility. But in the presence of the anionic surfactants sodium dodecyl sulfate (SDS), SDBS medium, the Co(II)-IIDE chromogenic system gives a low absorption, whereas in the presence of non-ionic surfactants or cationic surfactants, the absorption of the chromogenic system increases markedly. Various non-ionic surfactants and cationic surfactants enhance the absorbance in the following sequence. CTMAB>Tween-80>CPB>/Tween-20>/TritonX-100. Accordingly, CTMAB is the best additive. The addition of 4.0-/8.0 ml of CTMAB solution give a constant and maximum absorbance, and the use of additional 5.0 ml were recommended.

Effect of IIDE concentration

The addition of about 5.0 ml of 2.5×10⁻⁴ mol l⁻¹ of IIDE solution has been found to be sufficient for a complete reaction. Accordingly, 5.0 ml of IIDE solution was added in all further measurement.

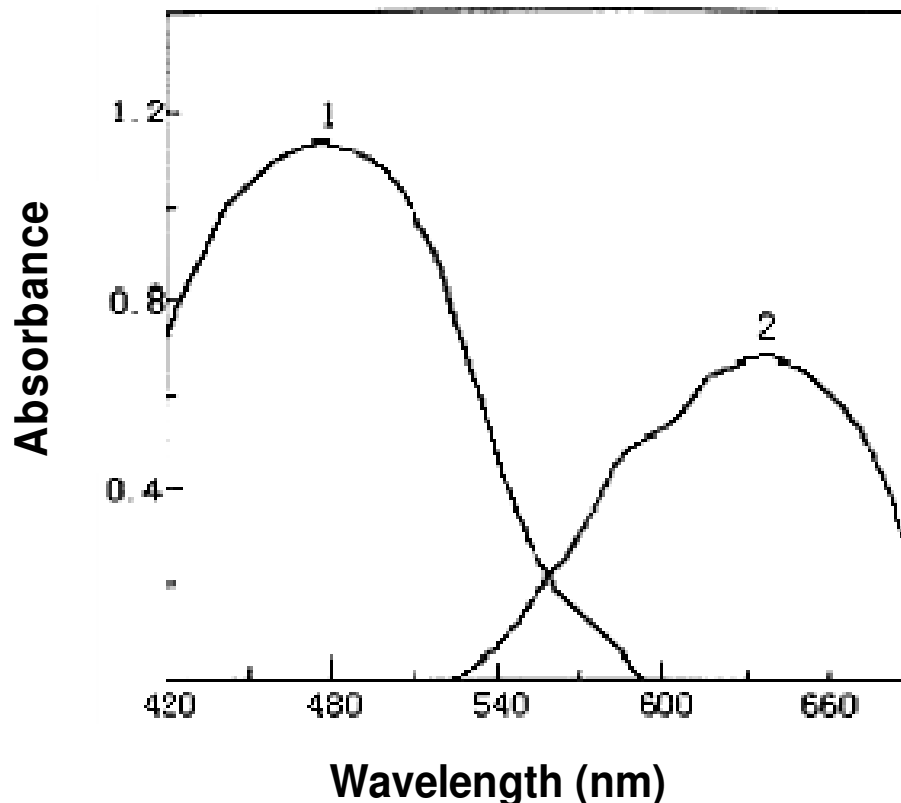


Figure 1. Absorption spectra of IIDE and its Co(II) chelate: (1) IIDE -CTMAB blank against water; (2) (IIDE) Co (II)- CTMAB complex against reagent blank.

Stability of the chromogenic system

After mixing the components, the absorbance reached its maximum within 5 min at room temperature and remained stable for at least 8 h in water solution. When extracted into the ethanol medium, the chelate could be kept stable for at least 15 h.

Solid phase extraction

Both the enrichment and the elution were carried out on a Waters SPE device, which can prepare 20 samples simultaneously. The flow rate was 50 ml min^{-1} when enrichment and 5 ml min^{-1} when eluted. Some experiments were carried out in order to investigate the retention of IIDE and its Co(II) chelate on the disk. It was found that the IIDE and its Co(II) chelate could be retained on disk quantitatively when they pass the disk as an aqueous solution. The capacity of the disk for IIDE was 25 mg and its Co(II) chelate was 20 mg in a 250 ml of solution. Under the circumstance of this experiment, the disk had adequate capacity to enrich the Co-IIDE chelate and the excessive IIDE. In order to choose a proper eluant for the retained IIDE and its Co(II) chelate, various organic solvents were studied. It was found that

the tetrahydrofuran, acetone, acetonitrile, ethanol and methanol could elute the IIDE and its Co(II) chelate from disk quantitatively. Ethanol had a low volatility, toxicity and price, so ethanol was selected. Co(II)-IIDE chelate had a good stability in weak acid medium. Containing 3-10% of acetic acid in ethanol could increase the stability of the Co(II)-IIDE chelate in the course elution. So ethanol (containing 5% of acetic acid) was selected as an eluant. Experiment shows that it was easier to elute the retained IIDE and its Co(II) chelate in reverse direction than in forward direction, so it is necessary to upturned disk during elution. Ethanol (2.5 ml, containing 5% of acetic acid) was sufficient to elute the IIDE and its Co(II) chelate from disk at a flow rate of 5 ml min^{-1} . The volume of 2.5 ml eluant was selected.

Calibration curve and sensitivity

The calibration curve (Figure 2) shows that Beer's law is obeyed in the concentration range of 0.01- 0.4 mg Co(II) ml^{-1} in the measured solution. The linear regression equation obtained was: $A = 2.475C \text{ (mg l}^{-1}\text{)} + 0.008$, ($r = 0.9999$). The molar absorptivity in the five measured solution was calculated to be $1.58 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 635 nm, and the sandell sensitivity was $3.67 \times 10^{-4} \text{ mg cm}^{-2}$.

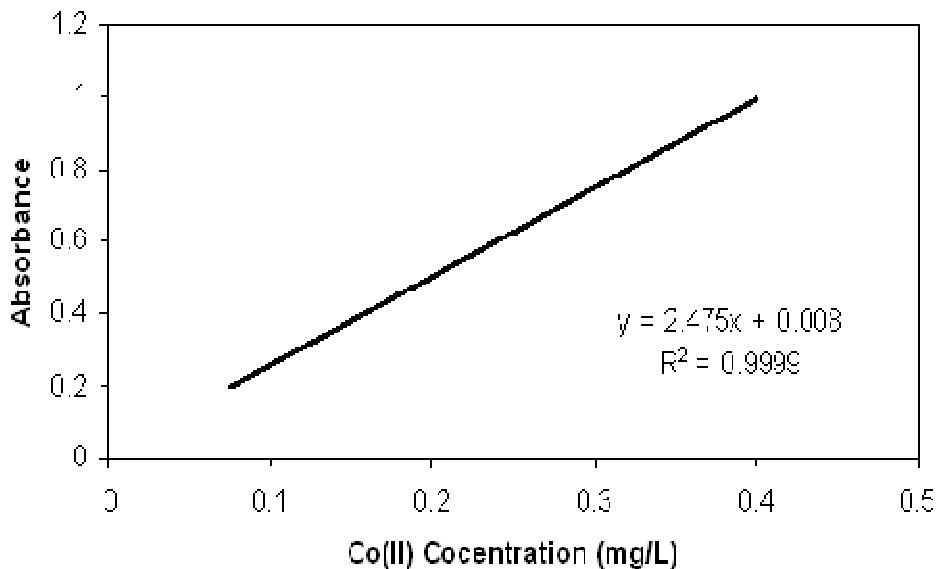


Figure 2. Calibration curve.

Table 1. Tolerance limits in the determination of 1 mg of Co(II) with IIDE (relative error $\pm 5\%$).

Tolerate (mg)	Ion added
100	SCN ⁻ , tartrate, thiourea, NO ₃ ⁻ , Cl ⁻ , Na ⁺ K ⁺ , borate oxalate
80	Citrate, benzoate, succinate, ascorbate, SO ₄ ²⁻ , NH ₄ ⁺
30	Li ⁺ , Al ³⁺ , PO ₄ ³⁻
10	F ⁻ , Br ⁻ , ClO ₄ ⁻ , Ca ²⁺ , Mg ²⁺
4	Sr ²⁺ , Ce(IV), Ba ²⁺ , Zr(IV)
1	Mn ²⁺ , W(VI), Mo(VI), Zn ²⁺
0.8	Ti(IV), Bi(III), V(V), Cr(VI), Zr(IV), Ni ²⁺ , Th(IV), Fe ³⁺
0.2	Ti(III), Ag ⁺ , Cd ²⁺ , Cr ³⁺ , Fe ²⁺ , La ³⁺ , Sn(IV), Pb ²⁺ , Cu ²⁺
0.6	Ru(III), Bi(III), Hg ²⁺ , Sb ³⁺ , Pd ²⁺ , Sn(IV)
0.05	Se(IV), U(VI), Te(IV), Au ³⁺ , Pt ²⁺
0.008	Os (VIII), Ir(IV), Sb(III)

The relative standard deviation at a concentration level of 0.01 mg ml⁻¹ of Co(II) ml⁻¹ (11 repeat determination) was 2.54%. The detection limit is 0.01 mg ml⁻¹ (in original samples).

Composition of the complex

The composition of the complex was determined by a continuous variation and the molar ratio method. Both showed that the molar ratio of Co(II) to IIDE is 1:2, which probably has the following structure.

Interference

The selectivity of the proposed method, investigated by

the determination of 1.0 mg Co(II) in the presence of various ions within a relative error of $\pm 5\%$ are given in Table 1. Result show that masked with Zn-EGTA and NaF, most foreign ions did not interfere with the determination. This method is highly selective.

Application

The proposed method has been successfully applied to the determination of cobalt in three real drinking water samples (tap water of Saveh, pure water (TWT Corporation of Varamin) and well water of Varamin). The results are shown in Table 2, together with results of a recovery test by adding a known amount of silver in water sample. A standard method with inductively coupled plasma mass spectrometry (ICP-MS) has also been used

Table 2. Determination of silver in the real sample.

Recovery	R.S.D.% (n=5)	This method ($\mu\text{g.g}^{-1}$)*	Reference method ($\mu\text{g.g}^{-1}$)*	Samples
98	3.0	10.8	11.9	Tap water
100	2.2	6.09	5.28	Pure water
96	2.1	19.0	18.5	Well water

as a reference method.

Conclusion

This method is highly selective and high in sensitivity. IIDE is one of the most sensitive and selective spectrophotometric reagents for cobalt. The molar absorptivity of the chelate reaches $1.58 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$. Most foreign ions do not interfere with the determination when masked with NaF and Zn- ethylene glycol tetraacetic acid (EGTA). By SPE with Waters Porapak Sep-Park C₁₈ disk, the Co(II) - IIDE chelate in 250 ml solution can be concentrated to 2.5 ml. The detection limit is $0.01 \mu\text{g l}^{-1}$ (in original samples), and $\mu\text{g l}^{-1}$ level cobalt in drinking water can be determined with satisfactory results. The consumption of organic solvents in this method is much lower than those consumed in liquid-liquid extraction method. Since ethanol has a lower volatility and toxicity, this method is more safe than methods that uses other organic solvents. By using Waters SPE device, 20 samples can be prepared simultaneously. This method is rapid for simultaneously preparing large amount of sample.

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REFERENCES

- Amin AS, Ahmed IS, Moustafa ME (2001). Selective spectrophotometric determination of cobalt (II) in synthetic mixtures and pharmaceutical formulates with 5-[o-carboxyphenylazo] 2, 4-dihydroxybenzoic acid. *Anal. Lett.*, 34: 759.
- Busev AI, Nemtseva ZI, Ivanov VM (1969). Spectrometric determination of 10-1 to 10-7 Percent cobalt in natural and industrial samples, using heterocyclic hydroxyl. 24: 1376.
- Carvalho MS, Fraga ICS, Neto KCL, Filho EQS (1996). Uranium determination at ppb levels by X-ray fluorescence after its preconcentration on polyurethane foam. 43: 1675.
- Chen JH, QF Hu, Yin JY, Guangpu S (2001). Study on the solid phase extraction of Co (II)-QADEAB chelate with C18 disk and its application to the determination of trace cobalt. *Chin. J. Spectrosc. Lab.*, 18(3): 341.
- Eskandari H, Ghaziaskar HS, Ensafi AA (2001). A sensitive and simple extractive-spectrophotometric method for the determination of microgram amount of cobalt by using benzilmonoxime. *Anal. Sci.*, 17: 327.
- Ferrira SLC, De Jesus DS, Braz J (1996). On-line preconcentration system for flame atomic absorption spectrometry using unloaded polyurethane foam: determination of zinc in waters and biological materials. *Chem. Soc.*, 7:109.
- Ghiasvand A, Rezaei B, Abbas MG (2006). Preconcentration, speciation and determination of ultra trace amounts of mercury by modified octadecyl silica membrane disk/electron beam irradiation and cold vapor. *Asian J. of Chem.*, 18 (32): 185.
- Hu QF, Yang GY, Tang DY, Yin JY, Fenxi H (2002). Square wave voltammetric determination of Hg(II) using thiol functionalized chitosan-multiwalled carbon nanotubes nanocomposite film electrode. *Chin. J. Anal. Chem.*, p. 30 in press.
- Hu QF, Yang GY, Tang DY, Yin JY, Ganhan HJ (2001). Study on determination of iron, cobalt, nickel, copper, zinc and manganese in drinking water by solid-phase extraction and RP-HPLC with 2-(2-quinolinyloxy)-5-diethylaminophenol as precolumn derivatizing reagent. *Chin. J. Arid Environ. Monit.*, 15 (4): 196.
- Hu QF, Yang GY, Tang DY, Yin JY, Ganhan HJ (2001). Study on the solid phase extraction of Co (II)-QADEAB chelate with C18 disk and its application to the determination of trace cobalt. *Chin. J. Arid Environ. Monit.*, 15 (4): 196.
- Khan MR, Khoo SB (1998). Differential pulse cathodic stripping voltammetric determination of manganese(II) and manganese(VII) at the 1-(2-pyridylazo)-2-naphthol- modified carbon paste electrode. *Analyst*, 123: 1351.
- Moghimi A (2006). Solid phase extraction of lead on octadecyl bonded silica membrane disk modified with Isopropyl 2- [(isopropoxy carbothioyl)disulfanyl]ethane thioate and determination by flame atomic absorption spectrometry. *Oriental J. of Chem.*, 22(3): 527.
- Moghimi A (November 2007a). "Preconcentration and Determination of Copper(II) Using Octadecyl Silica Membrane Disks Modified by 1,5-Diphenylcarbazyd and Flame Atomic Absorption Spectrometry. " *Chinese J. of Chem.*, 25(11): 1663-1668.
- Moghimi A (October, 2007b). Selective Pre-concentration and Solid Phase Extraction of Mercury(II) from Natural Water by Silica Gel-loaded (E)-N-(1-Thien-2'-ylethylidene)-1,2-phenylenediamine Phase. *Chinese J. of Chem.*, 25(10): 1536-1541.
- Moghimi A, Ghiasi R, Abedin AR, Ghammamy S (March, 2009). *Afr. J. of Pure and Appl. Chem.*, 3(3): 051-059.
- Moghimi A, Tehrani, MS, Waqif HS (2006). Preconcentration and Determination of Chromium Species Using Octadecyl Silica Membrane Disks and Flame Atomic Absorption Spectrometry. *Mater. Sci. Res. India* 3(1a): 27.
- Nayebi P, Moghimi A (2006). Solid phase extraction of trace Copper(II) using octadecyl silica membrane disks modified 5-(p-dimethylaminobenzylidene) rhodamine. *Oriental J. of Chem.*, 22(3): 507
- Park CI, Cha KW (1998). Spectrophotometric determination of trace amounts of cobalt with 2-hydroxybenzaldehyde-5-nitro-pyridylhydrazone in presence of surfactant after separation with Amberlite IRC-718 resin. 46:1515.
- Poursharifi MJ, Moghimi A (2009). Determination of Nickel in Natural Water Samples by Flow Injection- Inductively Coupled Plasma Optical Emission Spectrometry. *Asian J. of Chem.*, 21(4): 2533-2540.
- San Andres MP, Marina NL, Vera S (1994). Solid phase extraction and spectrophotometric determination of cobalt with 2-(2-quinolinyloxy)-5-dimethylaminobenzoic acid as chromogenic reagent 41: 179.
- Shen HX, Li JJ, Gaodeng X, Huaxue X (1988). Study of 2-(2-quinolinyloxy)-5-dimethylaminobenzoic acid as a new chromogenic reagent for the spectrophotometric determination of cobalt. *Chem. J. Chin. Univ.*, 9: 1007.
- Singh HB, Agnihotri NK, Singh VK (1999). Non-extractive derivative

spectrophotometric determination of cobalt in neutral micellar medium. 48: 623.

Siroki ML, Maric L, Stefanac Z, Herak MJ (1975). Solvent extraction of niobium-4-(2-pyridylazo) resorcinol complex and spectrophotometric determination of niobium in oxalato solutions. *Anal. Chim. Acta.*, 75: 101.

Tehrani MS, Moghimi A, Waqif HS (2005). Preconcentration and determination of trace amounts of heavy metals in water samples using membrane disk and flame atomic absorption spectrometry. *Mater. Sci. Res. India*, 3(2): 135.

Watanabe H (1974). A non-ionic surfactant as a new solvent for liquid-liquid extraction of zinc (II) with 1-(2-pyridylazo)-2-naphthol. 21: 295.

Zhao JW, Xu QH, Huaoxue S (1992). Solid phase extraction and spectrophotometric determination of cobalt with 2-(2-quinolinyloxy)-5-dimethylaminobenzoic acid as chromogenic reagent. *Chin. J. Chem. Reagent*, 14(6): 346.