Extractive Differential Pulse Polarography of Mo (VI) Oxinate in Chloroform and its Application in the Determination of Molybdenum in Steel

Pournaghi-Azar, Mohammad Hossein*[+]

Electroanalytical Chemistry Laboratory, Faculty of Chemistry, University of Tabriz, Tabriz, I. R. Iran

Nahalparvary, Hossein

Faculty of Chemistry, University of Tabriz, Tabriz, I. R. Iran

ABSTRACT: *The voltammetric characteristics of Mo (VI) oxinate at the mercury electrode, in the presence of tri-butylammonium perchlorate (tri-BAP) and piperidinium perchlorate (PP) + piperidine (P) as two different types supporting electrolytes, have been studied in chloroform. With the both supporting electrolytes a two electron irreversible process for the reduction of Mo (VI) oxinate was observed. Preceded by a solvent extraction of Mo (VI) oxinate in chloroform, the DP method was used for the determination of molybdenum. In the presence of 0.2 M tri-BAP as supporting electrolyte, the calibration graph was linear over the range 0.5 to 50 μM. and the detection limit was 0.16 μM about 10 times lower than the case of PP + P. The proposed method using Mo (VI) oxinate-tri-BAP system has been successfully applied for the determination of molybdenum in steel.*

KEYWORDS: *Chloroform, Steel, Differential pulse polarography, Oxinate, Molybdenum*

INTRODUCTION

Several sensitive methods have been developed for the determination of molybdenum in steel including; extraction spectrophotometry [1-5] or catalytic spectrophotometry [6-8], spectrofluorometry [9], atomic absorption spectrometry [10], mass spectrometry [11], polarography [12], capillary ion electrophoresis [13] and adsorptive stripping voltammetry [14].

Our previous studies revealed that a preliminary separation of neutral complexes of cations (chelates) by solvent extraction in chloroform or in dichloromethane and direct application of electroanalytical methods for the determination of analytes in pure extracts provide high selectivity [15-18].

In order to develop a selective extraction differential pulse polarographic procedure for the determination of trace amount of molybdenum, the present paper deals

* *To whom correspondence should be addressed.*
+ E-mail : pournaghiazar@Tabrizu.ac.ir
1021-9986/03/1/13 7/$/2.70

with a study of the polarographic behavior of Mo(VI) oxinate in chloroform in the presence of piperidinium perchlorate (PP) + piperidine (P) and tri-butylammonium perchlorate (tri-BAP) as two different type supporting electrolytes. Furthermore it is intended to demonstrate the suitability of the method for the determination of molybdenum in steel after dissolution of the sample and extraction of Mo (VI) oxinate into chloroform.

EXPERIMENTAL

Chemicals and reagents

Chloroform, perchloric acid, 8,Hydroxy quinoline (oxine) purified by recrystalization, tetrabutylammonium chloride (TBACl), piperidine and ammonium molybdate were from Merck (Darmstadt, Germany) or Aldrich (Milwaukee, WI, USA) p.a grade. The supporting electrolytes used were 0.2M tri-butylammonium perchlorate (tri-BAP) or 0.35M piperidinium perchlorate (PP) + 0.15M piperidine (P). PP and Tri-BAP was prepared as previously described [15,18].

Standard molybdenum solutions

A 10^{-2} M aqueous solution of ammonium molybdate was prepared as a stock solution. The standard solutions were prepared by successive dilution of this stock solution.

Extraction solution

A 0.01M solution of oxine in chloroform was prepared.

Standard oxinate solutions of Mo (VI)

A 10^{-3} M solution of Mo (VI) oxinate was prepared by direct dissolution of ammonium molybdate in the extraction solution**.** The standard solutions were prepared by successive dilution of this stock solution by the extraction solution.

Apparatus

All voltammograms were recorded with a three electrode system. A polarograph E 626 was used with a VA-Stand 663 (from Metrohm) for polarography. A multipurpose instrument from EG & G including; (a) potentiostat / galvanostat model 273, (b) electrochemical analysis software 3,00 model 270 coupled with an IBM personal computer and (c) Laser Jet 5L printer was used for controlled potential coulometry and cyclic voltammetry.

Electrodes

The reference electrode Ag/AgCl (sat.), TBACl (sat.) and tri-BAP 0.2M in chloroform in a separated compartment was directly immersed in the reaction cell. The working electrodes were dropping mercury electrode (DME) and hanging mercury drop electrode (HMDE), the auxiliary electrode was a platinum wire.

Procedures

Extraction and voltammetry of the Mo (VI) oxinate

A 5 ml portion of aqueous standard or sample solutions was transferred into a 100 ml separating funnel, EDTA was added up to 0.05 M and pH of the aqueous solution was adjusted by ammonia or hydrochloric acid solutions to 2 at which point the extraction of Mo (VI) oxinate is complete [19]. Mo (VI) was extracted four times with a 5-ml portion of 0.01M oxine in chloroform and the chloroform phases separated and collected. A 10-ml portion of the extract was pipetted into the voltammetric cell, a required amount of the supporting electrolyte added, nitrogen (99.999) pre-saturated with chloroform was administered through the solution for 20 min and the voltammograms recorded by sweeping the electrode potential over a desired potential range with a suitable scan rate depending on the technique used.

Dissolution of the samples

The sample (approximately 0.5 g) was placed in a 50-ml beaker of Teflon, followed by the addition of 10 ml of concentrated HNO_3 and $HClO_4$ mixture (1:1) The contents in the beaker were heated in a water bath. After the sample was dissolved, five drops of concentrated HF was added and the solution was evaporated to dryness at 150 ^{o} C, a white residue was obtained To the beaker,10 ml of 1 M HCl was added the contents were transferred into a 200 or 20-ml volumetric flask depending on the molybdenum amount in the sample and made up to volume with water. A 5-ml portion of the solution was subjected to the solvent extraction.

RESULTS AND DISCUSSION

Voltammetric behavior

In the presence of 0.35 M PP + 0.15 M P, direct current (DC) polarography of 0.1mM chloroform solution of Mo (VI) oxinate showed only one reduction wave with half wave potential of -0.41. DP polarography of 20 μM solution of Mo (VI) oxinate exhibited also one peak (Fig.1A). Cyclic voltammetry of 0.1 mM Mo (VI) oxinate at HMDE between 0 and -0.8 V showed one cathodic peak, while in the reversed scan no anodic peak was discernible (Fig1B). These observations confirm that the reduction of Mo (VI) oxinate occurs according to an irreversible process.

In the presence of 0.2M tri-BAP as a neutral supporting electrolyte, DC polarography of 0.1 mM chloroform solution of Mo (VI) oxinate showed two ill-resolved reduction waves with half wave potential of about -0.23 and -0.38 V. The cyclic voltammogram recorded under the same solution conditions exhibited two cathodic peaks with peak potentials of -0.25 and -0.42V and no anodic peaks were observed in reversed scan (Fig.2A). Coulometry at the level of the reduction wave (-0.5 V) in the presence of both supporting, electrolytes shows that two electrons per one mole of the starting Mo (VI) oxinate is needed. On the basis of the results obtained from the cyclic voltammetry and cotrolled potential coulometry the reduction step of Mo (VI) oxinate is a two electron irreversible process.

DP polarography of Mo (VI) oxinate shows also two peaks with peak potentials of -0.24 and -0.38V (Fig 2B). These peaks may be attributed to the reduction of two different forms of Mo (VI) oxinate in the presence of oxine and tri-BAP [20]. However as the concentration of oxine and tri-BAP in the solution is high, the C_{oxine} / $C_{tri\text{-}BAP}$ ratio and subsequently the i_1 / i_2 ratio for the polarograms recorded, maintained unchanged with respect to Mo (VI) concentration in the solution. Therefore each of these two peaks can be used for the analytical measurements.

Analytical approaches

Considering that Mo (VI) may be extracted into chloroform as oxinate [19],the possibility of developing a selective polarographic method for the determination of molybdenum in the chloroform extracts was examined. DP polarography of Mo (VI) oxinate in the presence of PP + P or tri-BAP as supporting electrolytes, exhibits one and two well-defined peaks respectively. The i_p values were linearly dependent on the Mo (VI) oxionate concentration in the range 1-50 μM with 0.35 M PP + 0.15 M P + 0.01 M oxine and 0.5-50 μM with 0.2M tri-BAP + 0.01M oxine. The regression equations

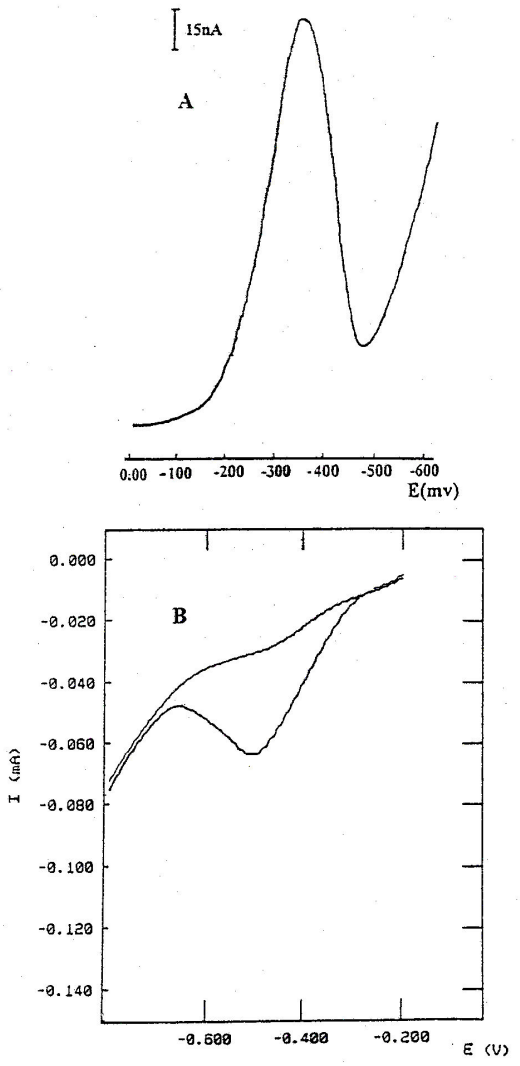

Fig.1: (A) DP polarogram of 20μM chloroform solution of Mo (VI) oxinate, Pulse amplitude: 50 mV, Sweep rate 5 mV s^{-1}, (B) Cyclic voltammogram of 0.1mM Mo (VI) oxinate solution, scan rate: 100 mV s^{-1} , in the presence of 0.35M PP + 0.15M P + 0.01M oxine.

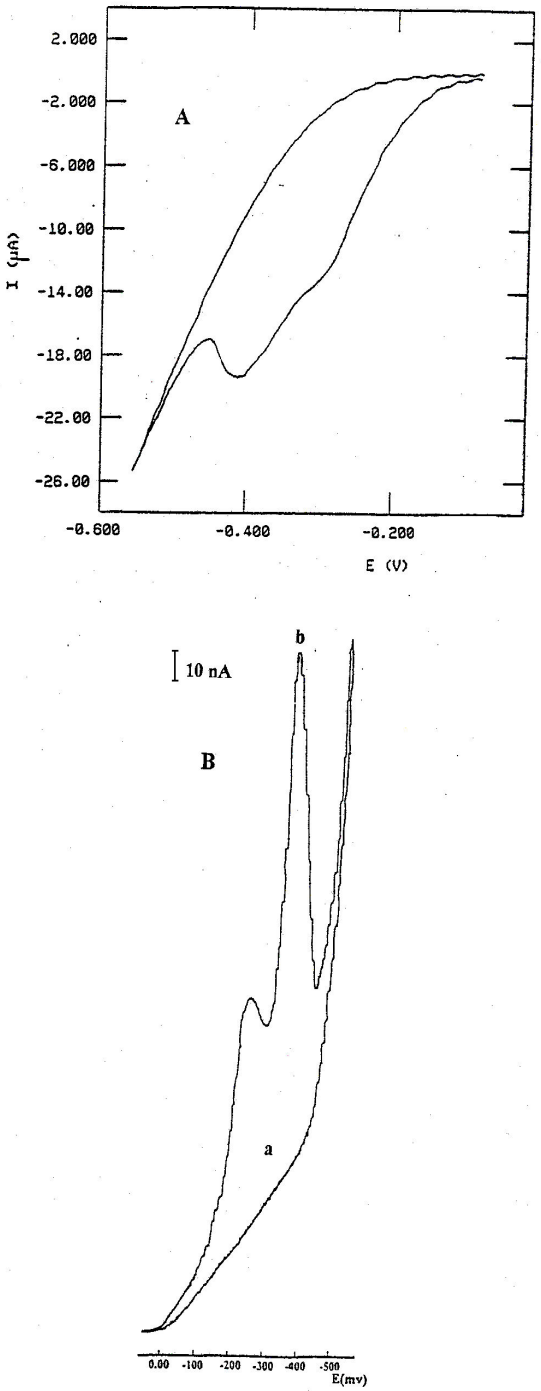

Fig.2: (A) Cyclic voltammogram of 0.1mM Mo (VI) oxinate solution, scan rate: 50 mV s^{-1} (B) DP polarogram of 7μM chloroform solution of Mo (VI) oxinate, Pulse amplitude: 50 mV, Sweep rate 5 mV s^{-1}. Supporting electrolyte 0.2 M tri-BAP + 0.01 M oxin.

of calibration graphs are I (nA) = 0.03 + 6.8 C (μM) and I (nA) = 0.7 + 13.7 C (μM) respectively, the detection limit of the method (LOD = $Y_B + 3S_{x/y}$) were found to be 0.32 μM and 0.16 μM, respectively. Note that in the case of tri-BAP the peak currents related to E_p of -0.38 V was considered for this purpose. As seen, the detection limit with tri-BAP is lower than with PP + P, therefore we have used the former for the analytical measurement of Mo (VI) oxinate.Fig.3 shows a typical example of DP polarograms of Mo (VI) oxinate in the presence of 0.35 M PP + 0.15 M P + 0.01 M oxine as supporting electrolyte.

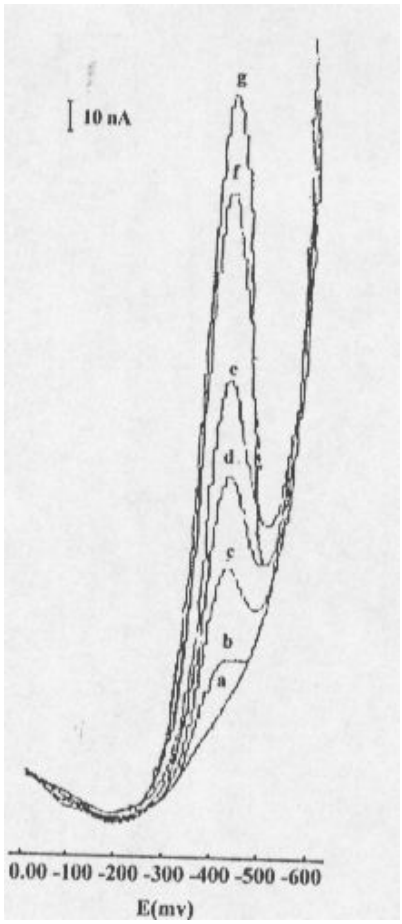

Fig.3: DP polarograms of Mo (VI) oxinate solutions over the concentration range 1-20 μM, (a) only supporting electrolyte, (b)1μM, (c) 2 μM, (d) 4μM, (e) 6μM, (f) 8μM and (g)10μM,. Supporting electrolyte: 0.35M PP + 0.15M P + 0.01M oxine, pulse amplitude: 50 mV,Sweep rate 5 mV s^{-1}.

Efficiency of Mo(VI) oxinate extraction

In order to utilize a simple standard addition method to the polarographic cell preventing the matrix effect on the analytical results of real samples, we have investigated the extraction efficiency of Mo (VI) oxinate from aqueous solution of pH 2. For this purpose we have extracted Mo (VI) oxinate from a 5 ml-portion of aqueous solution of 50 μM ammonium molybdate. The extraction efficiency was determined by three successive standard additions of standard chloroform solution of Mo (VI)oxinate to the extract. The average efficiency for three replicate determinations was 100.6% with a relative standard deviation of 2.2%.

Interference study

The preliminary experiments showed that among the metal ion-oxinates, which are extractable with a chloroform solution of oxine at pH range 0-4 [19], only Fe (III) and Cu (II) oxinates are electroreducible in chloroform, under the polarographic conditions for the determination of Mo (VI). The potential of the Cu (II) oxinate reduction is sufficiently different and hence does not cause any interference. However the presence of Fe (III) oxinate is undesirables, because the reduction peak of Mo (VI) oxinate overlapped with that of Fe (III) (see Fig 4). The masking effect of some compounds including, EDTA and ascorbic acid alone or together with 1,10- phenanthroline on the extraction of Fe (III) oxinate in chloroform was examined. We have found that in the presence of dissolved oxygen in the aqueous Fe (III) solutions, EDTA is suitable and 2 ml of 1M solution of EDTA per 10 mg of Fe in aqueous solution , masks Fe (III) and prevents the extraction of Fe. Furthermore the presence of EDTA in the aqueous solution does not perturb the quantitative extraction of Mo (VI) oxinate. At the experimental conditions optimized, the reliability of the method was investigated by analysis of a standard sample of marine animal's kidney (TORT1) containing a certified amount of molybdenum (1.5 ppm), Copper (439 ppm), iron (186ppm), cadmium (26 ppm), lead (10.4 ppm),manggaes (23.4), zinc (177ppm) and vanadium (1.4ppm), followed the wet dissolution and extraction processes as described in experimental section. As can be seen from the results shown in table 1, the agreement between the molybdenum amount, certified and obtained by means of the present method is good (student t test).

Application to the analysis of steel

It was intended to investigate the suitability of the present extraction DP polarography for the selective determination of molybdenum in steel. For this purpose the sample was dissolved and molybdenum was separated from the concomitant elements by solvent extraction into chloroform. DP polarograms of 10-ml portion of chloroform extract, obtained from the standard steel sample (NBS 165) in the presence of 0.2M tri-BAP as supporting electrolyte is shown in Fig. 5. As seen in Fig. 5, two peaks are observed, which are attributed to Mo (VI) oxinate, this was confirmed by comparing it with the polarogram, obtained for a standard solution of Mo (VI) oxinate in chloroform. Furthermore this Figure leads us to conclude that the concomitant elements even Fe in the samples (as matrix element) do not pose any problem in the determination of molybdenum in steel.

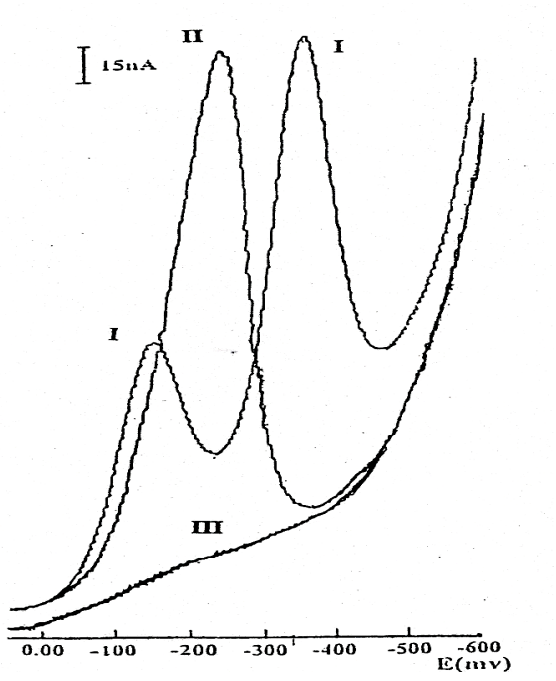

Fig.4: DP polarograms of: (I) Mo (VI) oxinate and (II, III) 10 μM Fe (III) oxinate (II) in the absence and (III) in the presence of 0.1 mM EDTA as masking agent. Supporting electrolyte: 0.2M tri-BAP + 0.1M oxine, experimental conditions as Fig.2.

Table1: Determination of molybdenum in standard samples

Sample	Certified amount %	Found amount %[a]	Rsd %	t^{b}_{exp}
TORT 1	0.00015	0.000155	2.4	2.75
NBS162 (steel)	0.005	0.0048	2.1	2.9
NBS165 (steel)	0.055	0.056	1.4	3.25

a: Mean of three replicate determinations
b: Critical value of t for p= 0.05 is 4.3

Using a standard addition method, to the polarographic cell as well as calibration graph , prepared by means of chloroform extracts obtained from the aqueous standard solutions of ammonium molybdate over concentration range 5×10^{-7} - 2×10^{-5} M, the average percent of molybdenum in the samples, obtained for three replicate determinations, are shown in Table1 for two standard steel samples. As seen in Table1 the results are precise and in good agreement with certified amounts.

CONCLUSIONS

The results obtained from voltammetry revealed that Mo (VI) oxinate extracted into chloroform is present in different chemical states depending on the type of supporting electrolyte used. In the presence of PP 0.35 M+ P 0.15 M only one reduction peak appears, for Mo (VI) oxinate, while its reduction in the presence of 0.2 M tri-BAP exhibits two reduction peaks related two different forms of Mo (VI) oxinate under the polarographic conditions.[20] The results obtained from the voltammetry suggest the possibility of developing a differential pulse polarographic method for the selective and rapid determination of molybdenum, after its extraction into chloroform as Mo (VI)oxinate. The detection limit of the method is low enough allowing trace determination of Mo and is comparable with the some methods cited in introduction. But the present method is highly selective for the determination of molybdenum in the complex matrices and in the presence of almost all metallic cations. Indeed the selectivity of the method due to both selective extraction and selective pulse polarography in non-aqueous media. The method was successfully applied to the selective determination of molybdenum in steel after its separation from the matrix and concomitant elements.

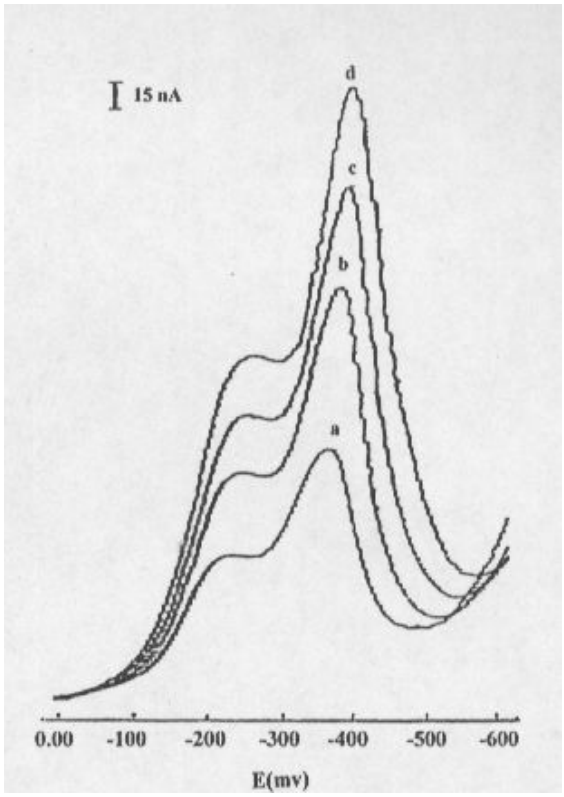

Fig.5: Dp polarogrms of (a) 10 ml chloroform extract obtained from 5 ml aqueous solution of digested steel sample NBS 165 (b-d) successive addition of 0.4ml standard solution of Mo(VI) oxinate in chloroform to solution a . Supporting electrolyte and experimental conditions as Fig.4. Standard solution of Mo (VI) oxinate 10^{-4}M.

Received: 1st Janurary 2002 ; Accepted: 28th October 2002

REFRENCES

[1] Soylak, M., Sahin, U., Elci, L. *Anal Chim Acta.* **322**, 111 (1996).

[2] Berhanu, B., Chandravanshi, B. S. *Anal Let.* **28**, 1681 (1995).

[3] RJR Mehta, *Feresenius J. of Anal Chem*. , **349**, 520 (1994).

[4] AKM. Atamjyot, ALJ . Rao. *indian J. of Chem. Inorg.,* Bioinorg, Phys Theor, 8*, Anal. Chem*., **312**, 480 (1992).

[5] Lahiri, S. , Ghosh, M. , *Indian J. of Chem.* , **30**, 989 (1991).

[6] Wang, J. H., He, RH. *Micro- Chem. J.*, **53**, 376 (1996).

[7] Jabbari, A., Shamsipour, M., *Ferisenius. J. of Anal. Chem.,* **374**, 269 (1993).

[8] Papadopoulos, CG., Zotou, Ac., *Microchim . Acta,* **106**, 203 (1992).

[9] Ensafi, A.A., *Anal. Let.,* **25**, 2339 (1992).

[10] Blanco, CC., Campana, AMG., Barrero, FA., Mr. Ceba, *Talanta,* **42**, 1037 (1995). [11] Kobayashi,T., Hasegawa, S., Yoshioka, T., Hasegawa, R. *J.of the Japan. Inst. of Metals* **58**, 789 (1994).

[12] Takahashi, T., Shimamura, T., *Anal., Chem.* **64**, 3247 (1994).

[13] Kumar, A., Agarwal, Rs., Puri, Bk., *Rev. Roumaine de Chimie,* **38**, 941 (1993).

[14] Jia, L., Zhang, HW., Hu, ZD., *J of Liquid. Chrom.& Related Technologie,* **19**, 565 (1996).

[15] Pournaghi-Azar, M.H., Zargharian, R., *Anal. Chim. Acta,* **328**, 33 (1996).

[16] Djozan, D., Pournaghi-Azar, M.H., Toutounchi-Asr, J., *Talanta,* **46**, 123 (1998).

[17] Pournaghi-Azar, M.H., Ansary-Fard, A.H., *Talanta,* **46**, 607 (1998).

[18] Pournaghi-Azar, M.H., Faradjenia, F., *Microchem. J.* **63**, 284 (1999).

[19] Stary, J., "The solvent extraction of metal chelates", Ed. H.Erving, First published, Pergamon Press.Ltd., (1964).

[20] Bilar, J.C., Emeleus, H.J., Nyholm, S.R., Trotman-Dickenson, A.F., Comprehensive Inorganic Chemistry, Pergamon Press Ltd, **3**, 734 (1975).