*Chimica Acta Turcica* 34 (2, 3) (200(j) 1-8

# SPECTROPHOTOMETRIC DETERMINATION OF COBALT, NICKEL, COPPER AND MOLYBDENUM USING AMMONIUM PYRROLIDINE CARBODITHIOATE IN THE PRESENCE OF SURFACTANTS

**Ashok Kumar Malik, Sanjiv Kumar Mehta, Varinder Kaur, Prem Lata* and A.L.J. Rao,**

Department of Chemistry, Punjabi University, Patiala.
Department of Applied Sciences. Punjab Engineering College, Chandigarh.

**Abstract:** A novel spectrophotometric method has been developed for the determination of microamounts of Co(II), Ni(II), Cut II), and Mo(VI) using ammonium pyrrolidinecarbodithioate as a reagent in the presence of surfactants as solubilising agent. The method is quite sensitive and has been applied for the determination of these metals in various alloys.

**Keywords:** Ammonium pyrrol idin ecarbodithio ate, surfactants, metal ions, environmental samples.

## INTRODUCTION

Dithiocarbamates are the important thio compounds and play a vital role in analytical chemistry due to highly sensitive colour reaction, stability and selectivity towards various metal ions". These compounds form water insoluble complexes with most of the metal ions, therefore, their complexes are either dissolved in water or extracted in a suitable organic solvent for their spectrophotometric determination, which is quite tedious and time consuming, thus there is need for more rapid and simple methods. In this method ammonium pyrrolidinecarbodithioate has been used as a complexing reagent for the spectrophotometric determination of Co(II), Ni(II), Cu(II) and Mo(VI) which form water insoluble complexes with these metal ions and can be solubilised in water using surfactants. The present method has been found to be simple, rapid and sensitive for the determination of these metal ions.

---

Chirnica Acta Turcica, ISSN 0379-5896, 2009 Printed in Turkey

F- 2

## EXPERIMENTAL

**Equipment:** A digital pH meter and an Varian Cary 2400 spectrophotometer were used for pH and absorbance measurements, respectively.

**Reagents:** All chemicals used were of analytical reagent (A.R.) grade and double distilled water was used throughout the study.

**Solution of ammonium pyrrolidinecarbodithioate:** A 0.2% solution of ammonium pyn-olidinecarbodithioate (Merck, OR) was prepared in distilled water and standardized titrimetrically$^{12}$ using mercuric acetate as a titrant and diphenylcarbazone as an internal indicator.

**Metal ion solutions:** Stock solutions of Co(II), Ni(II), Cu(II) and Mo(VI) were prepared separately in distilled water. The metal solutions were standardised" by known methods and further diluted as required.

**Solutions used for the study of pH effect:** Dilute solutions (0.1M) NaOH, perchloric acid and ammonia were used for the study of pH effect on absorbance. Sodium acetate-acetic acid (0.2 M, pH 5.0-5.8) was used for maintaining pH constant.

**Solutions of diverse ions:** A 10% (w/v) solution of alkali metal salts and 0.2% (w/v) solution of different metal salts were used to study the interference of diverse ions.

**Surfactants solutions:** Sodium dodecyl sulphate (SDS, 2%, w/v), Triton X-100 (TX-100, 5%, v/v) and cetyltrimethyl ammonium bromide (CTAB, 1%, w/v) were prepared in distilled water.

**General procedure:** Aliquots of Co(II), Ni(II), Cu(II), and Mo(VI) in the Beer's law range were taken separately in 10 ml measuring flasks and pH of the solutions was adjusted using 2.0 ml of acetate buffer in case of Co(II), Ni(II) and Cu(II) or with 5 M hydrochloric acid solution in case of Mo(VI). To these solutions a known volume of 0.2% ammonium pyrrolidine dithiocarbamate reagent solution was added and the complexes thus formed were solubilised in water by adding 1.0 ml of surfactant solution (table 1). The solution of each flask was made to mark with distilled water and the absorbance of portion of each solution was measured at its respective absorption maximum, against a reagent blank prepared under the similar conditions. The details of absorption maxima, pH ranges and volume of reagent used are summarized in table 1.

**Table 1.** Analytical characteristics of metal pyrrolidinecarbodithioate complexes in the presence of surfactants

| Characteristic | **Co(II)** | Ni(II) | **Cu(II)** | **Mo(VI)** |
|---|---|---|---|---|
| Beer's law range *(cg* gime | 0.3-3.5 | 0.2-3.7 | 0.2-3.0 | 0.35-8.0 |
| Absorption Maxima (.1g max, nm) | 328 | 330 | 438 | 402 |
| Molar absorptivity ( 1 mol$^{i}$crri$^{1}$ ) | 9.53x104 | 5.9x104 | 1.74x104 | 2.0x104 |
| Sandell's sensitivity (cg gicm-2) | 0.00062 | 0.0009 | 0.0036 | 0.0047 |
| pH range | 4.6-9.2 | 6.0-8.0 | 3.0-8.0 | 1.2-1.8 |
| Surfactant used * | SDS | SDS | SDS | TX-100 |
| Amount of 0.2% reagent used ( ml) | 1.0 | 1.0 | 1.5 | 1.0 |
| Relative standard deviation** (%) | 0.82 | 0.95 | 0.81 | 0.88 |

** SDS, TX-100 and CTAB were used for the study, however the best results were obtained with the given surfactant.*

*** Each result is average of five experiments.*

## RESULTS AND DISCUSSION

**Absorption spectra:** The absorption spectra of Co(II), Ni(II), Cu(II) and Mo(VI) pyn-olidinecarbodithioate complexes were recorded in the presence of surfactants against a reagent blank prepared under the similar conditions. The complexes absorb strongly at their respective absorption maxima in the presence of the surfactant (Fig 1-4).

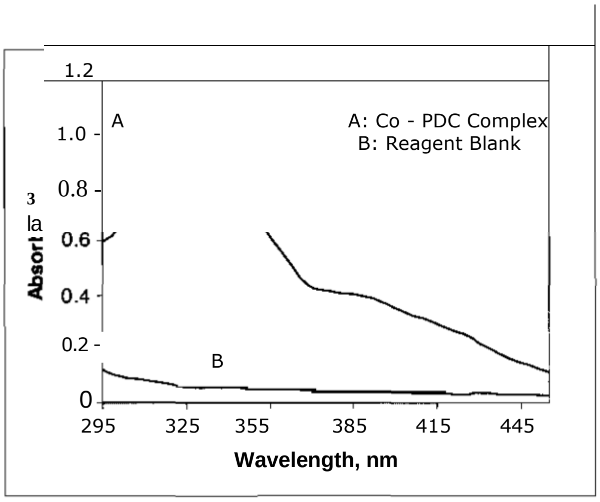

Fig. 1 : Absorption spectra of Co-PDC complex.

Conditions : Co = 6.0 pg, pH = 5.5, APDC = 1.0 ml (0.2%), SDS = 1.0 ml (2%, w/v), Total volume = 10 ml.

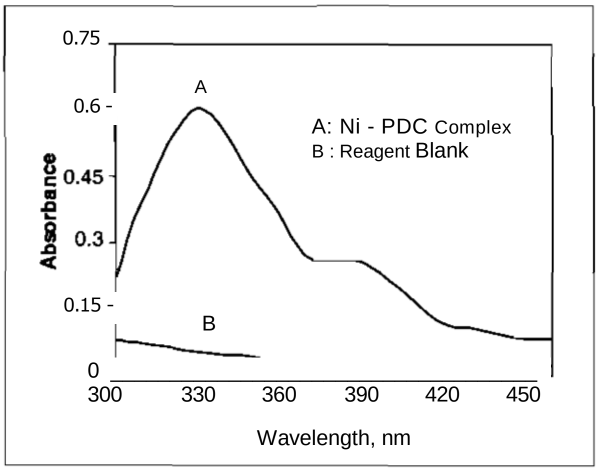

**Fig. 2: Absorption spectra of Ni-PDC complex.**

Conditions : Ni = 6.0 pg, pH = 5.5, APDC = 1.0 ml (0.2%), SDS = 1.0 ml (2%, w/v), Total volume = 10 mi.

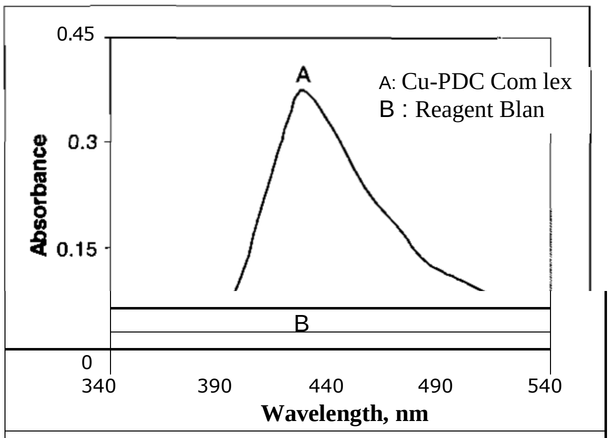

Fig. 3 : **Absorption spectra of Cu-PDC complex.**

Conditions : Cu = 13.5 pg, pH = 5.5, APDC = 1.5 ml (0.2%), SDS = 1.0 ml (2%, w/v), Total volume = 10 mi.

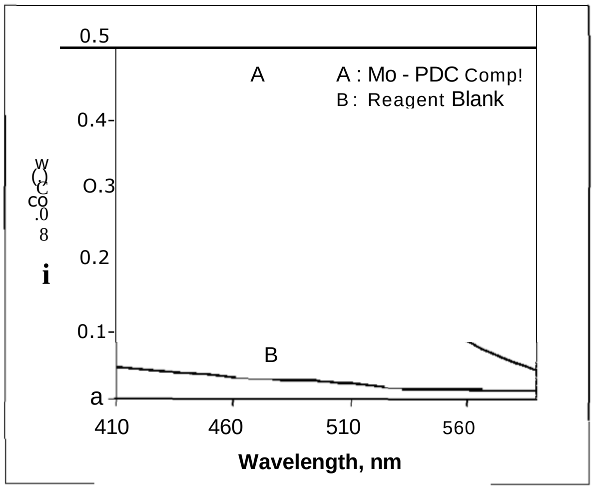

**Fig. 4 : Absorption spectra of Mo-PDC complex.**

Conditions : Mo = 21.0 pg, pH = 1.5, APDC = 1.0 ml (0.2%), Triton X-100 = 1.0 ml (5%, v/v), Total volume = 10 ml.

**Effect of pH:** The pH of metal complex solutions was adjusted using dilute solutions (0.1M) NaOH, perchloric acid and ammonia and effect on absorbance was studied. The absorbance of the complexes was maximum and constant in the pH range given in Table 1.

**Calibration curves:** The calibration curves were constructed at their respective absorption maxima and these were linear over wide concentration range as given in table 1 for each metal ion.

Table 2. Determination of metal ions in alloys

| Alloy | Certified (%) composition | | Amount of metal (i&')" | | RSD*(%) |
|---|---|---|---|---|---|
| | | | Taken | Found | |
| | | Determination of cobalt | | | |
| 175 607-6 | Co: | 4.72 | 5.00 | 5.0 | 1.96 |
| | V: | 0.82 | | | |
| | W: | 16.96 | | | |
| High Speed steel | Co | 9,25 | 11.0 | 11.2 | 1.94 |
| | Mn: | 040 | | | |
| | Si: | 0.005 | | | |
| | 5: | 0.05 | | | |
| | | 0.05 | | | |
| | Cr: | 4.1-4.2 | | | |
| | Mo: | | | | |
| | | 6.8-18.5 | | | |
| | | Determination of nickel | | | |
| Stainless Steel no 306 | Cr: | 16.5 | 14.5 | 14.1 | 1.56 |
| | Ni: | 12.0 | | | |
| | Mo: | 2.0-3.0 | | | |
| | Fe: | 70-71 | | | |
| Stainless Steel no. 304 | Cr.- | 18.0 | 17.0 | 172 | 1,65 |
| | Ni: | 8-12 | | | |
| | Fe: | 70-71 | | | |
| Mortal alloy 400 | NE: | 63 | 15.0 | 14.9 | 1.68 |
| | C: | 0.15 | | | |
| | | 0.0024 | | | |
| | Mn: | 0,07 | | | |
| | Si: | 0.5 | | | |
| | Fe: | 2.5 | | | |
| | | 31,0 | | | |
| | | Determination of copper | | | |
| Mollory | Cu: | 99.2 | 15.0 | 15.10 | 1.37 |
| | Cr: | 0,8 | | | |
| Steel | Cu: | 0.54 | 22.0 | 22.15 | 1.65 |
| | Ni: | 0.44 | | | |
| | 'Fe: | 44.0 | | | |
| | Ca,Si,Mn and Cr: | 55.02 | | | |
| | | Determination of molybdenum | | | |
| Stainless Steel no 306 | Cr: | 16.5 | 10.0 | 10.13 | 1_53 |
| | Ni: | 12,0 | | | |
| | Mo: | 2-3.0 | | | |
| | Fe: | 70.71 | | | |
| Eligiloy | Co: | 40_0 | 20.0 | 19.35 | 1.83 |
| | | 15.0 | | | |
| | Cr: | 20.0 | | | |
| | Mn: | 2.0 | | | |
| | Ma: | 7.0 | | | |
| | 'Fe: | 15.0 | | | |
| | Be: | 0.05 | | | |
| | C: | 0.15 | | | |

**Each result is average of five experiments; h: masked with 2.0 ml of 5% thiourea solution; c: masked with 2.0m1 of5% sodium fluoride solution.*

*It was standardized with reference 9.*

**Effect of reagent concentration:** Different amounts of 0.2% solutions of reagent were added separately to each metal ion solution and it was observed that the absorbance was constant and maximum in the range given in Table 1.

**Effect of time:** The absorbance of metal pyrrolidinecarbodithioate complexes was measured at different time of intervals and was found to be constant for more than 20 hr in case of Co(II), Ni(II) and Cu(II) however, molybdenum complex was stable for only one hour in the presence of surfactants.

**Effect of surfactants:** Different surfactants like SDS. TX-100 and CTAB were used to solubilize the insoluble metal complexes and absorbance was measured by general procedure. The complexes were readily soluble in the presence of these surfactants and increase in absorbance was observed in all cases due to micellar action. However, sodium dodecyl sulphate (SDS) was preferred over other surfactants in case of cobalt, nickel and copper and TX-100 in case of molybdenum due to more enhancement in absorbance as compared to other surfactants.

**Composition of the complexes:** The composition of metal pyrrolidinecarbodithioate complexes was determined by Job's and mole-ratio methods. A sharp peak at 0.33 mole fraction in Job's method of continuous variation and a break at 1:2 mole ratio in mole-ratio method indicated the formation of 1:2 (MI) complexes in all the cases.

**Beer's law and Sensitivity:** Under the optimum conditions described above calibration curves for Co(II), Ni(II), Cu(II) and Mo(VI) complexes with ammonium pyrrolidinecarbodithioate were constructed at 328, 330, 427 and 470 nm, respectively. Values of Beer's law range, molar absorptivity and Sandell's sensitivity of all the metal ions are given in Table 1.

**Interferences :** The effect of the diverse ions on the determination of these meal ions was studied in detail. To test the effect of diverse ions; Co(II) 612g, Ni(II) 30/2g, Cu(II) 13.5 *lig* and Mo(VI) 21/2g were determined by the general procedure, in the presence of respective foreign ions_ Each of these metal ions can be determined without any interference in the presence of 50 fold excess of the following cations; AMID, Bi(II1), Ba(II), Cd(II),Cr(III), Mg(II), Mn(II), Pb(II), Sr(II), Rh(III), Zr(IV) and Zn(II). Amongst the anions examined (amount mg shown in parentheses) the following anions did not interfere: acetate (100), sulphate(70), thiosulphate(20), metabisulphite(30), citrate (90), bromide (70), thiocynate(100), fluoride(95) and chloride(95). Iron (50 fold in excess) in the determination of these metal ions was masked with 2.0 ml of 5% sodium fluoride solution. Pd(II) in the determination of these metal ions was separated by pre-extraction into chloroform at pH 2.5 except molybdenum. EDTA interfered strongly in the determination of these metal ions due to its ability to form stronger complexes than ammonium pyrrolidinecarbodithioate.

## APPLICATIONS

**Determination of metals in the presence of metal ions and alloys :** A 0.1-0.5g of the alloy was taken in a beaker and to this was added 10-15 ml of concentrated HC1 and 5.0 ml of concentrated $HNO_3$. It was heated on a hot plate till dissolved and the final volume was reduced to about 5 ml. Then 10 ml of concentrated HC1 was added to it. It was diluted with distilled water and filtered. An aliquot of the resulting solution was determined by the general procedure. The results of the determinations are given in Table 2 which are comparable to the reported method[9] in which copper was extracted as potassium morpholine-4-carbodithioate complex into molten naphthalene and dissolved in $CIIC1_3$ and measured absorbance at 440 nm.

## Conclusion

The present method for the determination of cobalt, nickel, copper, iron, molybdenum and palladium is quite simple, rapid and sensitive and is comparable to other spectrophotometric methods reported in literature. The method has been applied for the determination of these metals in various alloys samples. A comparison of the present method with other existing methods is shown in Table 3-4. The wide applicability and simplicity of the method make it an excellent choice among available methods.

**Table 3.** Comparison of the present method with other spectrophotometric methods for the determination of Cobalt and Nickel

<table>
<tr><th colspan="5">Comparison of the present method with other spectrophotometric methods for the determination of Cobalt</th></tr>
<tr><th>Sr. No.</th><th>Reagent</th><th>Wavelength, nm</th><th>Molar absorptivity I moi$^{1}$ crril</th><th>Reference</th></tr>
<tr><td>1.</td><td>2-(2-benzothiazolylazo)-p-cresol</td><td>615</td><td>1.62 x $10^{4}$</td><td><b>14</b></td></tr>
<tr><td>2.</td><td>Sodium isoamylxanthate</td><td><b>400</b></td><td>1.92 x $10^{4}$</td><td>15, <b>16</b></td></tr>
<tr><td>3.</td><td>Isonitroso-5-methy1-2-hexanone</td><td>400</td><td>1.13 x $10^{4}$</td><td>17</td></tr>
<tr><td>4.</td><td>5-[o-carboxypheny1azo]-2,4-dihydroxybenzoic acid</td><td>555</td><td>1.64 x $10^{4}$</td><td>18</td></tr>
<tr><td>5.</td><td>m-Benzil monoxime</td><td>380</td><td>255 x $10^{4}$</td><td>19</td></tr>
<tr><td>6.</td><td>Pyridoxa1-4-phenyl-3-thiosemicarbazone</td><td>450</td><td>1.4.0 x $10^{4}$</td><td>20</td></tr>
<tr><td>7.</td><td>Ammonium pyrrolidine dithiocarbamates (APDC)</td><td>328</td><td>9.53 x $10^{4}$</td><td>Present Method</td></tr>
<tr><th colspan="5">., Comparison of the present method with other spectrophotometric methods for the determination of Nickel</th></tr>
<tr><td>1.</td><td>Sodium isoamylxanthate</td><td>360</td><td>1.2 x $10^{4}$</td><td>15, <b>16</b></td></tr>
<tr><td>2.</td><td>Cyclohexylxanthate</td><td><b>415</b></td><td>0.50 x $10^{4}$</td><td>21</td></tr>
<tr><td>3.</td><td>4-(2'-benzothiazolylazo) salicylic acid</td><td>525</td><td><b>0.6</b> x $10^{4}$</td><td>22</td></tr>
<tr><td>4.</td><td>3-(4'-fluoropheny1)-5-(2'-carboxyphenylazo)-rhodarnine</td><td><b>440</b></td><td>2.3 x $10^{4}$</td><td>23</td></tr>
<tr><td>5.</td><td>benzene</td><td>66665</td><td>1.30 x $10^{4}$</td><td>24</td></tr>
<tr><td>6.</td><td>Ammonium pyrrolidine dithiocarbamates (APDC)</td><td>330</td><td>.9x $10^{4}$</td><td>Present Method</td></tr>
</table>

**Table 4.** Comparison of the present method with other spectrophotometric methods for the determination of Copper and Molybdenum

| Comparison of **the present method** with other **spectrophotometric methods for the determination** of **Copper** | | | | |
|---|---|---|---|---|
| Sr. No. | Reagent | Wavelength, nm | Molar absorptivity I mo1$^{-1}$ crril | Reference |
| 1. | lead 4-benzylpiperidinedithiocarbamate | 437 | $0.81 \times 10^4$ | 25 |
| 2. | 1,3,8-trihydroxy-6-methylanthraquinone | 572 | $0.55 \times 10^4$ | 26 |
| 3. | 5(4-dimethylaminobenzylidene) rhodanine | 480 | $0.76 \times 10^4$ | 27 |
| 4. | 1-phenyl-1,2-propane dione-2-oxi *me* thiosemicarbazone | 465 | $0.58 \times 10^4$ | 28 |
| 5. | 2-carboxybenzaldehyde thiosemicarbazone | 346 | $1.2 \times 10^4$ | 29 |
| 6. | Ammonium pyrrolidine dithiocarbamate (APDC) | 427 | $1.74 \times 10^4$ | Present Method |
| **Comparison of the present** method with **other spectrophotometric methods for the determination of Molybdenum** | | | | |
| 1. | Sodium isoamylxanthate | 470 | $1.13 \times 10^4$ | 15, 16 |
| 2. | N1-(o-chloropheny1)-N1-hydroxy-N2-(o-methylphenyl)benzamidine hydrochloride | 470 | $0.77 \times 10^4$ | 30 |
| 3. | 2'-hydroxyacetophenone benzoylhydrazone | 390 | $0.85 \times 10^4$ | 31 |
| 4. | 00$^1$-bis(2-ethy1hexyl) dithiophosphoric acid<br>5,7-Dibromo-8-hydroxyquinoline | 503 | $0.96 \times 10^4$ | 32 |
| 5. | Ammonium pyrrolidine dithiocarbamate (APDC) | 401 | $0.41 \times 10^4$ | 33 |
| 6. | | 470 | $2.0 \times 10^4$ | Present Method |

## RE'FERENCES

1. Puri B.K., Sethi C.L. and Kumar A., J. Chinese Chem. Soc., **29,** 173 (1982).
2. Livingstone S.K., Quart. Rev., 19, 386 (1965).
3. Bag S.P. and Bhattacharya B., J. Indian Chem. Soc., **60(6),** 596 (1983).
4. Yamamoto D. and Tskada M. and Hiraoka S., Bunseki Kagaku, 29, 396 (1980).
5. Safavi, A. and Parham H., Anal. Chim. Acta., 157(2), 369 (1984).
6. Salinas F, Martinez Vidal J.L. and Gouzalez-Parra J., An. Quim. Sci. Sr., 2, 190 (1986). Chem. Abstr., 4, 106, 27039p (1987).
7. Satake M. Yoshida N., Div. Appl. Sci. Fukui Univ. Fukui, Japan, 28(2), 207 (1980). Chem. Abstr., **95,** 108037 (1981).

8. Looyeng R.W. and Boltz D.F., Talanta, 19, 82 (1972).

9. Gautam M., Bansal R.K. and Puri B.K., Bull. Chem. Soc. Japan, 54, 3178 (1981).

10. Sethi C.L. and Puri B.K., Micro Chem. Acta., 1, 361 (1983).

11. Maklokova V.P. and Ryazaner 1.P., Zavod. Lab., 34, 1049 (1968).

*12. Rao A. L. J. and Malik A.K. and Paul* Y., J. Ind. Acad. Forensic Sc.,./9, *31* (1992).

13. Vogel, Al.,. A text book of quantitative inorganic analysis, r$^{i}$ edn., Longman, London, 1969.

14. Carvalho M. S., Fraga I. C. S., Neto K. C. M. and Filho E. Q. S., *Talanta,* 43, 1675 (1996).

15. Malik A. K., *Ann. Chim. (Rome),* 90, 581 (2000).

16. Malik A. K., Kaul K. N., Lark B. S., Faubel W. and Rao A. L. *J., Turk J. Chenz.,* 25, 99 (2001).

17. Jadhav S. B., Tandel S. P. and Malve S. *P Talanta,* 55, 1059 (2001).

18. Amin A. S., Ahmed I. S. and Moustafa M. E., *Anal. Lett.,* 34, 749 (2001).

19. Eskandari H., Ghaziaskar H. S. and Ensafi A. A., *Anal. Sci.,* 17, 327 (2001).

20. Sarma L. S., Kumar J. R., Kumar C. J. and Reddy A. V., *Anal. Lett.,* 36, 605 (2003).Atamjyot, Sharma J. D. and Rao A. L. J., *Indian J. Chem.,* 36, 725 (1997).

21. Hashem E. Y., Abu-Bakr M. S. and Hussain S. M., *Spectrochim. Acta,* 59, 761, (2003).

22. Yu J. II., Ou Q. Y., Peng S. Y. and Wang L. G., *Laura Jianyan, Huaxue Fence,* 40, 75, 81 (2004).

23. Hashem E. Y., Abu-Bakr M. S. and Hussain S. M., Ann. *Chim.,* 94, *571* (2004).

24. Cesur H. and Bati B., *Turk. J. Chem.,* 26, 599 (2002).

25. Paz T. and Jana N. R., *Talanta,* 40, 1519 (1993).

26. Ojeka E. O. and Iyun J. F., *Global Journal of Pure and Applied Sciences, 10,* 577 (2004).

27. Hussain Reddy K. and Prasad N. B. L., *Indian J. Chem.,* 43, 111 (2004).

28. Lopez-de-Alba P., Loper-Martinez L. and Arnador-Hernandez J., *Bol. Soc. Chil. Quim,* 44, 469 (1999).

Mishra I. and Mohabey H., *Bull. Chem. Soc. Jpn.,* 66, 1533 (1993).

30.31. R. Das, J. R. Mehta, *Bull. Chem. Soc. fpn.,* 66, 1086 (1993).

32. Y. Sasaki, S. Tagashira, Y. Murakami, M. Ichikawa, *Anal. Sci.,* 14, 603 (1998).

33. Ahmed M. J. and Hague M. E., *Anal. Sci.,* 18, 433 (2002).