

Determination of Co(II) in water and soil samples using spectrophotometry coupled with preconcentration on 4-amino methyl pyridine anchored silica gel column

C. Sivani^a, G. Ramakrishna Naidu^a, J. Narasimhulu^b, D. Reklam^c,
J. Dilip Kumar^c, P. Chiranjeevi^{c,*}

^a Department of Environmental Sciences, S.V. University, Tirupati 517502, A.P., India

^b Department of Chemistry, JNTU, Anantapur, AP, India

^c Environmental Monitoring Laboratory, Department of Chemistry, S.V. University, Tirupati 517502, A.P., India

Received 28 October 2006; received in revised form 29 November 2006; accepted 30 November 2006

Available online 6 December 2006

Abstract

4-Amino methyl pyridine anchored silica gel (4-AMPS) was used as a sorbent in a simple sensitive spectrophotometry determination of Co(II) in various samples using piperazine dithiocarbamate as a color developing agent ($\lambda_{\max} = 330$ nm) at pH 5.0 ± 0.2 . Beer's law was obeyed over the range of 0.1 – $5.0 \mu\text{g ml}^{-1}$. The molar absorptivity and Sandell's sensitivity were $1.257 \times 10^5 \text{ l mol}^{-1} \text{ cm}^{-1}$ and $0.006145 \mu\text{g cm}^{-2}$, respectively. Under these conditions, the preconcentration factor obtained was 10, and the detection limit achieved was 5.0 ng ml^{-1} . The detailed study of various interfering ions made the method more sensitive and selective. The recovery of Co(II) from various samples range from 97.50 to 99.66%. The present method was successfully applied for the determination of Co(II) in various water and soil samples. The proposed method was compared with reported methods in terms of Student's 't'-test and 'F'-test which indicates that there is no significant difference between proposed and literature method at 95% confidence level.

© 2006 Elsevier B.V. All rights reserved.

Keywords: 4-Aminomethyl pyridine–silica gel (4-AMPS); Preconcentration; Piperazine dithiocarbamate; Cobalt(II); Spectrophotometer; Water and soil samples

1. Introduction

Cobalt is an essential element for human and animals because it is associated with the synthesis of Vitamin B₁₂. Cobalt is used in the manufacture of alloys, permanent magnets, paint driers and as industrial catalyst in processes such as manufacture of NH₃ and alcohol. It deficiency is exhibited by retarded growth rate, loss of appetite and pernicious anemia in human beings. Chronic exposure of cobalt may lead to cancer disease. Ingestion of excessive amounts of cobalt causes intercellular hypoxia and polycythemia. At high concentrations, it inhibits heme-biosynthesis and enzyme activities. Moreover, the element is toxic, when taken directly.

Several analytical techniques have been reported for the determination of cobalt(II) in various environmental samples, such as AAS, ICP-AES, X-ray fluorescence spectroscopy, spectrofluorimetry and spectrophotometry. Thiosemicarbazone is an important sulphur containing organic reagent. The metal chelate of this reagent find a wide range of application in medicine [1,2] and agriculture [3]. The use of thiosemicarbazones in inorganic analysis has been reviewed [4–6] and the survey of literature reveals that only a few reagents have been employed for the determination of cobalt(II) in various samples [7–18]. Above reported methods have certain limitations such as less stability, selectivity, sensitivity, serious interference of foreign species with chelating agent and high reagent consumption.

In this investigation the novel, facile and sensitive sorbent, 2-aminomethylpyridine grafted silica gel (AMPSG) was successfully anchored for the preconcentration of Co(II) in various water and soil samples. Optimum experimental conditions were

* Corresponding author. Tel.: +91 877 2250556; fax: +91 877 2261274.
E-mail address: chiranjeevipattam@gmail.com (P. Chiranjeevi).

investigated with respect to a standard solution of the same matrix, in order to examine the possibility to obtaining the maximum extraction efficiency with minor sample treatment and minimal experimental conditions. Under these conditions, the preconcentration factor obtained was 80, and the detection limit achieved was 5.0 ng ml^{-1} . The method was successfully applied for the determination of Co(II) in various water and soil samples.

2. Experimental

2.1. Apparatus

A HITACHI U 2001 spectrophotometer with 1.0 cm path length was used for electronic spectral measurements. An Elico Li-129 model pH meter along with glass-calomel combined electrode was used for all pH measurements.

2.2. Reagents

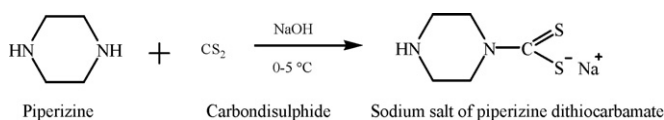
All the reagents used were analytical grade and double distilled water was used through out the experiment.

2.3. Solution

Solutions containing 2.0 M of nitric acid (Merck, Mumbai, India) were used as eluent. A stock solution of cobalt (II) (0.01 M) was prepared by dissolving 2.380 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (Merck, Germany) in deionised doubly distilled water in 1000 ml standard flask. Cobalt (II) working standard stock solutions were prepared afreshly by appropriate dilution of the standard stock solution with deionised doubly distilled water. Piperazine dithiocarbamate (0.03 M) solution was prepared afreshly by dissolving 1.208 g of piperazine dithiocarbamate in 5 ml of methanol and this solution was mixed with 150 ml of hot water ($70\text{--}80^\circ\text{C}$), filtered into a 250 ml volumetric flask, and the volume was made up to the mark with double distilled water.

2.4. Synthesis of sodium piperazine dithiocarbamate reagent

Carbon disulphide (80 g) was slowly added to a solution of piperazine (12.5 g) in 100 ml of water at 5°C with constant stirring, followed by 40 g of sodium hydroxide dissolved in 20 ml of water to form sodium salt of piperazine dithiocarbamate as shown in Scheme 1. The product was warmed to room temperature and washed 2–3 times with purified acetone. The reaction product was purified by recrystallization in acetone. The purified compound has a melting point of $209\text{--}212^\circ\text{C}$ at 740 mm pressure.



Scheme 1. Synthesis of sodium salt of piperazine dithiocarbamate.

2.5. Synthesis of 4-amino methyl pyridine–silica gel sorbent organo fictionalization

A sample of 20 g of activated silica gel was suspended in 100 ml of dry toluene and 20 ml (108 mol) of 3-chloropropyltrimethoxy silane was added to this suspension. The mixture was mechanically stirred under reflux of the solvent in an inert atmosphere for 72 h the suspension was filtered and the solid was washed with toluene and dried under vacuum at 40°C for several hours, to give the modified silica named silica [19].

2.6. Incorporation of 4-amino methyl pyridine

A sample of 5.0 g of silica reacted with 150 ml (0.034 mol) of the compound 4-AMP in 50 ml of toluene, containing 5.0 ml of triethylamine in order to facilitate the reaction equilibrium [20]. The suspension was kept under reflux and mechanically stirred for 72 h at 40°C . The final product 4-AMP–silica gel was filtered, washed with toluene followed ethanol, and dried under vacuum at 40°C for 24 h.

2.7. General procedure

4-AMP (1.0 g) were first packed in a glass column (glass column with stopcock and a porous disk, was 10 cm long and 1.5 cm internal diameter. A small amount of glass wool was placed at the disk to prevent disturbing of the 4-AMP–silica gel-reagent during the sample loading) between frits, using the method recommended by the manufacturer [21]. The column was treated with 2 M HNO_3 (25 ml) and washed with double distilled water until free from acid. A suitable aliquot of the sample solution containing Co(II) in the concentration range of $200\text{--}800 \mu\text{g ml}^{-1}$ was passed through the column after adjusting its pH to the optimum range (acetate buffer of $\text{pH } 5.0 \pm 0.2$) with a flow rate of $1.0\text{--}5.0 \text{ ml min}^{-1}$. The column was washed with double-distilled water to remove free metal ion. The bound metal ion Co(II) was stripped from the column with 2 M HNO_3 (5–10 ml) passed at a flow rate of $2.0\text{--}4.0 \text{ ml min}^{-1}$. The eluent was then mixed with 0.03 M piperazine dithiocarbamate to form yellow colored product, which was measured spectrophotometrically at wavelength 390 nm against reagent blank as shown in Fig. 1.

2.7.1. Determination of cobalt(II) in natural water samples

Different river, lake and spring water samples were collected from various places in and around Tirupati, A.P., India. The samples (150 ml) were stored at $0\text{--}5^\circ\text{C}$ in metal free polyethylene bottles. Water samples were filtered through Whatman filter paper no. 41 and clean solution is collected into 250 ml beaker. The contents are diluted up to the mark with deionised doubly distilled water. Fifteen millilitres of this solution is further diluted to get working solution for determination of cobalt(II) as described in above procedure and compared with the reported method. The results were summarized in Table 1.

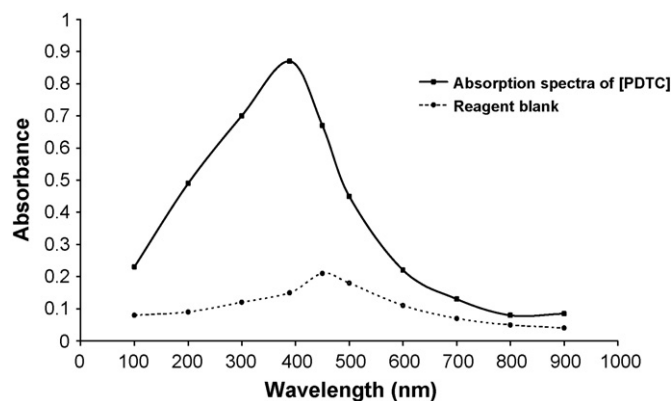


Fig. 1. Absorption spectra of [Co(II)-piperazine dithiocarbamate] complex.

2.7.2. Determination of cobalt(II) in soil samples

Soil samples were collected from Rangampet area, A.P., India. The sample was homogenized in the laboratory, using a fissile and motor and air-dried for 24 h approximately, before analysis. An aliquot of 500 mg of finely pulverized soil is digested with 5 ml of nitric acid (65%) in metal free Teflon vessel. The sample is digested for about 1 h in a microwave oven and again re-digested at 160 °C for 15 min. After treating with double distilled water, the supernatant liquid was made up to the mark in a 25 ml standard flask. The aliquot was analyzed for cobalt(II) using piperazine dithiocarbamate, following the recommended procedure and results were tabulated in Table 1.

3. Result and discussion

3.1. Effect of pH

The effect of pH on the peak height of Co(II) at different concentrations was investigated with a fixed 0.05 M piperazine

Table 2
Optical characteristics of [Co(II)-PDTC] and precision data

Optical characteristics of present method	
Color	Green
λ_{\max} (nm)	390
Stability	More than 7 days
Beer's law range ($\mu\text{g ml}^{-1}$)	0.1–5.0
Molar absorptivity ($1 \text{ mol}^{-1} \text{ cm}^{-1}$)	1.257×10^4
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.006145
Regression equation (Y) ^a	
Slope ^b	0.1519
Intercept ^d	0.0172
Regression coefficient (r)	0.999
Standard deviation (%) ^c	0.09
Range of error (95% confidence level)	± 2
% Error	0.05754

^a $Y = ax + b$, where x is the concentration of cobalt(II) ($\mu\text{g ml}^{-1}$).

^b Experiments performed under optimized conditions (see text) with 5 ml of 0.01 M $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution.

^c $n = 4$.

dithiocarbamate concentration (Table 2). The pH of acetate buffer was changed in the range of 3.0–7.0 and the peak height was measured for each concentration level of Co(II). At all concentration levels of Co(II) maximum peak height were found between 4.0 and 6.0. Therefore, a pH 5.0 ± 0.2 of acetate buffer system was chosen for the throughout the study and it was represented graphically in Fig. 2.

3.2. Effect of piperazine dithiocarbamate concentration

The effect of concentration of piperazine dithiocarbamate on the peak height was investigated at pH 5.0 ± 0.2 by using 2.0 and 3.5 $\mu\text{g ml}^{-1}$ Co(II) solutions. The concentration of piperazine dithiocarbamate was varied in the range 0.001 M–0.10 M. Maximum peak height was obtained at a concentration of

Table 1
Determination of cobalt(II) in various environmental samples

Samples	Proposed method					Reported method [18]	
	Cobalt(II) added ($\mu\text{g ml}^{-1}$)	Cobalt(II) found ($\mu\text{g ml}^{-1}$)	Mean recovery (%) ^a	<i>t</i> -Test	<i>f</i> -Test	Cobalt(II) found ($\mu\text{g ml}^{-1}$)	Mean recovery (%) ^a
Spiked water-I	2.0	0.975	97.50 ± 0.36	1.05	0.048	0.97	97.0 ± 0.45
Spiked water-II	3.0	2.99	99.66 ± 0.14	0.56	0.035	2.92	97.33 ± 0.07
River water ^b	–	9.42	–	–	–	9.40	–
	5.0	14.27	98.0 ± 0.35	0.49	0.29	14.20	96.0 ± 0.18
Lake water ^c	–	5.06	–	–	–	–	–
	7.0	13.89	99.52 ± 0.09	–	–	–	–
Spring water ^d	–	2.91	–	–	–	–	–
	9.0	11.7	98.61 ± 0.25	–	–	–	–
Soil sample ^e	–	10.85	–	–	–	11.40	–
	11.0	21.75	99.50 ± 0.21	0.51	0.63	22.14	97.63 ± 0.18

^a Mean ± standard deviation ($n = 4$).

^b Collected from Chandragiri area.

^c Collected from Chandragiri area.

^d Collected from Narsingapuram area.

^e Collected from Rangampet area.

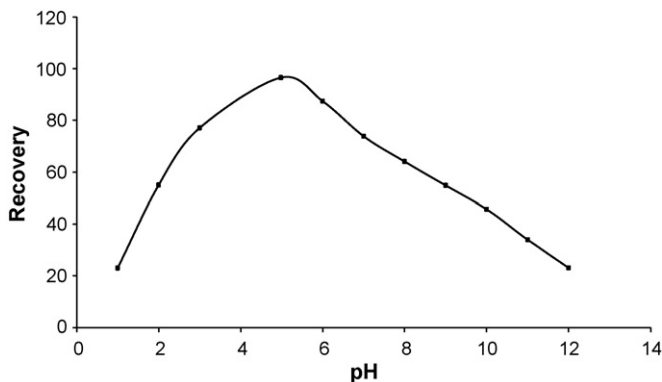


Fig. 2. Effect of pH on the complexation of Co(II) with piperazine dithiocarbamate.

0.03 M piperazine dithiocarbamate as color developing reagent for lower concentration level of Co(II) solution.

3.3. Efficiency of elution

The choice of selecting an eluent was a difficult problem. In addition to an eluent should not destroy the solid support in the column. Hence, for the determination of the preconcentrated Co(II) by spectrophotometry, the elution was performed with 0.5–3.0 M HNO₃ and is dependent on the concentration of HNO₃ as solution in Fig. 3 quantitatively Cobalt(II) was achieved for 6 ml of 5–10 M HNO₃. Hence, 6 ml of 2 M HNO₃ was chosen the optimum eluent for the Co (II) determination and recoveries were higher than 99%.

3.3.1. Effect of volume of a sample on elution

The effect of the sample volume on the extraction of Co(II) was studied by taking different volumes of water samples in the range of 100, 200, 300, 400, 500 and 600 ml. As the volume of sample increases, the recovery of metal ion increases gradually. In this case the recovery obtained was higher than 99% at 500 ml volume. However, the efficiency of recovery slightly decreases when the sample volume more than 600 ml. Hence, the 500 ml of water sample was chosen for the present study.

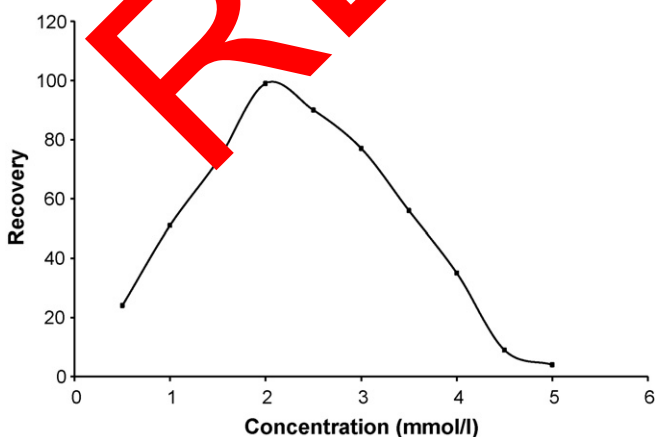


Fig. 3. Concentration of HNO₃ on elution of Co(II).

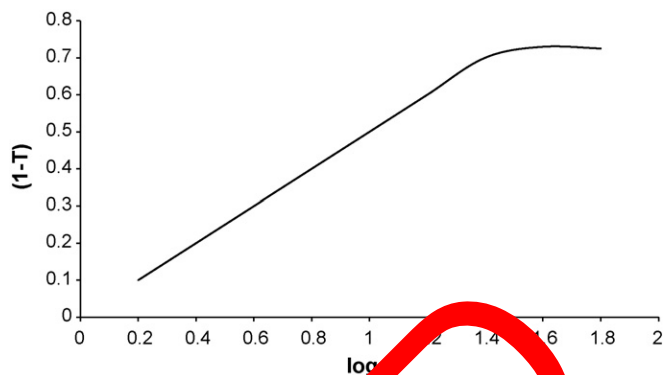


Fig. 4. Ringbom's plot of Co(II) with piperazine dithiocarbamate complex.

3.3.2. Effect of volume of an eluent on percentage of elution of Co(II)

The effect of volume of eluent on elution of Co(II) for various water and soil samples on 4-aminomethylpyridin–silica gel measured at 30–35 °C. It can be observed that the percentage of recovery increases with the increase in the volume of eluent to some extent. After increasing the volume of an eluent, the elution percentage slightly decreases. Thus 6.0 ml of 2 M HNO₃ was chosen for 100% recovery of Co(II) ion.

3.4. Ringbom plot for red colored derivative

Ringbom's plot is the established standard adopted to know the optimum range of concentration for a system that obeys Beer's law. The plot is drawn between log *C* of Co(II) and (1 – *T*) (where *T* is the transmittance). The plot has a sigmoid shape with a linear segment at intermediate absorbance values (0.4–0.8) and concentration values (0.4–1.6 μg ml⁻¹). The slope of Ringbom plot from Fig. 4 is 0.5840. Hence, the ratio between the relative error in concentration and photometric error is 0.80, for a concentration of 0.95, for 0.6% photometric error.

3.5. Calibration graph

The extraction of a typical calibration is $p = 5031c + 4.93r$ = 0.999 (where *p* is the peak height and *c* is the concentration). The calibration graph was obtained at the optimum working conditions; piperazine dithiocarbamate concentration 0.03 M, sample volume 500 ml; eluent concentration 2 M HNO₃ and volume of eluent 6.0 ml.

3.6. Effect of column performance

In order to examine the long term stability of the support, it was subjected to successive adsorption and desorption cycles (six runs in a day and the next six runs another day, and so on, total 30 runs) by 500 ml of metal solutions through the column. The stability and potential recycle ability of the column containing support were assessed by monitoring the change in the recoveries of the analyte. After 15 runs, the recoveries of the analyte slightly decreased to <95%.

Table 3
Effect of foreign species for the determination of cobalt(II) with spectrophotometry

Ions	Tolerance limit ($\mu\text{g ml}^{-1}$)
As(III), Mg(II), Mn(II), Zr(IV), Ba(II), Ti(I), As(V)	4500 ^a
Hg(II), Th(IV), Al(III), V(V), Be(II), U(VI)	3000 ^b
Cu(II), Ni(II), Fe(II), Cd(II), Fe(III), Pd(II)	5000 ^c
F ⁻ , SCN ⁻ , thiosulfate	4000
Chlorides, tartrate, thiourea and bromide	2000

^a Masking with 200 $\mu\text{g ml}^{-1}$ 1% citrate.

^b Masking with 20 $\mu\text{g ml}^{-1}$ 1% flourides.

^c Masking with 20 $\mu\text{g ml}^{-1}$ of 0.5% EDTA.

3.7. Effect of the flow rates of sample solution

The effect of the flow rate of the sample solution on the recovery of the metal ion was investigated under the optimum conditions (pH, eluent type, etc.). The sample solution was passed through the column with the flow rates adjusted in a range of 2.0–4.0 ml/min. At flow rates greater than 3 ml/min, there was a decrease in the recovery of metal ion. The reason for this decrease is probably insufficient contact of the metal ion and the adsorbent to reach equilibrium. Therefore, a flow rate of 2.0 ml/min was applied for determination cobalt(II) in through out the experiment. The flow rate of the elution solution was 2.0 ml/min.

3.8. Effect of foreign species

Several anions and cations were studied in detail. Table 3 summarizes the tolerance limits of interfering ions in the determination of 50 $\mu\text{g l}^{-1}$ Co(II). The tolerance limits was taken as the amount causing an error of $\pm 2\%$ at the peak height.

3.9. Applications and statistical comparison of the present method with literature method

The proposed preconcentration method for the determination of Co(II) has been employed for water and soil samples were presented in Table 1. The obtained results were compared with reported methods [18] in terms of student's 't'-test and Variance ratio 'f'-test. The analytical data summarised in Table 1 suggests that the average recovery of Co(II) from water and soil samples range from 97.50 to 99.66% which is more reliable and sensitive than the reported methods [18].

4. Conclusion

The proposed preconcentration spectrophotometric method is simple, highly sensitive and selective for the determination of Co(II) in water and soil samples. Synthesis of color forming reagent (sodium salt of piperazine dithiocarbamate) was economically feasible at ordinary laboratories and highly selective towards metal ion. The limit of detection of the proposed method is superior when compared to reported method [18]. The column employed in this method is highly stable and can be regenerated several times. The efficiency of column was 95% for 15 cycles. The proposed method is an additional method to the existing literature method.

References

- [1] I.H. Hall, C.B. Leskey, D. Kuster, R.W. Dorrham, E.M. Joud, M. Khan, D.X. Thanh, S. Jebbar-Singh, Benali-IBouch, G.M. Buet, *Pharmazie* 55 (2000) 937.
- [2] M.C. Michel, K. Bastow, C.N. Srinivasan, J.R. Vance, D.X. West, I.H. Hall, *Anti Cancer Res.* (1998) 4131.
- [3] Ph.Ng. Buu-Hoi, T. T. Le, D.Ng. Xuong, *Bull. Soc. Chem. Fr.* 1 (1955) 177.
- [4] J.M.C. Pavon, *Micro Chem. J.* 26 (1981) 155.
- [5] B.S. Garg, V. Jain, *Micro Chem. J.* 38 (1988) 144.
- [6] J.S. Casas, M. Garcia-Tasenda, J. Sardo, *Coord. Chem. Rev.* 209 (1981) 197.
- [7] S. Soylok, Akkaya, L. Eici, *Trace Elements Electrolytes* 20 (2003) 16.
- [8] K.S. Kim, I.M. Pak, *J. Korean Chem. Soc.* 43 (1999) 644.
- [9] M. Soylok, *Asian J. Chem.* 15 (2003) 1780.
- [10] S. Soylok, L. Eici, M. Dogan, *Anal. Lett.* 30 (1997) 623.
- [11] L. Subramanyam Sarma, J. Rajesh Kumar, C. Jaya Kumar, A. Varadha Reddy, *Anal. Lett.* 36 (3) (2003) 605.
- [12] F. Salinas, M. Jimenez-Ahemed, Iduram, *Micro Chem. J.* 33 (2) (1986) 194.
- [13] B.K. Reddy, C.J. Kumar, L.S. Reddy, A.V. Reddy, *Asian J. Chem.* 9 (3) (1997) 487.
- [14] A. Aamhieh, A.H. Laila, R. Salim, *Spectrosc. Lett.* 21 (5) (1988) 411.
- [15] F. Salinas, J.C.J. Sanchez, J.M.C. Gallago, M. Jose, *Ann. Chim Rome* 76 (7–8) (1986) 301.
- [16] B.K. Reddy, C.J. Kumar, L.S. Sarma, A.V. Reddy, *Asian J. Chem.* 9 (3) (1997) 487.
- [17] F. Salinas, M. Jimenez-Arrabal, I. Duram, *Micro Chem. J.* 33 (2) (1986) 194.
- [18] L.S. Sarma, J.R. Kumar, C.J. Kumar, A.V. Reddy, *Anal. Lett.* 36 (3) (2000) 605.
- [19] A.G.S. Prado, L.N.H. Arakaki, C. Airoidi, *Green Chem.* 4 (2002) 42.
- [20] A.G.S. Prado, C. Airoidi, *J. Colloid Interface Sci.* 236 (2001) 161.
- [21] P.K. Tewari, A.K. Singh, *Analyst* 124 (1999) 1847.