International Journal of ChemTech Research
CODEN(USA): IJCRGG ISSN : 0974-4290
Vol.2, No.1, pp 295-302, Jan-Mar 2010

Differential pulse polarographic determination of Cr(VI) in various environmental and soil samples using 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol

P.R. Prasad, S. Rajasekar Reddy, M. Chandra Mohan and N.Y. Sreedhar*

Department of Chemistry, Electroanalytical lab, S.V.University, Tirupati, A.P, India.

****E-mail : sreedhar_ny@rediffmail.com,***
Tel: +910877 2289303

ABSTRACT: A simple and sensitive differential pulse polarographic method has been developed for the determination of Cr(VI) using 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol as a complexing agent. The differential pulse polarogram exhibited a well defined peak observed with Ep at -0.85V versus Ag-Agcl electrode. The optimum conditions for the analysis of Cr(VI) include 0.3 mM of 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol, 0.4 mM of ammonium acetate buffer (pH-8.0), pulse amplitude of 50mV and scan rate of 12 mV/sec. The peak current is proportional to the concentration of chromium over the concentration range of 1–25 ppm with a limit of detection was found to be 0.06 µg mL^{-1} for Cr(VI) respectively. The proposed enrichment method was applied successfully for the determination of Cr(VI) ions in environmental and soil samples.
KEYWORDS: Differential pulse polarography (DPP), Soil and Chromium (VI).

INTRODUCTION

Chromium is widely distributed in the food supply, but most foods provide only small amounts (less than 2 micrograms [mcg] per serving). Meat and whole-grain products, as well as some fruits, vegetables, and spices are relatively good sources[1]. Normally, chromium complexes in different valent states coexist in the above products, both trivalent and hexavalent chromium in most cases, but the toxicity of these species differ significantly. Cr(III) is an essential material for humans and animals, and plays an important role as a glucose-tolerance factor (GTF) in insulin, lipin, and protein metabolism.[2,3] On the other hand, Cr(VI) is very toxic for humans and living organisms.[4,5] The most elevated concentrations of Cr(VI) found in the environment are the result of industrial pollution.[6]

Chromium (VI) is known to be a strong oxidizing agent, posing a high risk to humans and animals due to its car-cinogenic and mutagenic properties.[7] That is why the determination of chromium in environmental and biological samples is of great interest. Few serious adverse effects have been linked to high intakes of chromium, so the Institute of Medicine has not established a Tolerable Upper Intake Level (UL) for this mineral.[8,9] Chromium content can be determined in various techniques such as NAA, UV-visible, ICP-MS and AAS, with high sensitivity for the determination of chromium reported so far [10-13] need complicated and expensive equipment. Moreover, such techniques are usually not available in most laboratories. The proposed differential pulse polarographic technique is not time consume and less expensive technique.

Chromium is one of the essential trace elements in the human body, as it appears to play a role in the metabolism of glucose and some lipids (mainly cholesterol).[14-18] However, adverse effects may occur at higher concentrations.[17] Excessive amounts of Chromium, particularly in the more toxic Cr(VI) valence state, may be involved in the

pathogenesis of some diseases such as lung and gastrointestinal cancers.[19,20] Electrochemical techniques are considered to be the most powerful methods. In particular, differential pulse polarography (DPP) is of interest due to its high sensitivity and selectivity.

The objective of this investigation was to devise simple, sensitive and economically viable procedures that could be used to deter mination of Cr(VI) using 2,2'-{benzene-1,2-diylbis (nitrilomethylylidene]}diphenol analytical reagent in environmental and soil samples.

EXPERIMENTAL

Apparatus

Analysis were carried out with an Elico Model CL-362, three electrode system consisting of a dropping mercury electrode (DME) as the working electrode, an Ag/AgCl reference electrode and platinum counter electrode. It was outfitted with a Model EPSON LX-300^{+} X–Y recorder. A Perkin-Elmer ® Model 2380 Flame atomic absorption spectrometry (FAAS) with air-acetylene flame and hallow cathode lamp was used for the determination of metal ion. The instrumental parameters were set as recommend by the manufacturer. Elico Li-129 Model glass calomel combined-electrode was employed for measuring pH values.

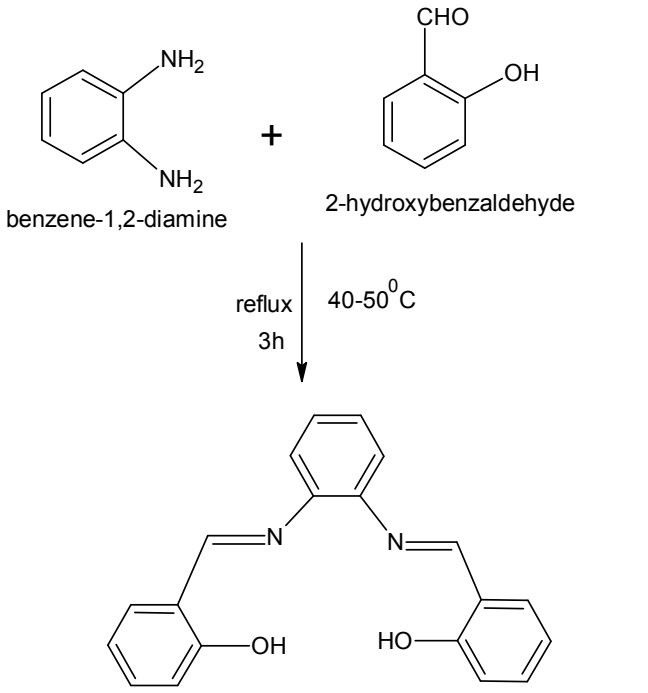
Reagents and solutions

All chemicals used were of analytical reagent grades. All the containers (glassware, polyethylene bottles, etc.) were cleaned, soaked overnight in 10% HNO_3, and were rinsed with distilled water prior to use. A potassium chromate (K_2CrO_4) solution was prepared by dissolving their (Merck Chemicals, Mumbai., India) analytical-grade samples in double-distilled water and standardized by established methods.[21] A 3mM solution of 2,2'-{benzene-1,2-diylbis (nitrilomethyl-ylidene]}diphenol was prepared by using appropriate amount of ethanol. Buffer solution of pH-8.0 was prepared by mixing 0.4 M ammonia and 0.4 M ammonium acetate solutions in the appropriate ratio.

Preparation of 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol

Benzene-1,2-diamine(0.1mol) and 1-hydroxy benzaldehyde (0.2 mol) were taken in to1: 2 ratio added ethanol were refluxed for 3 hours, and the contents were cooled to room temperature for separating the formed yellow solid product was filtered, washed with water, dried and recrystallized from hot aqueous methanol. Yield=92% and m.p=160-162^{0}C, Infrared spectrum (cm^{-1} KBr disk): v(O-H) 3290s, v(C=N)1640 v(C-O)1290.The preparation as it shown in Figure 1.

Figure 1: Scheme of the preparation of 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol.



General procedure

A 10 ml volume of a supporting electrolyte solution (0.4 mM of ammonium acetate buffer solution pH-8.0) and 0.5ml of 0.3mM; 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol was pipetted into the polarographic cell and 5 µg/ml solutions of Cr(VI) were added to the volumetric flask. The differential pulse polarogram were recorded after oxygen was removed by passing nitrogen gas for 10–15 min. The amalgamate Cr(VI) was differential by pulse polarography by scanning of potential of the electrode between −500 to −1600 mV with a scan rate of 12 mVs^{-1} and pulse amplitude of 50mV. The Cr(VI) peak was scanned at about -0.85V and its current used as a measure of analytical signal. All data were obtained at room temperature. The standard addition method was used for the determination of chromium content in the samples. Typical differential pulse polarogram of Cr(VI) are shown in Figure 2.

RESULTS AND DISCUSSION

Effect of buffer solution and pH

The influence of pH on the DPP peak of Cr(VI) was investigated for a solution containing 0.3mM of 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol and 5.0 µg/ml of Cr(VI) in 0.4 mM of ammonium acetate buffer, as preliminary tests showed that this buffer improved the DPP peak height and shape, the DP peak height for Cr(VI) was strongly affected by pH, with a maximum at pH±8.0 and a sharp decrease at higher and lower pH values. The peak current increased with increasing pH up to 8.0 and then decreased. This was due to the increasing complex formation of Cr(VI) with the ligand at the electrode surface with increasing pH to 8.0. The peak potential for the Cr(VI) complex is shifted to more negative potentials with increasing pH (Figure 3). Therefore, a ammonium acetate buffer, with a pH of 8.0 was selected as the optimum pH for the study.

Effect of ligand concentration

The concentration of 2,2'-{benzene-1,2-diylbis (nitrilomethylylidene]}diphenol has a great influence on the sensitivity of Cr(VI) determination. To 10 mL of 0.4 mM ammonium acetate buffer solution containing 5.0 µg/ml Cr(VI) at pH 8.0, varying concentrations of 2,2'-{benzene-1,2-diylbis (nitrilomethylylidene]}diphenol were added in the range 0–1.2 mM. No peak was obtained in the absence of 2,2'-{benzene-1,2-diylbis (nitrilomethyl-ylidene]}diphenol, but a distinct peak was observed after its addition. The peak current increased upto ligand concentration of 0.3 mM and then remained almost decrease in peak current at ligand concentration above 0.3mM (Shown in Figure 4.), has been attributed to competitive adsorption of 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol on DME. In all further studies, 0.3 mM of 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol was selected as optimum ligand concentration.

Effect of scan rate

The scan rate was also investigated from 2 to 25mV/sec. The peak current increased with increasing the scan rate, after that 12 mV/sec the peak current decreased. For that reason, 12mV/sec was selected for further studies. The results are shown in Figure 5.

Effect of foreign ions

The selectivity of the proposed method was investigated by the determination 4.0 µg/ml of Cr(VI) in the presence of various ions within a relative error of ±5%, the results are given in Table 1. At the nearly same concentration of Fe(III) or Ti(IV) as that of Cr(VI), the two metal ions seriously interfere with the determination of Cr(VI). Fe(III) was masked with 3ml of 5% NaF solution and Ti(IV) was masked with 3ml of a 1% $Na_2S_2O_3$ solution. It was found that most of foreign ions did not interfere for the determination of Cr(VI) in environmental and soil samples.

Procedure for the determination of Cr(VI) in environmental water samples

Different water samples (tap water, river water, boar water, polluted water and sea water) were collected from various places in around Tirupati and Nellore, A.P., and India. The samples (150 mL) were stored at 0-5 ^{0}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 double distilled water. 10 mL of this solution is further diluted to get working solution for determination of Cr(VI) as described in above procedure. The validity of the proposed method was tested by spiking known concentrations of Cr(VI) in water samples. The recovery of Cr(VI) was found to be quantitative with an average relative standard deviation of 2.3% for five replicate measurements. The results obtained were compared with AAS method and were in good agreement with each other (Table 2).

Determination of Cr(VI) in soil samples

A known amount of (1g) air dried homogenized soil samples, spiked with known amounts of Cr(VI) was taken and then fused with 5g anhydrous sodium carbonate in a nickel crucible and evaporated to dryness after the addition of 25 mL of water. The dried material was dissolved in water, filtered through whatman No. 40 filter paper in to 25 mL calibrated flask and neutralized with dilute ammonia. It was then diluted to a known volume with double deionised water. An aliquot of this sample solution described general procedure. The results obtained were compared with AAS method and were in good agreement with each other (Table 3).

Calibration plot

The calibration plot for the determination of Cr(VI) was prepared according to the general procedure under the optimum conditions developed above from its differential pulse polarogram with different concentrations. A typical polarogram for Cr(VI) is given in Figure 6. The linearity was maintained in the concentration range of 0.2–100 µg/ml chromium in final aqueous solution with a correlation factor of 0.9998(y=2.908x – 1.0262). The detection limit was 0.06 µg/ml with standard deviations varied from ±0.08 and ±0.82%, respectively. The proposed method good precision and accuracy for the reported methods.

CONCLUSIONS

The proposed procedure provides a simple, sensitive, precise and accurate technique for the determination of Cr(VI) in environmental and soil samples. Chromium concentration was determined by applying the calibration curve and standard addition methods. Recovery tests for the analyzed samples were satisfactory (about 94.0– 105.0%) with relative standard deviations of 0.46 – 4.79%. The proposed method possesses a low detection limit satisfactory for given application, high precision and simple instrumentation.

Table 1: Tolerance limits for the determination of 5µg/ml of Cr(VI) with 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol (relative error ±5%)

Ion added	Tolerate/mg
$(NH4)_2SO_4$, NH_4Br	500
Li^{+}, Al^{3+}, PO_4^{3-}, NO_2^{-},SO_4^{2-}, ClO_4^{-}	250
Ga(III), Al(III) ,	100
Mg(II), In(III), Rh(III), Ru(III), Fe(III)[a],Ce(IV)	50
U(VI), V(V), Te(IV), Zr(IV)	10
Sn(II), Sb(III),Ag(I)	5
Mn(II), Ti(IV)[b], Mo(VI), Bi(III) , As(III),Cr(III)	4
Cu(II), Zn(II), Cd(II), Pd(II)	3
Ni(II), Co(II), Cr(III)	1.0

[a]Masked with 3ml of 5% NaF solution., [b]Masked with 1ml of 5% (w/v) $Na_2S_2O_3$ solution.

Table 2: Determination of Cr(VI) in real water samples

Environmental samples	Proposed method			AAS Method	
	Cr(VI) added (µg/ml)	Found (µg/ml)	Recovery[a] (%)	Found (µg/ml)	Recovery[a] (%)
Industrial waste water	-	0.72	--	0.76	--
(Renigunta industrial area,	1.0	1.73	101.0±0.54	1.76	100.0±0.12
Tirupati)	5.0	5.74	100.4±0.42	5.80	100.8±0.10
River water	-	0.54	--	0.62	--
(Penna river)	1.0	1.52	98.00±0.46	1.61	99.00±0.18
	5.0	5.53	99.80±0.32	5.62	100.0±0.12
Tap water	-	0.38	--	0.41	--
(S.V.U Chemistry Lab)	1.0	1.32	94.00±0.74	1.35	94.00±0.82
	5.0	5.44	99.20±0.60	5.33	98.40±0.62
Sea water	-	0.53	--	0.52	--
(Bay of Bengal)	1.0	1.51	98.00±0.46	1.51	99.00±0.44
Upper level	5.0	5.53	100.0±0.12	5.51	99.80±0.32
Well water	-	0.42	--	0.46	--
	1.0	1.49	97.00±0.58	1.44	98.00±0.46
	5.0	5.40	99.60±0.63	5.43	99.40±0.33
Polluted water	-	0.68	--	0.72	--
	1.0	1.67	99.00±0.44	1.69	97.00±0.67
	5.0	5.67	99.80±0.51	5.68	99.20±0.39

[a]Mean±standard deviation of five determinations

Table 3: Determination of Cr(VI) in soil samples

Soil samples	Proposed method			AAS method	
	Added (µg/ml)	Found (µg/ml)	Recovery[a] (%)	Found (µg/ml)	Recovery[a] (%)
Renigunta Industrial Area	2.0	2.01	100.50±0.14	2.10	105.00±0.08
	4.0	4.03	100.75±0.11	4.06	101.50±0.12
S.V.University Campus Area	2.0	1.94	97.00±0.68	1.92	96.00±0.76
	4.0	3.99	99.50±0.46	3.94	98.50±0.51
Agricultural Area (Pudi)	2.0	1.99	99.50±0.46	1.96	98.00±0.54
	4.0	4.00	100.00±0.10	3.98	99.50±0.32

[a]Mean± standard deviation of five determinations

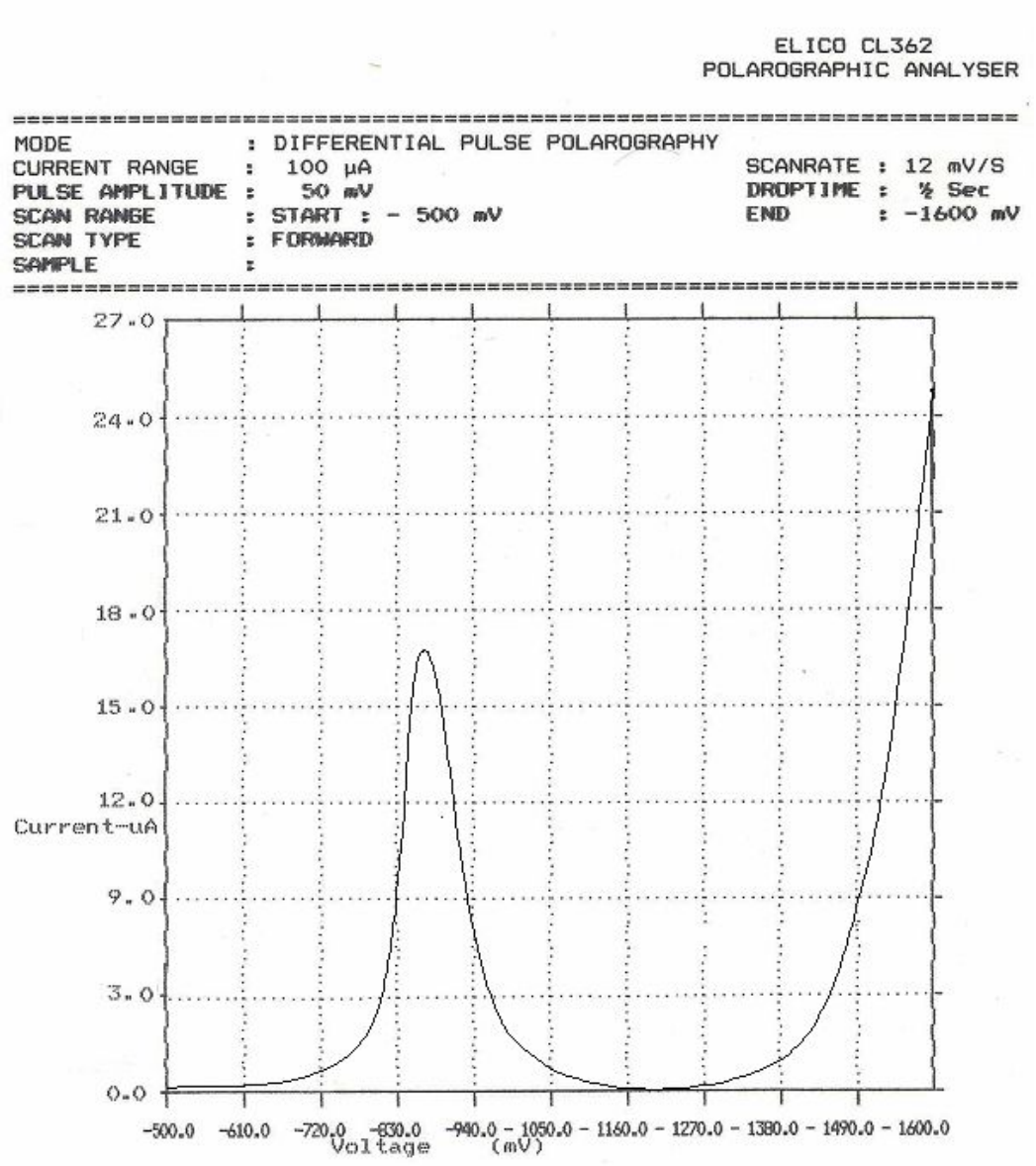


Figure 2: The differential pulse polarogram of Cr(VI). Conditions: 0.3mM of 2,2'-{benzene-1,2-diylbis(nitrilomethylylidene]}diphenol; 4.0 µg/ml of Cr(VI); 0.4mM of ammonium acetate buffer at pH 8.0. Instrumental settings: scan rate=12mV/sec, drop time = 0.5 sec, pulse amplitude = 50mV.

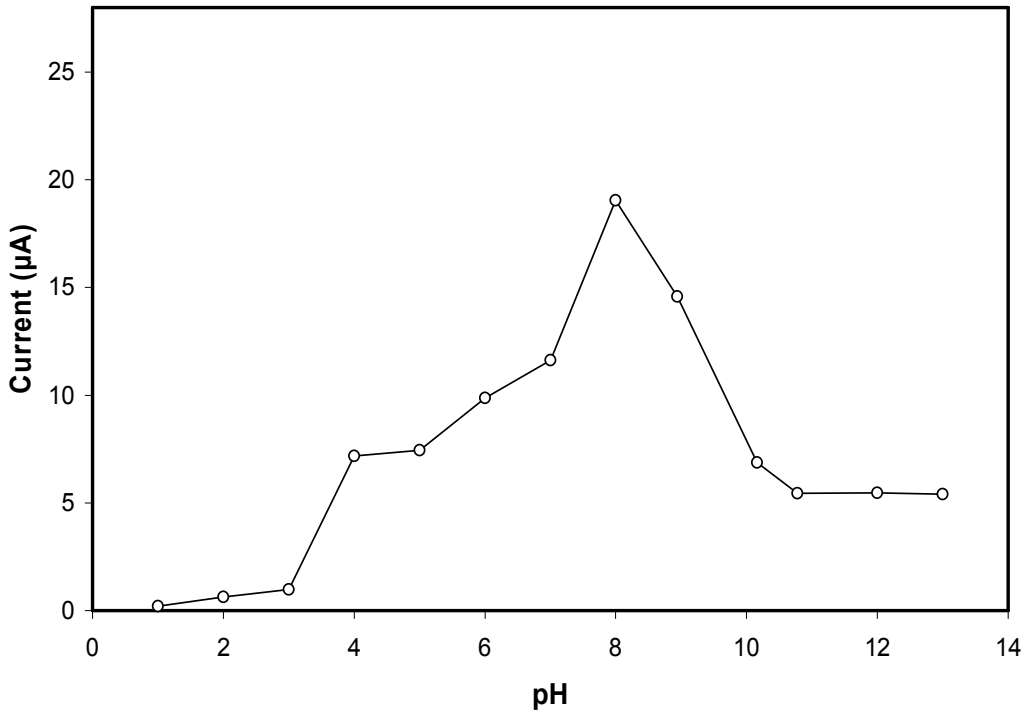


Figure 3: Effect of pH on the determination of Cr(VI); Conditions and standard instrumental parameters were used.

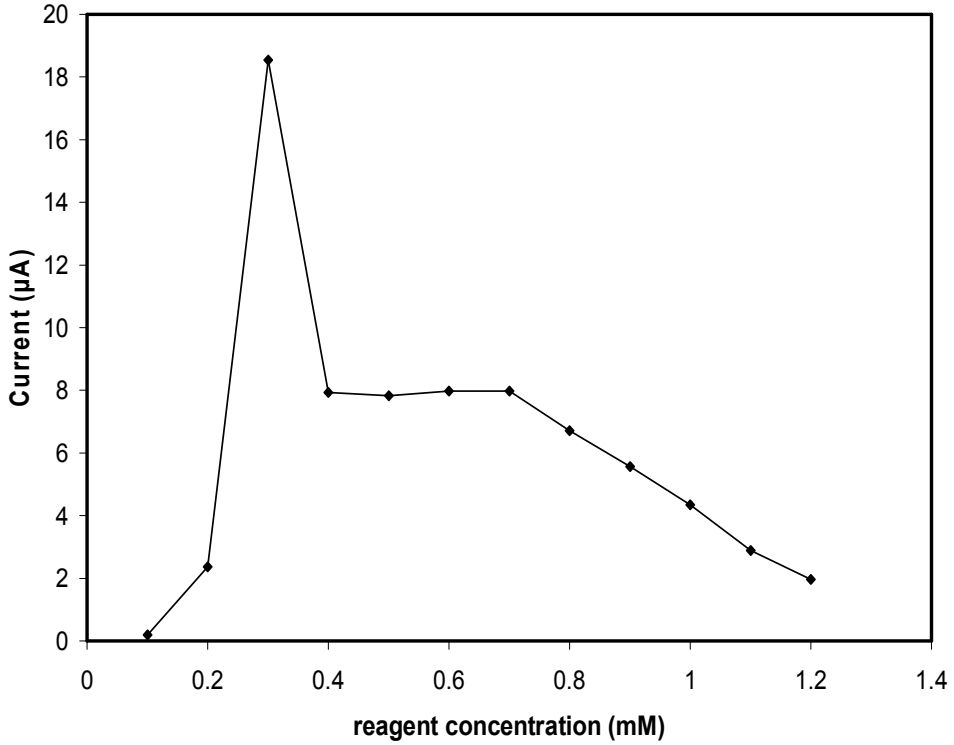


Figure 4: Effect of reagent concentration; Conditions and standard instrumental parameters were used.

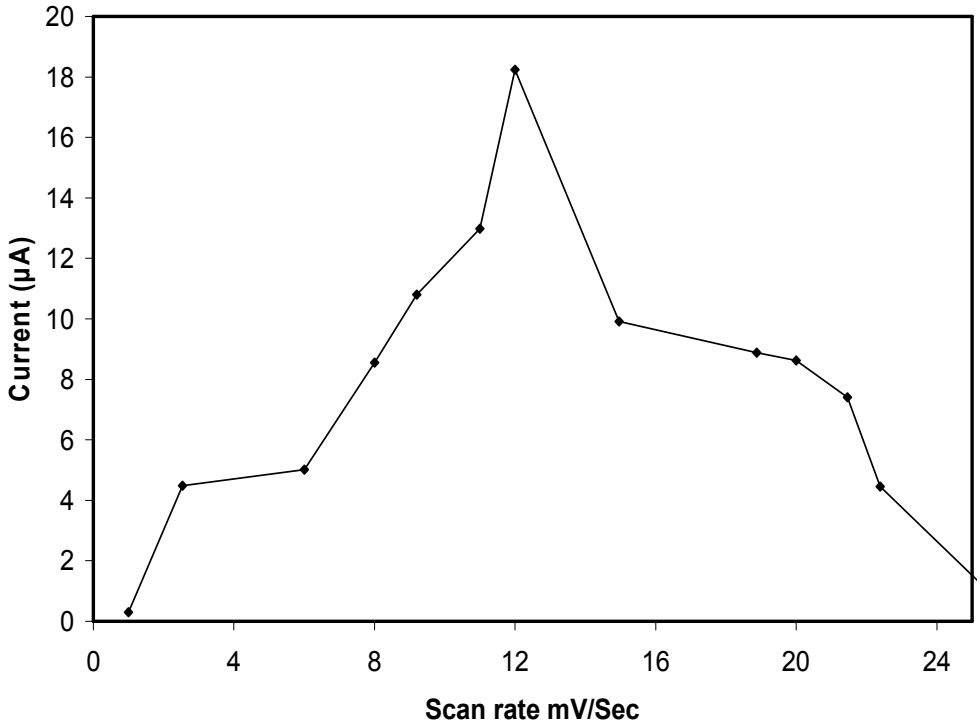


Figure 5: The effect of scan rate. Conditions and standard instrumental parameters were used.

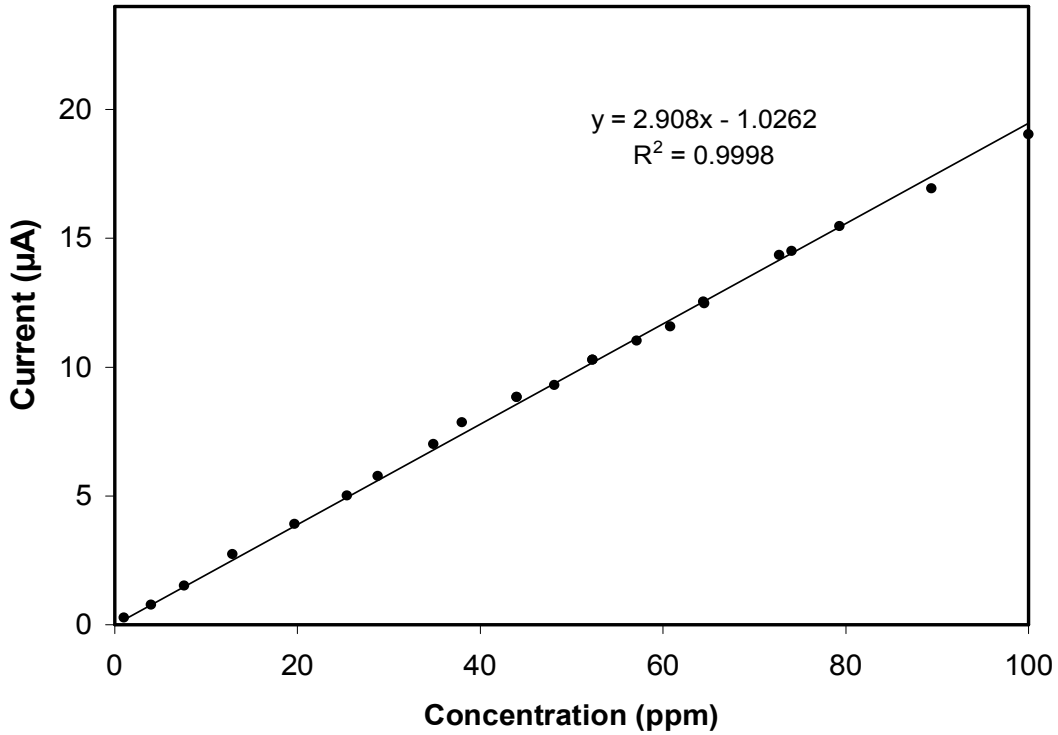


Figure 6: Calibration curve for Cr(VI); Conditions and standard instrumental parameters were used.

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