



Research Article

ISSN: 2321-3132

**International Journal of Chemistry and
Pharmaceutical Sciences**

www.pharmaresearchlibrary.com/ijcps


Determination of Chromium (VI) in Industrial Effluents and Agricultural materials using Catalytic hydrogen currents at DME
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Received: 7 February 2014, Accepted: 9 March 2014, Published Online: 27 April 2014

Abstract

A simple and sensitive catalytic polarographic method for the determination of Cr (VI) is developed based on the catalytic currents of Cr(VI)-amine complexes in the presence of ammonium chloride-phosphate buffer as supporting electrolyte at PH 8.2 for nBA and 8.4 for 2-MBI. The Cr (VI)-amine complexes produces a catalytic hydrogen waves at -1.36 V Vs SCE for nBA and -1.38V Vs SCE for 2-MBI in the presence of ammonium chloride and phosphate electrolyte. The proposed method is sensitive with the lowest detection limit up to 0.1 ppm. The proposed method is free from interference of many meta ions except MO(VI). The developed method is applied for the determination of Cr(VI) in industrial effluents and agricultural products. The method is first of its kind in the Polarographic Analysis.

Keywords: Polarographic catalytic hydrogen waves. Chromium (VI), nButyl amine, 2-Mercaptobenzimidazole, ammonium chloride, phosphate electrolyte, industrial effluents, Agricultural materials.

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Manuscript ID: IJCPS2017



PAPER-QR CODE

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1. Introduction

Chromium is one of the essential trace metal nutrients for animals and man. The tolerance limits of chromium contents according to US Public Health Service is 0.05 mg/l for drinking water and 2.1 mg/lL for industrial effluents discharged into sewages. Chromium metal and Cr(III) are relatively nontoxic [1-3] whereas water soluble chromium (VI) is extremely irritating and toxic to human body tissue [4-5]. In tannery industries severe environmental contamination [6-7], the corrosive active hexavalent chromium induces chronic ulcers in workers and cancer to the nose and lungs [8] among the workers is also reported. The developed method is simple, sensitive, selective and rapid procedure for the determination of chromium in water and agricultural samples using n-Butyl amine and 2-Mercaptobenzimidazole as reagents by simple d.c polarographic technique.

Chromium gives catalytic currents at mercury electrode in the presence of organic reagents such as amines and arsines. The Chromium (VI) and (III) content in water samples have been studied by polarographic catalytic waves

using the system, ethylene diamine-sodium nitrate at pH 8 [9]. Chromium in mineral samples is estimated by Chou and Pao [10] using N-nitrosophenyl-hydroxyl amine-ammonium chloride-ammonium hydroxide medium. The adsorption of the reduced form of the complex of chromium with As (III) in ammonium or borate buffer was found to give a catalytic hydrogen wave in d.c.polarography and was used for the determination of chromium at concentrations as low as 10^{-8} M [11]. The chromium content of clays and ores was determined by the catalytic wave of chromium in an electrolyte solution of sodium nitrate-O-phenanthroline-ammonium chloride-ammonium hydroxide at pH 9.3 [12]. Lin et al. [13] reported the study of traces of chromium in sea water using ethylene diamine- NaNO_2 -EDTA system. The chromium (VI) content in water samples is estimated by Su et al. [14] using ammonium acetate – cupferron at pH 6-6.5. The mechanism of the catalytic wave of chromium in 1, 10-phenanthroline-nitrite-ammonium chloride-ammonia medium at pH 9.4 was explained by Han et al. [15]. Trace amounts of Cr (VI) in steel and water was determined by using a catalytic polarographic method of O-phen- NaNO_2 -CTAB [16].

Catalytic hydrogen waves of organic thio compounds in the presence of Cr (VI) and Cr (II) at DME have been reported from these laboratories [17-21]. Catalytic hydrogen currents of metal ions with amines have also been suggested [22] but so far there is no reference available on this. An attempt has been made with n-Butyl amine and 2-Mercaptobenzimidazole and found to give catalytic hydrogen currents and the potential range is -1.36 and -1.38 V Vs SCE with Cr (VI) in the presence of NH_4Cl and Phosphate electrolyte at pH 8.2 and 8.4 respectively [Fig:1&2] and the corresponding Differential pulse polarogram curves are shown in [3&4]. The quantitative experimental conditions have therefore been developed and the details are shown in Table:1.

2. Materials and Methods

Reagents:

The chemicals used are of analytical reagent grade (E.Merk, India). The solutions are prepared in distilled water and diluted to required strength. 5% NH_4OH and 1% HCl are used for pH adjustments. Gelatin and TritonX-100 are prepared and diluted as per requirements. The stock solution of 2-mercaptobenzimidazole is prepared by taking 0.1% w/v in mixed solvents of 60:40 methanol and double distilled water and diluted to required strengths. Phosphate buffer is prepared by mixing potassium dihydrogen phosphate and sodium hydroxide. Dry ash [23] method is used for agricultural products.

Apparatus:

The equipment used is D.C.polarograph model CL-358 coupled with model LR-101 P strip chart recorder and Differential Pulse Polarography (DPP) model CL-362 coupled with optional printer supplied by Elico Private Limited (Hyderabad, India) is used as supporting technique. The pH meter; model LI-120 (Elico Private Limited) with glass electrode at pH range 0-13. The temperature is maintained at $25 \pm 0.2^\circ\text{C}$ and the flow of mercury at 2.5 S per drop.

Applications of the catalytic method to real samples

The developed method is applied to the analysis of trace quantities of chromium in drinking water samples, industrial effluents, tannery waste water and agricultural materials.

Drinking water samples

One litre of the samples collected from Kalyani Dam, Bore wells and Kapilatheertham water falls (Tirupati, Chittoor (Dt)) are preconcentrated to 100 ml.

Agricultural material

10 g of *Oryza sativa* (Unpolished rice) collected from Tirupati Town, Chittoor District are digested by dry ash method and brought into solution. (10g Unpolished rice/ 25 ml double distilled water). Aliquots of the above solution are taken in a beaker and the quantitative experimental conditions are maintained as already mentioned in the previous pages. The precipitates of metal amines given by interfering metal ions are filtered off and the filtrate is polarographed after deaeration. The results are presented in table 2, 3 &4. The standard addition method is used for the analysis of chromium content in all the samples. A known amount of standard Cr (VI) is added to the sample, which is then polarographed for the total amount of metal ion present. The difference between the results obtained with and without the added Cr (VI) gives the amount of the metal ion present in the sample. These results are further supported by the values obtained using differential pulse polarography method.

Table 1. Quantitative experimental conditions for Cr (VI) determination through Chromium (VI) - Amine catalytic hydrogen waves.

Conditions	nBA
pH	8.2
NH_4Cl , M	0.3
Amine, mM	0.5
Cr (VI), ppm	0.1-8.0

Conditions	2-MBI
pH	8.4
Phosphate supporting electrolyte, M	0.4
Amine, mM	0.6
Cr (VI), ppm	0.1-8.0

Table 2. Determination of chromium (VI) in water samples of Tirupati town

S.No	Cr (VI) added, ppm	nBA		2-MBI		DPP method		
		Cr(VI),ppm found	% Recovery	Cr(VI),ppm found	% Recovery	Cr(VI),ppm found	% Recovery	
I	1	0.8	0.80	100.00	0.80	100.00	0.80	100.00
	2	1.0	0.98	98.00	1.00	100.00	0.98	98.00
	3	1.2	1.20	100.00	1.18	98.33	1.20	100.00
	4	1.4	1.38	98.57	1.38	98.59	1.40	100.00
	5	1.6	1.60	100.00	1.60	100.00	1.59	99.33
		Average 99.31		Average 99.38		Average 99.46		
II	1	0.8	0.80	100.00	0.80	100.00	0.80	100.00
	2	1.0	0.98	98.00	0.98	98.00	0.98	98.00
	3	1.2	1.19	99.16	1.19	99.16	1.20	100.00
	4	1.4	1.38	98.57	1.40	100.00	1.38	98.57
	5	1.6	1.60	100.00	1.58	98.66	1.59	99.33
		Average 99.15		Average 99.16		Average 99.18		

I. Kalyani Dam II. Bore Well

	Supporting electrolytes	Amine, mM	pH
A. nBA	0.3M NH ₄ Cl	0.5	8.2
B. 2-MBI	0.4 M phosphate electrolyte	0.6	8.4

The results in table 2 show that the drinking water drawn from bore wells and supplied to Tirupati town by municipality from Kalyani Dam is free from chromium content. Though the water from the water falls of Kapilatheertham of Tirupati town (Table 3) is found to have traces of chromium but is within the tolerance limits. The chromium levels analysed in agricultural samples (Table 4) are in agreement with the reported values. The results obtained using two ligands are in good agreement with differential pulse polarography.

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

Sample* / Amine		Cr (VI) , ppm		Cr (VI) in the sample, ppm	
		Added	Total found**	Catalytic method	DPP method
I	a	0.5	0.86	7.50	7.66
	b	0.5	0.87	7.30	

Kapilatheertham water falls–Tirupati Town

	Supporting electrolytes	Amine, mM	pH
A. nBA	0.3M NH ₄ Cl	0.5	8.2
B. 2-MBI	0.4 M phosphate electrolyte	0.6	8.4

*5 ml of concentrated sample is used.

**Average of five individual determinations.

Table 4. Determination of Chromium (VI) in Agricultural Material

Sample* / Amine		Cr (VI) , ppm		Cr (VI) in the sample, ppm/g	
		Added	Total found**	Catalytic method	DPP method
I	a	1.0	1.056	0.14	0.145
	b	1.0	1.053	0.13	

Oryza Sativa (Unpolished rice)

	Supporting electrolytes	Amine, mM	pH
A. nBA	0.3M NH ₄ Cl	0.5	8.2
B. 2-MBI	0.4 M phosphate electrolyte	0.6	8.4

*1.0 (l) ml of the sample is used

**Average of five individual determinations

The method reported here may therefore, be successfully applied for the determination of traces of chromium in water samples and agricultural materials without interference from other transition metal ions excepting molybdenum.

3. Results and Discussion

Effect of pH

The effect of pH on the catalytic current is examined by recording the current-voltage curves at various pH values (5.0 to 10.0) keeping Cr (VI) ion at 3.0 ppm and amine concentration 0.5 mM for nBA in 0.3 M NH₄Cl and 0.6 mM for 2-MBI in 0.4 M Phosphate medium adjusting the pH with ammonium hydroxide. The shape of the wave remained unchanged, but the peak height increased gradually up to pH values of 8.2 (nBA) and 8.4 (2-MBI) and decreased beyond these pH values. These pH values at maximum current are therefore selected as optimum PHS for all other studies. The peak potential shifted to more negative values with increasing pH.

Effect of supporting electrolyte concentration

The wave height of the catalytic hydrogen wave is not only dependent on pH but also depend on sodium acetate and phosphate electrolyte concentration. These concentrations are varied from 0.1-0.8 M maintaining the metal ion concentration at 3.0 ppm, amine concentration at 0.5 mM (nBA) and 0.6 mM (2-MBI) and adjusting the pH of the solution with ammonium hydroxide to pH 8.2 for nBA and 8.4 for 2-MBI. The wave height increased up to 0.3 M NH₄Cl in the case of nBA and 0.4 M phosphate medium in the case of 2-MBI and decreased beyond these concentrations for both the amines. Hence, 0.3 M ammonium chloride and 0.4 M phosphate electrolyte concentration is fixed as the analytical concentration of the supporting electrolytes for all studies. The peak potential of the catalytic wave shifted considerably towards negative potentials with increase in supporting electrolyte concentrations.

Effect of reagent concentration

The influence of concentration of nBA and 2-MBI on the polarographic catalytic waves of the chromium (VI)-amine complexes is investigated in detail. 3.0 ppm of Cr (VI) in 0.3M ammonium chloride at pH 8.2 for nBA and 0.4 M phosphate supporting electrolyte of pH 8.4 for 2-MBI is used varying the concentration of amines from 0.1 to 1.0 mM. The wave heights obtained at 0.5 mM for nBA and 0.6 mM for 2-MBI are maximum and with further increase in amine concentration the wave height is not proportional to concentration and remain almost constant at much higher concentration of ligand. The peak potential is shifted towards more negative potentials on increasing the amine concentration.

The variation of the wave height as a function of amine concentration is not linear but tends to a limiting value at higher concentration of amine which is a typical of catalytic waves. The maximum shape of the waves is indicative of adsorption. The non-linear portion has the shape of a curve resembling a Langmuir adsorption isotherm, and the plot of $\{[amine]/i_p\}$ Vs $\{amine\}$ is a straight line (Fig.5). The relationship shows the involvement of adsorption process in the electrode mechanism [24].

Supportive evidence of catalytic hydrogen waves

The catalytic behavior of chromium-amine systems are further supported by the effect of mercury column height on the peak current and temperature coefficient values. The catalytic current as well as i_c/\sqrt{h} decreased with the increase of the mercury column indicating that the current is catalytic in nature. The diminishing of wave height increased with increase in temperature and temperature coefficient values decreased gradually from 15 to 30^o C. The surfactant like gelatin suppresses the catalytic wave sharply up to 0.01% and by about 2% beyond and up to maximum permissible concentrations. The suppression with Triton X-100 is small when compared to gelatin. The peak potential shifted towards less negative potentials in both cases. It could be shows that the wave is of catalytic in nature and adsorption involved in these waves.

Effect of chromium (VI) on peak current

Maintaining all the optimum conditions previously selected, the concentration of chromium is varied and the sensitivity is tested. The peak current increased proportionally with the concentration of Cr (VI) in the range of 0.1 to 8.0 ppm for both nBA and 2-MBI. The linear relationship obtained between the catalytic current and metal ion concentration within a limited range [Fig.6] as is expected with catalytic currents indicates that the method can be used successfully for the determination of microgram quantities of Cr (VI) in agricultural samples using amines as complexing agents is possible.

Interference Studies

Most of the transition metal ions do not interfere with catalytic wave of Cr (VI) under the conditions developed and Ni (II) gets precipitated which can be removed by filtration. The only metal ion, Mo (VI) interferes seriously by increasing the wave height of Cr (VI). Anions such as carbonate and EDTA interfere by completely suppressing the chromium catalytic wave whereas nitrite and nitrate interfere as they also give catalytic current with chromium (VI).

Effect of indifferent cations

The effect of indifferent cations is tested at constant pH, supporting electrolytes, amine and Cr (VI) concentrations. The alkali chlorides used are lithium, sodium, potassium and divalent calcium. The presence of an indifferent electrolyte diminishes the wave height. The figure proves that with the same ionic strength the divalent cation, Ca^{2+} has a greater suppressing effect on the catalytic maximum than the monovalent cations. The wave height decreases continuously when the chloride concentration is increased and the peak potential shifted towards less negative potentials in all cases. The suppression of wave height in the presence of indifferent electrolyte shows that the chromium-amine complexes have adsorption properties on the mercury electrode.

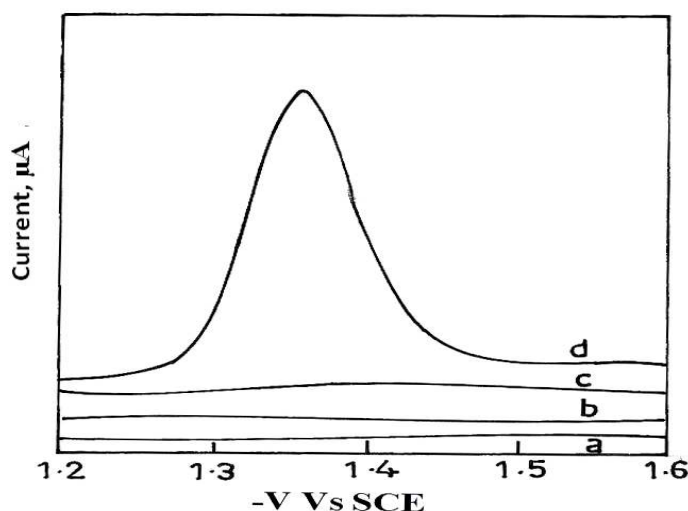


Figure 1

Polarographic curves of Cr (VI)

- a) 0.3 M NH_4Cl , pH 8.2 b) a + 0.5 mM nBA
 c) a + 3.0 ppm Cr (VI) d) b + 3.0 ppm Cr (VI)

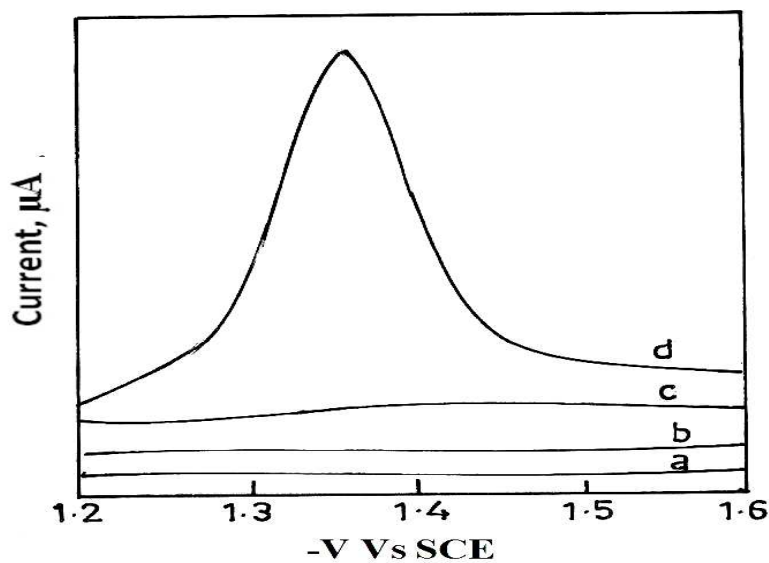


Figure 2

Polarographic curves of Cr (VI)

- a) 0.4 M Phosphate electrolyte, pH 8.4 b) a + 0.6 mM 2-MBI
 c) a + 3.0 ppm Cr (VI) d) b + 3.0 ppm Cr (VI)

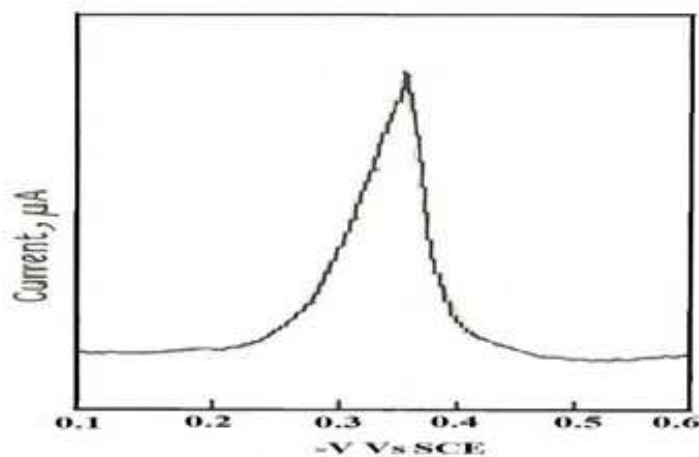


Figure 3

Typical Differential Pulse Polarogram

NH₄Cl, M : 0.3 nBA, mM: 0.5
 Cr (VI), ppm : 0.1 pH : 8.2

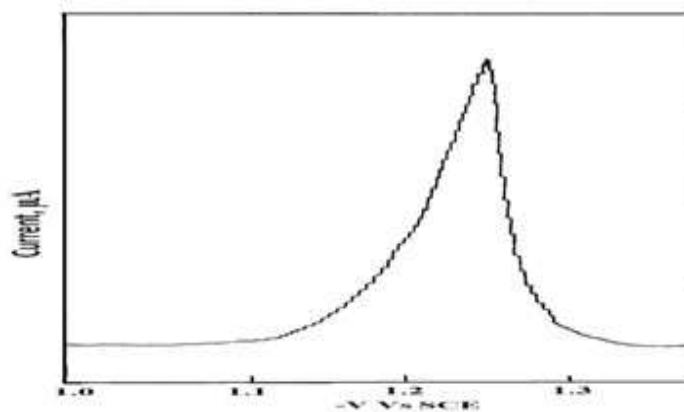


Figure 4

Typical Differential Pulse Polarogram

Phosphate Electrolyte, M: 0.4 2-MBI, mM : 0.6
 Cr (VI), ppm : 0.1, pH : 8.4

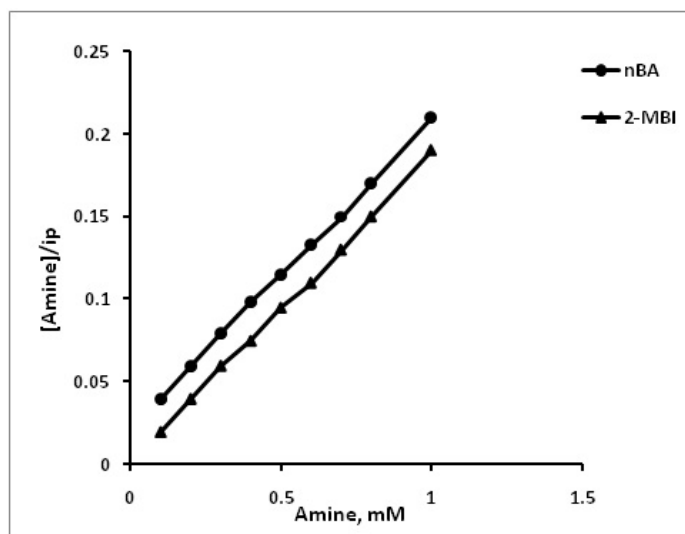


Figure 5. Langmuir adsorption isotherm plot

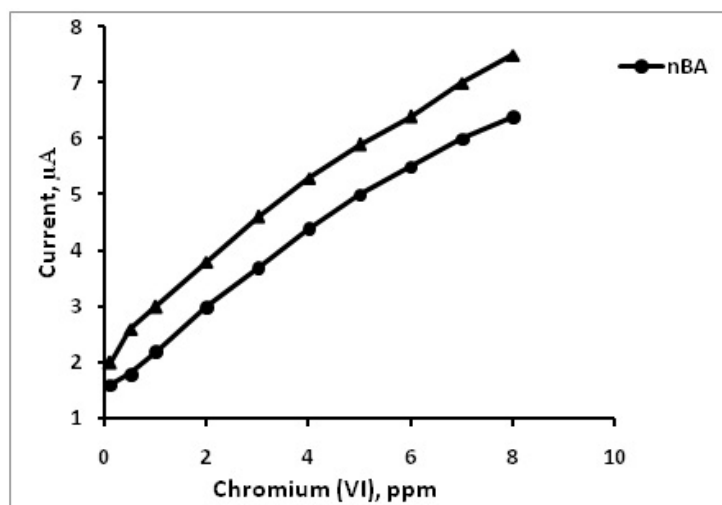


Figure 6. Effect of Cr (VI) on peak current

4. Conclusion

The result of this investigation shows that chromium (VI) gives catalytic hydrogen waves in the presence of amine at DME due to chromium-amine complex formation. The linear dependence of the current on the pH and ligand concentration up to certain values shows that the waves are catalytic in nature due to chromium complexes with the amines and adsorption phenomenon is involved. The effect of the height of the mercury reservoir and temperature coefficient values is also indicative of catalytic nature of the waves. Further support of adsorption is indicated by the Langmuir adsorption isotherm curve. Yet another support for the idea about participation of adsorption of the catalytic metal-amine complexes in catalytic hydrogen waves is seen with the decrease of the height of the peak current with indifferent electrolytes. From the results obtained for Cr (VI)-amine complex study it may be concluded that the procedure developed for the determination of Cr (VI) using the catalytic hydrogen waves at DME in the presence of nBA and 2-MBI is selective without much interferences due to other metal ions except Mo (VI). The method is also sensitive with the lowest detection limit of 0.1 ppm, rapid and specific compared to diffusion current of Cr (VI) in d.c. polarography.

5. Acknowledgement

One of the authors, T. Niranjan is thankful to UGC for granting BSR fellowship.

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