



ISSN: 2321-4902

Volume 1 Issue 4

Online Available at [www.chemijournal.com](http://www.chemijournal.com)

## International Journal of Chemical Studies

### Voltammetric Studies On Method Development For Determination Of Chromate In Natural Waters

P.Sharma <sup>1\*</sup>, R. Bais <sup>1</sup>, K.Songara <sup>1</sup>, Mohd. Raees <sup>1</sup>

1. Electroanalytical Research Laboratory, Department of Chemistry, J. N. V. University, Jodhpur- 342005, India.  
[E-mail: [sharma\\_pk00@yahoo.com](mailto:sharma_pk00@yahoo.com)]

---

A detailed electrochemical study of chromate ion was carried out in presence of potassium nitrate. It has resulted in development of a voltammetric method for determination of submicrogram level chromate using differential pulse polarography. Linearity of the calibration curve was achieved upto 14 ppm with a limit of determination of  $0.05 \mu\text{g mL}^{-1}$ . The possible interference of coexisting metal ions was examined where copper, lead and zinc did not interfere. The method has been successfully applied for the analysis of chromate in natural waters. The validity of the results has further been established by comparing the results of DPP with UV-Vis spectrophotometric method.

---

**Keyword:** Chromate, Voltammetry, DPP, Real Samples.

#### 1. Introduction

The study of elements of variable oxidation states has become increasingly important because a change in oxidation state is usually associated with the change in chemical and other properties. Arsenic, chromium, mercury and selenium are rather more concerned species due to their toxicity and adverse effects<sup>[1]</sup>. In the present work attention was focused on chromate ion which is highly toxic (chromium limit in water,  $0.05 \text{ mg/L}$ ) and a possible carcinogen. Chromate dust causes lung cancer. Chromium in the form of Cr(III) is comparatively harmless since it is readily hydrolysed to an insoluble hydroxide<sup>[2]</sup>. The dissolved hexavalent chromium is determinable in the form of chromate ion in natural waters as recommended in US-EPA methods<sup>[3]</sup>.

Voltammetric methods such as pulse polarography and stripping voltammetry have proved more suitable methods in such determinations<sup>[4]</sup>. These methods can identify and

determine different ionic forms of an element due to the selectivity of redox potential, as in case of chromium which exists in three oxidation states of +2, +4, and +6<sup>[5]</sup>. Voltammetric data revealed that the electroreduction of chromate ion at mercury electrode in different media showed well defined polarographic waves<sup>[6]</sup>. A pulse polarographic determination method of chromium(VI) in sodium fluoride medium is reported by Cox *et al*<sup>[7]</sup>. Svancara<sup>[8]</sup> *et al* have studied the determination of chromium as chromate at a carbon paste electrode modified with surfactants. Mu *et al*<sup>[9]</sup> have investigated transparent chromate (III) passive films on electroless Ni-P coating by electrochemical and XPS methods. A crown ether based electrochemical sensor for detection of chromate ion is given by Singh and coworkers<sup>[10]</sup>. In the same manner Jain *et al*<sup>[11]</sup> have reported a PVC based sensor for chromate ions. A cytochrome based biosensor for determination of chromate by

using amperometry is presented by Michel *et al*<sup>[12]</sup>.

We have also reported voltammetric determination of chromium in industrial wastes<sup>[13]</sup>. However, due to the close peak potential of Cu(II) and Cr(VI) in ammonium tartrate buffer medium, method could not be used for analysis of chromium in natural waters which usually contains copper at very low concentration. Herein, detailed investigations of  $\text{CrO}_4^{2-}$  ion in different supporting electrolytes have enabled its determination in real samples of tap water, pond water and sea water using differential pulse polarography (DPP). The Voltammetric determination of arsenic<sup>[14]</sup>, mercury<sup>[15]</sup> and tellurium<sup>[16]</sup> was reported earlier.

## 2. Methods and Materials

### 2.1 Sample collection and sample preparation

Samples of tap water and pond water were collected from University Campus and Jodhpur city, respectively. Sea water sample was also taken from Arabian Sea, Mumbai. Collected samples were filtered in order to separate any suspended particulate matter and acidified with HCl to pH  $\sim$  2 for storage purpose. A measured volume of the sample was then spiked with known concentration of chromate for polarographic analysis.

### 2.2 Instrumentation

A microprocessor based pulse polarographic analyzer (Model CL-362) with a drop-timer of Elico Limited, Hyderabad, India, was employed for voltammetric measurements. The current voltage curves were recorded by an Epson printer (Epson-LX-300+II). The instrumental settings for DPP were as follows: pulse amplitude, 25 mV; drop time, 0.5 sec; scan rate, 12 mV/sec and charging current compensation, 20%.

### 2.3 Voltammetric Set-up

A three electrode assembly was used for carrying out the polarographic experiments. The working electrode was a dropping mercury electrode (DME) while the potentials were measured against a saturated calomel electrode (SCE). A platinum wire acted as counter electrode

throughout. The inlet and outlet tubes were provided for nitrogen purging.

Test solutions were deaerated by bubbling purified nitrogen for 20 mins, prior to the voltammetric measurements. Traces of oxygen present in nitrogen were removed by passing the gas through a vanadous chloride scrubbing solution kept in contact with amalgamated zinc<sup>[17]</sup>.

### 2.4 UV-Vis spectrophotometer

A UV-Vis spectrophotometer (Model SL-160) of Elico was also used for sample analysis. It covers wavelength range from 190–1100 nm. The tungsten-halogen deuterium lamp and wide range photomultiplier were used as the light source and detector, respectively. The spectral band width of resolution was 0.5 nm.

The analysis was based on the reaction of chromate with diphenylcarbazide in test solution to produce red violet color. The absorbance of the species was measured at 540 nm<sup>[18]</sup>.

### 2.5 pH meter

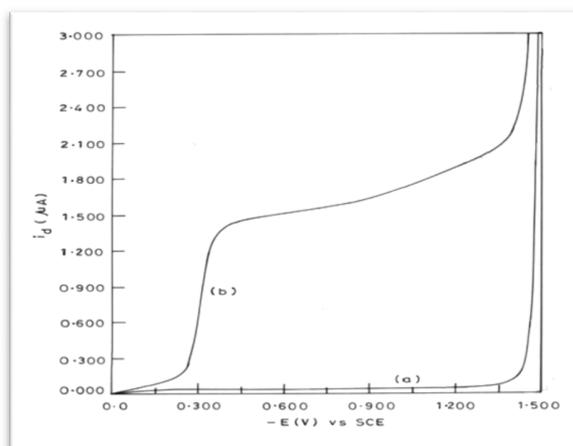
The pH measurement was made by using a digital pH meter (Model 5000) of Lab India.

### 2.6 Chemicals and standard solution

A Quality Assurance System (Model- A643) of Millipore, France was used to obtain milli-Q-water. All standard solutions were prepared in milli-Q-water. Stock solution of chromate was prepared from potassium chromate. Chemicals used were of analytical grade. All experiments were carried out at  $\pm$ 298 K.

## 3. Results and Discussion

Preliminary investigations on electroreduction of chromate at mercury electrode revealed that in presence of potassium nitrate in ammonia-ammonium chloride medium (pH 9.5),  $\text{CrO}_4^{2-}$  gave a well-defined polarographic wave at a potential of -0.28 V as shown in Fig. 1. The wave height increased linearly with the concentration of chromate in range  $(0.30-9.0) \times 10^{-4}$  M. The plot of  $E$  vs  $\log i/(i_d-i)$  indicated that electrode reaction was not fully reversible; however, the wave appeared to be diffusion controlled.

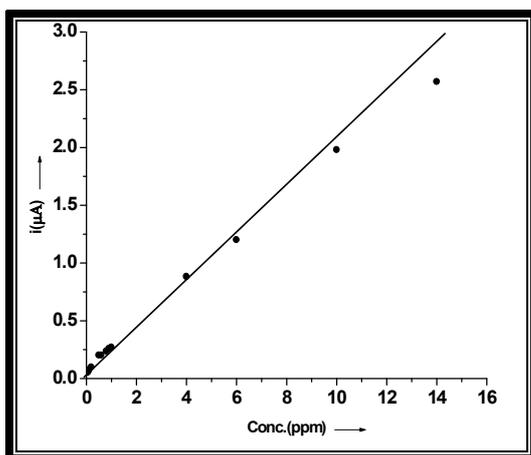


**Fig 1:** DC polarogram of chromate in presence of  $1 \times 10^{-3}$  M  $\text{KNO}_3$  in 0.1 M ammonia- 1 M ammonium chloride buffer (pH 9.5)

(a) Blank solution of supporting electrolyte  
(b)  $0.9 \times 10^{-4}$  M  $\text{CrO}_4^{2-}$  in supporting electrolyte

### 3.1 Optimal Conditions for Chromate Determination

$\text{CrO}_4^{2-}$  also showed sharp differential pulse peak (DP) at -0.28 V. A linearity of peak current was observed in the 0.05-14.0 ppm range of chromate concentration. The characteristics of the calibration curve (Fig. 2) are given in Table 1. The limit of determination of  $0.05 \mu\text{g mL}^{-1}$  was achieved under the experimental conditions.



**Fig 2:** Calibration curve of chromate (concentration vs peak current)

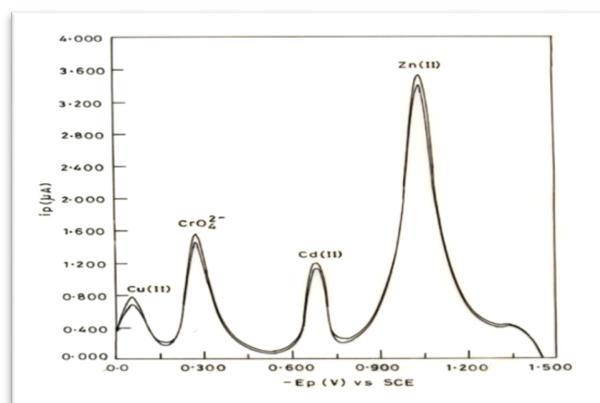
### 3.2 Interferences

The coexisting major ions such as copper, lead and zinc were tested for interference during the determination of chromate. The DP peak of

$\text{Cu(II)}$  in presence of potassium nitrate in ammonia-ammonium chloride medium was noticed at -0.60 V, which is well-separated from that of  $\text{CrO}_4^{2-}$  at -0.28 V. Similarly, peak potential of  $\text{Pb(II)}$  and  $\text{Zn(II)}$  were found to be -0.75 V and -1.03 V, respectively, illustrating no interference. It has been clarified in Fig. 3.

**Table 1:** Calibration characteristics of chromate

	Parameter	Characteristic
1.	Slope	0.18
2.	Intercept	0.08
3.	Coefficient of correlation (r)	0.99
4.	Standard deviation ( $\pm$ )	0.81



**Fig 3:** DP polarogram of chromate in presence of copper, lead and zinc  $\text{Cu(II)}$ , 7.0 ppm;  $\text{Pb(II)}$ , 16 ppm;  $\text{CrO}_4^{2-}$ , 9.0 ppm and  $\text{Zn(II)}$ , 5.0 ppm. Polarographic medium:  $1 \times 10^{-3}$  M  $\text{NO}_3$  in ammonia-ammonium chloride (pH 9.5) Modulation amplitude, 50 mV; pulse duration, 57 ms; drop time, 0.5 s; scan rate, 12 mV/s.

## 4. Analytical Applications

The devised optimum conditions in terms of polarographic medium, calibration linearity and limit of determination were applied to determine chromate in spiked samples of tap water, pond water and sea water.

### 4.1 Voltammetric Measurements

A measured volume of the prepared water sample was taken in polarographic cell with  $1 \times 10^{-3}$  M  $\text{KNO}_3$  in ammonia-ammonium chloride medium (pH 9.5). DP polarograms were recorded from 0.0 to -1.2 V. Peak currents were measured at -0.28 V after making the blank correction. The concentrations were determined by standard

addition method<sup>[19]</sup>. The results of determination of chromate in different water samples are summarized in Table 2.

**Table 2:** DPP determination of chromate in different water samples

Sample	CrO <sub>4</sub> <sup>2-</sup> (µg mL <sup>-1</sup> )		
	DPP ± SD	RSD (%)	Relative error (%)
Tap water <sup>a</sup> (2.0)	1.98 ± 0.02	0.80	1.0
Pond water <sup>b</sup> (1.0)	0.98 ± 0.03	3.00	2.0
Sea water <sup>c</sup> (1.4)	1.41 ± 0.01	1.06	0.7

N= number of determination; 3  
 Values shown in parentheses is chromate concentration (µg mL<sup>-1</sup>) spiked in sample  
 a= water sample collected from University Campus  
 b= water sample collected from pond in Jodhpur city  
 c= water sample collected from Arabian Sea, Mumbai

#### 4.2 Validation

The validity of the measurements has been demonstrated by comparing the results of DPP

with UV-Vis spectrophotometric method. The data so obtained are compared in Table 3.

**Table 3:** Comparison of results of determination of chromate by DPP and UV-Vis spectrophotometry

Water sample	DPP (µg mL <sup>-1</sup> )	UV-VIS (µg mL <sup>-1</sup> )
	1.	1.98
2.	0.98	0.99
3.	1.41	1.40
Sample 1, 2, 3 of tap, pond and sea water, respectively		

#### 5. Conclusion

The present DPP method for the determination of chromate is specific, rapid and convenient due to the simple sample preparation and no interference from major ions. Further, voltammetric measurements made by present method are in good agreement with other techniques including differential pulse polarography in terms of detection limit ( $1.5 \times 10^{-8}$  M) reported by Cox *et al* <sup>[7]</sup>.

#### 6. Acknowledgement

Authors acknowledge the UGC, New Delhi for the financial support to K. Songara under the scheme of Rajeev Gandhi National Fellowship.

#### 7. Reference

- Harrison RM. Pollution: Causes, Effects and Control. Edn 2, The Royal Society of Chemistry, Cambridge 1990; 28-31.
- Bailey RA, Clarke HM, Ferris JP, Krause S, Strong RL. Chemistry of the Environment. Edn 1, Academic Press, New York 1978, 389.
- Blowes D. Tracking hexavalent chromium in groundwater. Science 2002; 295 (5562):2024-25.
- Kissinger PT, Heineman WR. Laboratory Techniques in Electroanalytical Chemistry. Edn 2, Marcel Dekker, New York, 1996, 152-155.
- Bard AJ, Parsons R, Jordan J. Standard Potentials in Aqueous Solutions, Marcel Dekker, New York, 1985, 475-483.
- Lingane JJ, Kolthoff IM. Polarographic study of the reduction of chromate ion at the dropping mercury electrode. J Am Chem Soc 1940; 62(4):852-858.
- Cox JA, West JL, Kulesza PJ. Determination of chromium (VI) by differential pulse polarography with a sodium fluoride supporting electrolyte. Analyst 1984; 109:927 - 930.
- Svancara I, Foret P, Vytras K. A study on the determination of chromium as chromate at a carbon paste electrode modified with surfactants. Talanta 2004; 64(4):844-852.
- Mu S, Li N, Li D, Zou Z. Investigation of a transparent chromate (III) passive film on electroless Ni-P coating by XPS and electrochemical methods. Electrochim Acta 2009; 54(26):6718-6724.
- Singh LP, Bhatnagar JM, Tanaka S, Tsue H, Mori M. Selective anion recognition: Charged diaza crown ethers based electrochemical sensors for chromate ions. Anal Chim Acta 2005; 546(2):199-205.
- Jain AK, Gupta VK, Singh LP, Srivastava P, Raisonni JR. Anion recognition through novel C-thiophenecalix

- [4] resorcinarene: PVC based sensor for chromate ions. *Talanta* 2005; 65(3):716-721.
12. Michel C, Brunet FB, Minh CT, Bruschi M, Ignatiadis I. Amperometric cytochrome C<sub>3</sub>- based biosensor for chromate determination. *Biosensors and Bioelectronics* 2003; 19(4):345-352.
  13. Sharma P, Kapoor RC. Polarographic determination of chromium in aqueous matrices at micro levels. *Int J Environ Anal Chem* 1987; 30:51-57.
  14. Sharma P. Sequential trace determination of arsenic (III) and arsenic (V) by differential pulse polarography *Anal Sci* 1995; 11(2):261 -262.
  15. Sharma P, Vyas S, Sangneria S. Microdetermination of mercury in industrial waste waters by stripping voltammetry. *Int J Environ Anal Chem* 1997; 68:391-395.
  16. Sharma P, Agarwal A. Voltammetric ultra trace determination of tellurium. *Anal Lett* 2006; 39:1421-1427.
  17. Kapoor RC, Agarwal BS. *Principles of Polarography*. Wiley Eastern Ltd., New Delhi 1991, 17-18.
  18. Greenberg AE, Connors JJ, Jenkins D. (eds.) *Standard Methods for the Examination of Water and Waste Water*. Edn 15, American Public Health Association, New York 1981, 187-190.
  19. Vogel AI. *Textbook of Quantitative Inorganic Analysis*. Edn 4, Longman, London, 1982, 645.