

## ANODIC STRIPPING VOLTAMMETRY (ASV) OF CHROMIUM (VI) IN METAL FINISHING EFFLUENTS

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### ABSTRACT

Hexavalent chromium is a highly toxic pollutant in industrial electroplating and metal finishing effluents. Even though several colorimetric procedures are available for the estimation of hexavalent chromium, electrochemical methods for its estimation are scanty. In the present work conditions were standardised for estimating  $\text{Cr}^{6+}$  by ASV. The method is applicable over different pH ranges and linear calibration plots are obtained in the range  $5 \times 10^{-6}$  to  $10^{-4} \text{M}$  of  $\text{Cr}^{6+}$

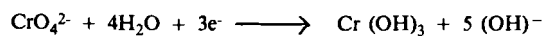
**Key Words:** Anodic stripping voltammetry, Cr (VI) estimation, metal finishing effluents

### INTRODUCTION

Hexavalent chromium in metal finishing effluents is very conveniently estimated by colorimetric procedure using diphenylamine indicator [1]. The first electrochemical stripping method [2] for the estimation of hexavalent chromium consisted of the reduction of hexavalent chromium to give chromium trihydroxide film and its subsequent anodic stripping. A procedure for trivalent chromium has also been reported recently [3]. Hexavalent chromium is highly toxic and its monitoring assumes importance in environmental samples and industrial effluents. During the course of our work on the development of electroanalytical procedures for monitoring environmental pollution caused by heavy metals, we have been assessing various electroanalytical methods for chromium. In this context the ASV procedure reported earlier has been found to be lacking in many important details like sensitivity and improvements that could be obtained with enhanced sweep rates. These aspects together with the use of other forms of carbon electrodes as working electrodes have been examined in the present work and reported.

### PRINCIPLE OF THE METHOD AND EXPERIMENTAL

Description of the determination of elements of varying valencies with their preconcentration in the form of their hydroxides on graphite has been described earlier [4]. In a subsequent work [2] the progress of the reaction



has been studied in buffered and unbuffered solutions. The chromium trihydroxide formation takes place between -0.6 to -1.0 V and the electrodisolution potential of the film occurs over the potential range +0.6 to +1.0 V depending on the pH of the medium.

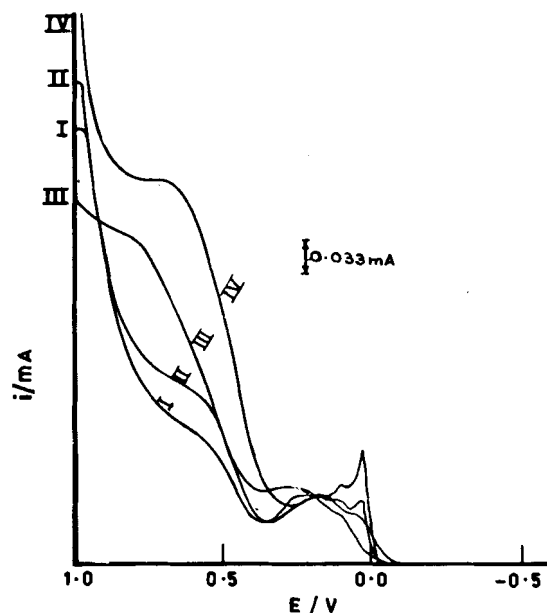
In the actual ASV analysis, a closed cell having suitable ground joints on the cover to introduce the working electrode, reference electrode and deaeration inlets was employed. The auxiliary platinum electrode was fused to the side wall of the cell to encircle the working electrode. Suitable Luggin capillary were provided adjacent to the working electrode surface. Standard solution of potassium chromate and background solution were prepared from A.R. grade chemicals. Glassy carbon embedded in teflon and fixed to glass body was used as working electrode. Electrical contact to the electrode was given through mercury.

Preelectrolysis of the standard solutions were carried out for the stipulated

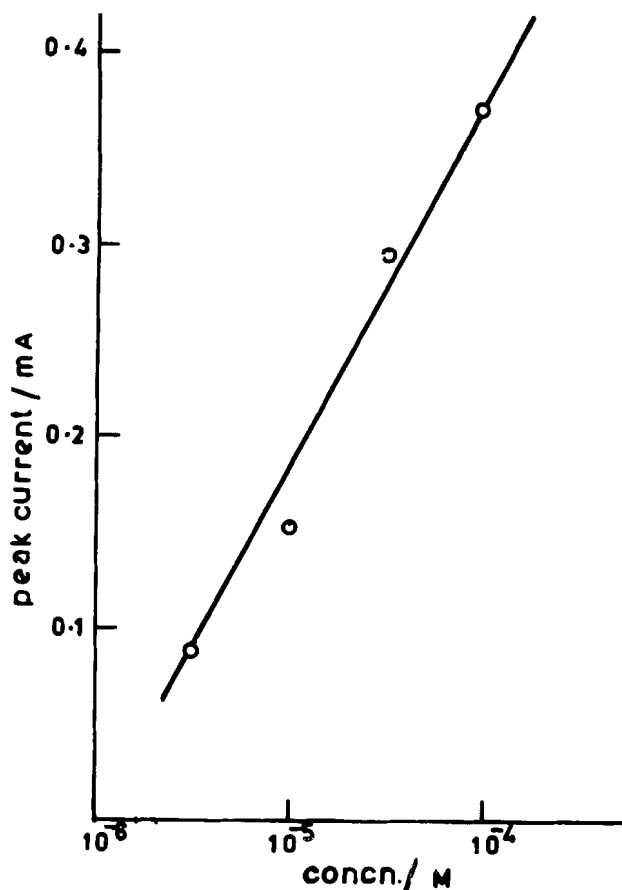
time under hydrodynamic conditions. A magnetic stirrer was employed to stir the solution. During stripping process, the stirring was stopped. The entire ASV experiment was carried out with Wenking Potentiostat Generator (POS73) and the voltammograms were recorded with RW 201 Rikadenki X-Y Recorder.

### RESULTS AND DISCUSSION

The anodic stripping voltammograms for  $\text{Cr}(\text{OH})_3$  film deposited from chromate solution in the concentration range  $10^{-4} \text{M}$  to  $5 \times 10^{-6} \text{M}$  are represented in Fig. 1



1. Anodic stripping voltammograms for  $\text{Cr}(\text{OH})_3$  film deposited from different concentrations of  $\text{K}_2\text{CrO}_4$  in  $0.4 \text{M NH}_4\text{Cl} + 0.1 \text{M NH}_4\text{OH}$   
 I -  $5 \times 10^{-6} \text{M Cr}^{6+}$     II -  $10^{-5} \text{M Cr}^{6+}$   
 III -  $5 \times 10^{-4} \text{M Cr}^{6+}$     IV -  $10^{-4} \text{M Cr}^{6+}$



2. Linear calibration plot of anodic stripping current vs concentration of Cr<sup>6+</sup> in the range  $5 \times 10^{-6}$  M to  $10^{-4}$  M.

It is clear from the voltammograms that stripping signal occurs over a potential range from +0.3V to +0.8V. Potential region over which the stripping signal occurs is larger at higher concentrations (waves III & IV) than at lower concentrations (I and II). It is also noticed from the stripping voltammograms that only a plateau somewhat pronounced at higher concentrations (III & IV) is obtained even at a scan rate as high as 200 mV/sec at all the concentrations. All the above observations may be attributed to the highly irreversible nature of the Cr<sup>3+</sup>/Cr<sup>6+</sup> system. The heights of the stripping currents, however, were found to increase in proportion to the concentration of chromate in solution and the linear calibration graph correlating stripping current and concentration is represented in Fig.2 (linear over  $5 \times 10^{-6}$  M to  $10^{-4}$  M Cr<sup>6+</sup>). In earlier reports the scan rate employed were very low corresponding to only 10 mV/sec necessitating the measurement of very low currents by resorting to special techniques such as derivative methods. On the other hand, by employing faster scan rates it has been possible in the present work to get large currents for stripping which enabled reaching even lower concentration range for estimation of Cr. For example, it was possible to get stripping current for Cr<sup>6+</sup> concentration below  $10^{-6}$  M and upto  $10^{-8}$  M. However, the entire lower concentration range has to be studied under separate experimental conditions and this will be taken up in future. Application of the method reported here for the estimation of hexavalent chromium in natural and simulated samples, will also be attempted.

#### REFERENCES

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