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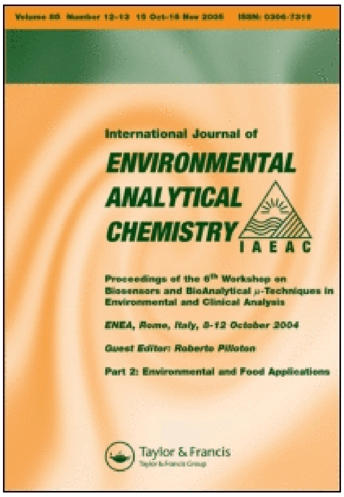

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Sharma, P. and Kapoor, R. C.(1987) 'Polarographic Determination of Chromium in Aqueous Matrices at Micro Levels', International Journal of Environmental Analytical Chemistry, 30: 1, 51 — 57
To link to this Article: DOI: 10.1080/03067318708075455
URL: http://dx.doi.org/10.1080/03067318708075455

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Intern. J. Environ. Anal. Chem., 1987, Vol. 30, pp. 51–57
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Polarographic Determination of Chromium in Aqueous Matrices at Micro Levels

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(*Received August 14, 1986; in final form November 22, 1986*)

The polarographic reduction of chromium(VI) was studied by dc polarography, differential pulse polarography and cyclic voltammetry. Conditions have been standardised in which ppm concentration of chromium could be estimated in aqueous matrices by the DPP technique.

KEY WORDS: Chromium trace analysis, cyclic voltammetry, DPP, industrial waste waters samples.

INTRODUCTION

Due to rapid growth of industrialisation, natural water sources like ground water are being subjected to pollution load from the flow of industrial effluents comprising of organic and inorganic constituents. Significant inorganic constituents are toxic metals like cadmium, lead, chromium, mercury etc. which act as poisons and are non-degradable. Thus they adversely affect the ecosystem.[1] It is therefore appropriate to monitor the concentration of toxic metals in industrial waste water. The determination of cadmium and lead has already been reported by authors elsewhere.[2] In the present communication, a method has been proposed for the determination of chromium.

Lingane and Kolthoff[3] studied the reduction of chromate ion at dropping mercury electrode in different media. A differential pulse polarographic method has been reported by Jindal and Bhatnagar[4] for simultaneous determination of zinc and chromium in ammonia buffer. The authors have found ammonium tartrate buffer as the suitable supporting electrolyte for chromium determination. Detailed observations have been made at different pH to enable the determination of chromium along with cadmium, lead and zinc simultaneously employing DPP. Further polarographic and cyclic volammetric studies were made to study the nature of electrode reactions. Industrial waste water samples of Jodhpur were analysed for their chromium contents.

EXPERIMENTAL

Instrumentation

A PAR polarographic analyzer (174-A) along with a drop timer (Model 174/70) and X-Y recorder, was used to record dc and dp polarograms. Natural drop time was employed for dc polarography while one second drop time was chosen for DPP. Cyclic voltammograms were recorded with a BAS-100 electrochemical analyzer in which a platinum disc electrode was used as the working electrode and Ag/AgCl as the reference electrode. In all other experiments, a saturated calomel electrode (SCE) was used as the reference electrode. Further a platinum wire was used as the auxillary electrode.

All chemicals used were of reagent grade purity. The solutions were deaerated by bubbling pure nitrogen for 20 minutes prior to experiments.

All experiments were made in an air-conditioned room at a temperature of $27 \pm 1°C$.

RESULTS AND DISCUSSION

Chromate ion, in presence of ammonium tartrate buffer (pH 9.5) displayed a single reduction wave due to the reduction of Cr(VI) to Cr(III). Its half wave potential was observed at -0.81 V vs. SCE. A typical dc polarogram is shown in Figure 1.

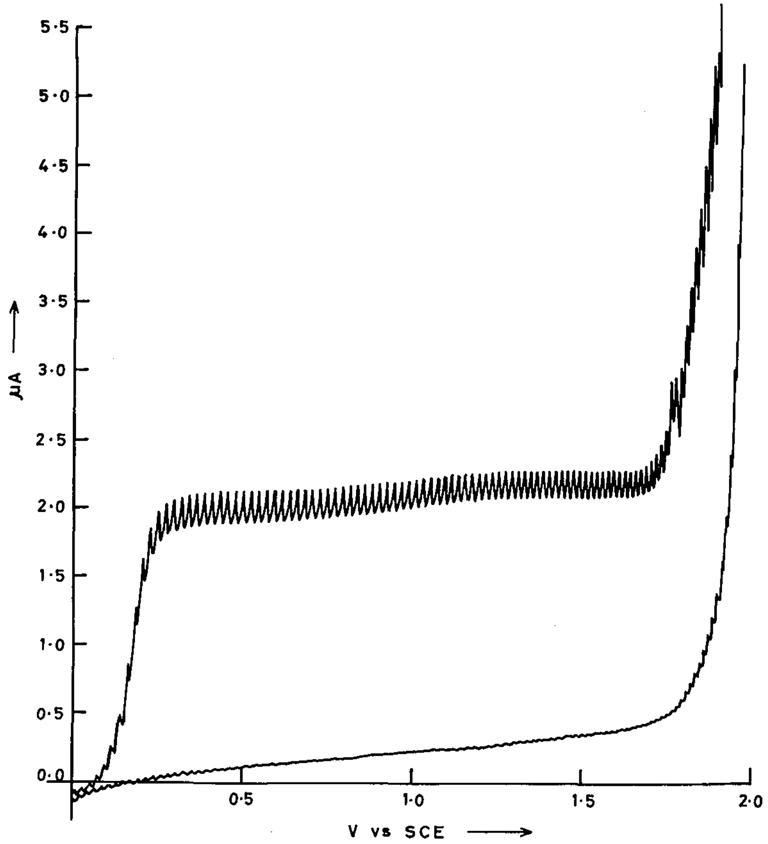

Figure 1 DC polarogram of Cr(VI) in ammonium tartrate buffer Cr(VI) = 0.8×10^{-4} M, pH = 9.5.

Influence of pH

The half wave potential of the wave was found to be dependent on the pH of the solution. At pH 8.1 there appeared a very high background current which resulted in an ill-defined reduction wave of chromate ion. It did not appear to be a suitable medium for analytical purposes since no dp peak was observed. At higher pH (10.5 or more), the polarogram of chromate ion consisted of three waves at −0.23, −1.15 and 1.35 V vs. SCE. The limiting current also did not appear to be linear to the chromate ion concentration.

At pH 9.5 a single reduction wave was observed, which appeared to be diffusion controlled. This wave was chosen for other studies and was made a basis for the determination of chromate ion employing DPP. The reversibility of the process was checked by making a cyclic voltammetric study, wherein only one cathodic peak appeared. A typical cyclic voltammogram of Cr(VI) is shown in Figure 2.

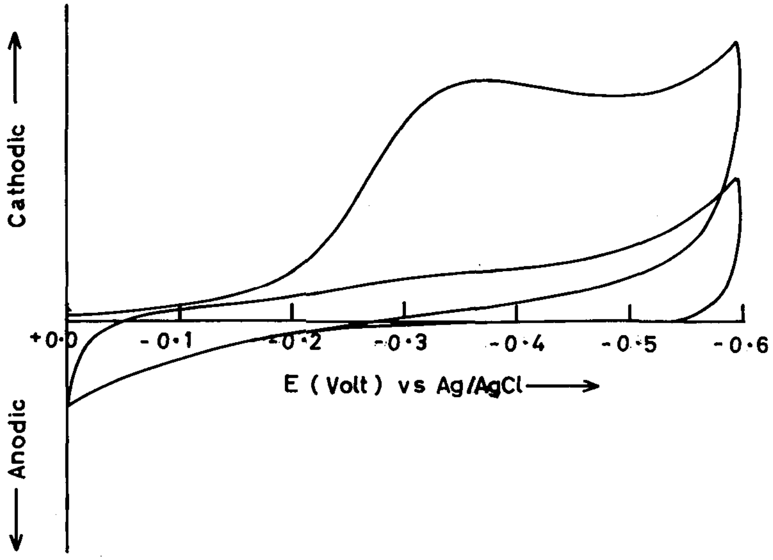

Figure 2 Cyclic voltammogram of Cr(VI) in ammonium tartrate buffer Cr(IV) = 1.6×10^{-4} M, pH = 9.4. Scan rate ≈ 80 mv/sec.

Voltammograms were also recorded at different scan rates. Both the peak potential and peak current changed with scan rate. The observations confirmed the irreversible nature of the system.

The chromate ion in ammonium tartrate buffer medium (pH 9.5) gave a sharp dp peak at a potential of -0.20 V vs. SCE. The peak potential appeared dependent on the pH of the solution. Conditions were standardised at pH 9.5 for the estimation of chromium contents in low concentration in aqueous matrix. Under these conditions, the dp peak-height appeared proportional to the concentration of chromate ion in the range 0.05–17.2 ppm. Figure 3 shows that

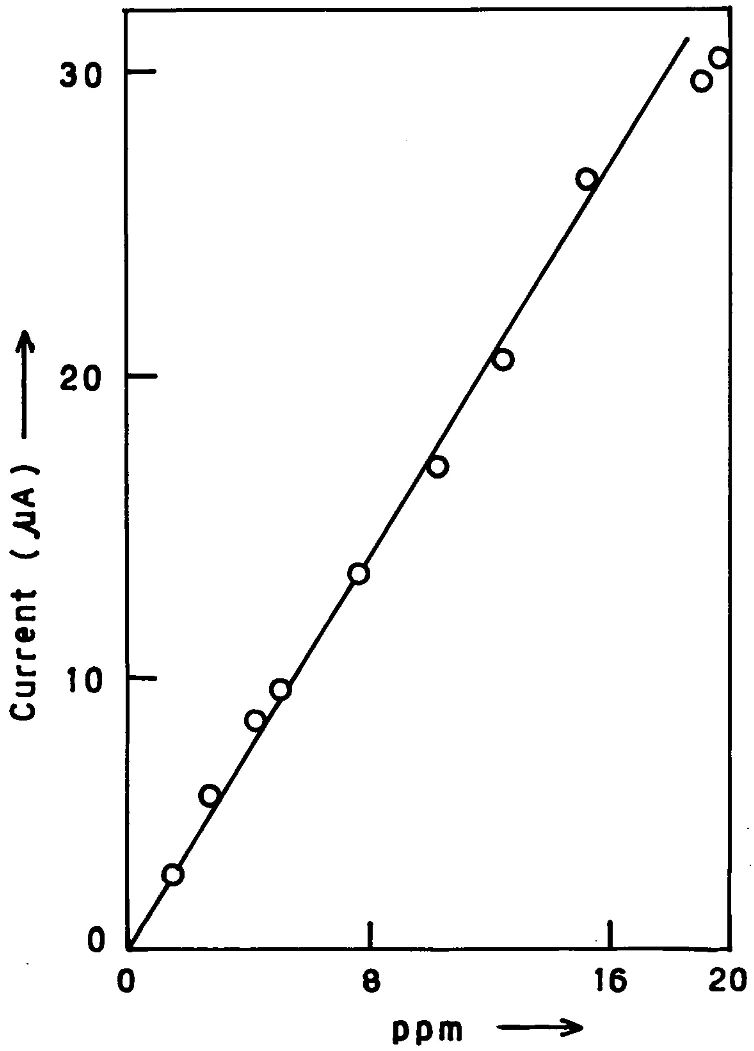

Figure 3 The plot of calibration curve, concentration vs. peak current.

current increased regularly in proportion to the added amount of chromate ion up to 17.2 ppm. Subsequent addition of Cr(VI) did not bring a linear increase in current. However, the concentrations were determined by standard addition method.[5]

dp polarograms were also recorded for a mixture containing chromium(VI), lead(II), cadmium(II) and zinc(II). The dp peaks for these metal ions were distinguishable from each other with the following peak potentials.

Metal ions	*Peak potentials vs. SCE*
Chromium	−0.20 V
Lead	−0.55 V
Cadmium	−0.70 V
Zinc	−1.25 V

A dp polarogram of a solution containing Cr(VI), Pb(II), Cd(II) and Zinc(II) is shown in Figure 4.

The limit up to which a measurable dp peak of Cr(VI) was observed was taken as its detection limit. The minimum amount which thus could be determined was found to be 0.020 ppm.

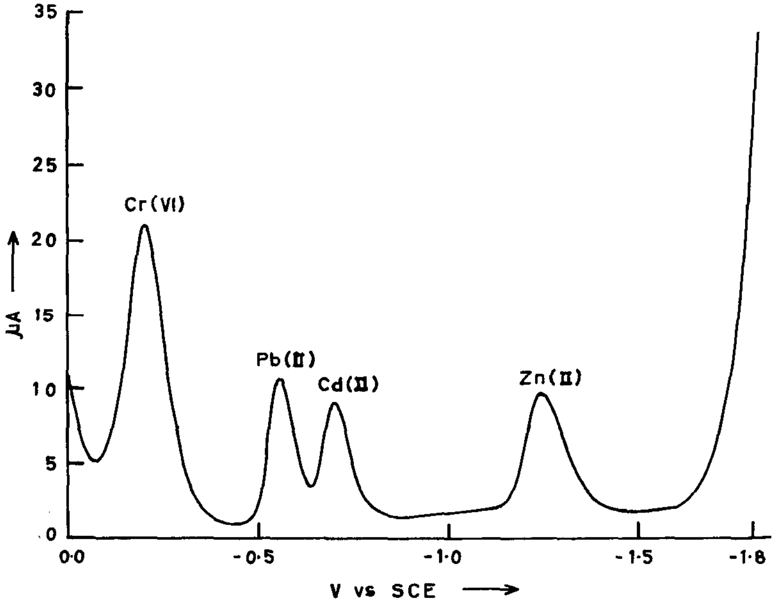

Figure 4 DPP of solution containing Cr(VI), Pb(II), Cd(II) 8.8×10^{-5} M each and 1.06×10^{-4} M Zn(II), pH = 9.5. Scan rate = 5 mv/sec, modulation amplitude = 50 mv, pulse duration = 57 ms, clock time of pulse = 1 sec.

ESTIMATION OF CHROMIUM IN WATER SAMPLES

The reduction of Cr(VI) to Cr(III) has been made the basis for determination of chromium contents in micro amounts employing dpp technique. For this purpose, the industrial waste water samples were concentrated by reducing their volumes to 1/5 times to obtain detectable quantities of chromium. The water samples were digested with hydrogen peroxide in basic solution to oxidise all the chromium to hexavalent state, the excess amount of hydrogen peroxide was decomposed by heating. The samples were then diluted to the desired volume,[6] and taken in the polarographic cell. The pH was adjusted to 9.5 by adding ammonium tartrate and the dp polarograms were recorded in the potential range 0.0 to -0.5 V. The peak currents were measured at -0.20 V after making blank correction. The concentration of chromium was determined in 40 samples of industrial waste waters in this manner within the following limits.

Minimum amount found = 0.027 ppm

Maximum amount found = 0.097 ppm

Standard deviation = $\pm 6\%$.

Acknowledgement

Thanks are due to the DRDO, Ministry of Defence, Government of India, for the sanction of a project (Sanction No. DTT/80843/50/RD-82/719/D(R&D) which made this work possible.

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