Highly Sensitive Adsorptive Stripping Voltammetric Method for the Ultra-trace Determination of Chromium(VI)

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A rapid differential pulse adsorptive stripping voltammetric method has been developed for the ultra-trace determination of chromium using 2,2'-bipyridine. The base electrolyte used is 0.1 M NH₄Cl (pH 6.0). The peak current was found to increase substantially with the addition of nitrite ions. A well-defined peak was observed at -1.3 V. Parameters, like concentration of the ligand, concentration of nitrite ion, accumulation potential, accumulation time, rest period, drop size, scan rate, pulse amplitude *etc.* have been optimized. Under the optimum conditions, the 3 σ detection limit was found to be 0.02 ppb (3.8×10^{-10} M). The method is highly selective and sensitive, and has been applied to the determination of Cr(VI) in spiked water, effluents and ore samples.

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Introduction

Chromium exists in +3 and +6 oxidation states. Cr(VI) is known to be carcinogenic when ingested, even in very small quantities. Most harmful effects are on vital organs, like the liver and kidney. It causes marked irritation of the respiratory tract, ulceration and perforation of the nasal septum.¹

The chromium content can be determined in various samples by neutron activation analysis.^{2,3} However, this technique is very expensive and requires quite a long time (5–6 weeks). Atomic absorption spectroscopy is another technique used for the determination of total chromium. To distinguish Cr(III) and Cr(VI), the separation of the two species is necessary.^{4,5} Colorimetric methods generally suffer from the disadvantage of interference from other species present.⁶

Tanaka and Ito⁷ first reported that Cr(III) and Cr(VI) give exceptionally high polarographic currents in the presence of a solution of EDTA and nitrate ions as a supporting electrolyte. High polarographic currents have been reported to be produced due to a catalytic effect of nitrate ions, which reoxidize the Cr(II)-EDTA complex. In recent years, methods using cupferron,⁸ diphenylcarbazide⁹ and polyamino acids, like DTPA¹⁰ and TTHA,¹¹ have been reported owing to the high adsorption properties of these complexes. These methods make use of nitrate ions as catalytic agents.

Palrecha and Mathur¹¹ have studied the mechanism of Cr(VI)-TTHA voltammetry in the presence of nitrate ions. Cr(VI) reduces at the surface of the electrode to Cr(III), which forms a complex with TTHA immediately, and then gets reduced at the surface of the electrode to Cr(II) during a cathodic scan. The reduction product is reoxidized by nitrate ions to enhance the peak current by catalytic action. Misiego *et al.*¹² have made a comparative account of square wave *versus* the differential pulse voltammetric behavior of Cr(VI)-TTHA. Li and Xue¹³

have reported the use of DTPA for speciation studies of chromium. A catalytic enhancement of the reduction current due to the presence of nitrite ions has already been studied for the Co(II)-bipyridine complex.¹⁴ In the present work, 2,2'-bipyridine was used as a ligand for the determination of Cr(VI), while nitrite ions were used as a catalytic agent. This method resulted in a still better sensitivity and selectivity.

Proposed mechanism of the reaction is:

Experimental

Apparatus

Differential pulse adsorptive cathodic stripping voltammetric (DPAdCSV) studies were carried out using Metrohm Polarecord E-506 serie-03 working on 220 volts stabilized AC mains. To it was connected the Metrohm polarography stand E-505. The instrument was kept in an air-conditioned room maintained at $25 \pm 10^\circ\text{C}$, and the humidity was between 50 to 60%.

The electrode assembly consisted of a hanging mercury drop electrode (Kemula Type) as the working electrode, an Ag/AgCl (sat. KCl) electrode as a reference electrode and a platinum

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Fig. 1 Typical voltammograms of (A) 0.1 M NH_4Cl containing 0.5 μM bipyridine and 0.4 M NaNO_2 with (B) 0.2 ppb and (C) 0.4 ppb Cr(VI) .

Fig. 2 Effect of the pH on the peak current in 0.1 M NH_4Cl , 0.4 M NaNO_2 and 0.5 μM bipyridine solution with 0.2 ppb and 0.4 ppb Cr(VI) .

electrode as an auxiliary electrode. Nitrogen gas was used for deaeration and a micropipette (25 μl) was used for adding the Cr(VI) solution. Mercury was purified by an aeration method, and then distilled under reduced pressure in a mercury distillation unit.

Reagents and solution

All of the chemicals used were of AR grade. The solutions were prepared in double-distilled water. A stock solution of 100 ppb Cr(VI) was prepared and desired dilutions were made as per the requirements. A 0.5×10^{-3} M solution of 2,2'-bipyridine was prepared in 100 ml of distilled water.

General procedure

In each determination, 0.1 M NH_4Cl and 0.4 M NaNO_2 were maintained at a total volume of 25 ml. The pH was adjusted to 6.0 using a diluted NH_3 and HCl solution. To it 25 μl of a 2,2'-bipyridine solution was added using a micropipette, which made the concentration of the ligand 0.5 μM . A chromium solution of the desired concentration was added using a micropipette. The solution was deaerated with nitrogen for 10 min before actual recording. In all cases, blank recordings were performed and necessary corrections were made in the calculations. Typical voltammograms obtained for a blank as well as two concentrations of Cr(VI) are shown in Fig. 1.

Results and Discussion

NH_4Cl was selected as a base electrolyte that gives a smooth baseline for the entire potential range of studies. The

Fig. 3 Effect of the concentration of nitrite ions on the peak current in 0.1 M NH_4Cl and 0.5 μM bipyridine solution (pH 6.0), with 0.2 ppb and 0.4 ppb Cr(VI) .

Fig. 4 Effect of the concentration of bipyridine on the peak current in 0.1 M NH_4Cl , 0.4 M NaNO_2 solution (pH 6.0), with 0.2 ppb and 0.4 ppb Cr(VI) .

concentration of NH_4Cl was varied from 0.02 M to 0.20 M with other parameters kept constant. The peak current was found to increase with the concentration of NH_4Cl up to 0.1 M, and remained constant thereafter. The peak potential (-1.3 V) was not affected by any variation in the concentration of NH_4Cl . The peak signal was found to be symmetrical for all concentrations of NH_4Cl . In the present studies, 0.1 M NH_4Cl was selected as a supporting electrolyte.

The pH was varied from 5.0 to 8.0 using diluted ammonia and diluted HCl solutions, and voltammograms were recorded for 0.2 ppb and 0.4 ppb Cr(VI) . The peak height was found to increase substantially up to pH 6.0, and decreased above it, probably due to a higher stability of the complex at pH 6.0. A sharp and symmetrical peak was obtained at pH 6.0, which was selected for all studies (Fig. 2). The peak potential was found to be unaffected by a change in the pH and remains at -1.3 V.

The concentration of sodium nitrite was varied from 0.1 M to 0.8 M. It was observed that the peak current increased up to 0.4 M, and remained constant above this concentration (Fig. 3). A sharp single peak was obtained at 0.4 M NaNO_2 , which was maintained for all of the studies. An increase in the peak current with nitrite clearly showed catalytic action of nitrite ions.

To a solution containing 0.1 M NH_4Cl , 0.4 M NaNO_2 and 25 μl 0.2 ppm Cr(VI) solution with pH 6.0, varying concentrations of 2,2'-bipyridine were added in the range 0–1 μM . No peak was observed when 2,2'-bipyridine was absent, but a distinct peak was obtained after the addition of 2,2'-bipyridine. The peak current increased up to a ligand concentration of 0.4 μM , and remained constant above this value. A similar trend was observed with 0.4 ppb Cr(VI) (Fig. 4). In all further studies, 0.5

Fig. 5 Effect of the accumulation potential on the peak current in 0.1 M NH_4Cl , 0.4 M NaNO_2 and 0.5 μM bipyridine solution (pH 6.0) with 0.2 ppb and 0.4 ppb Cr(VI).

Fig. 6 Effect of the accumulation time on the peak current in 0.1 M NH_4Cl , 0.4 M NaNO_2 and 0.5 μM bipyridine solution (pH 6.0) with 0.2 ppb and 0.4 ppb Cr(VI).

μM bipyridine was selected as the optimum concentration.

An adsorptive accumulation of the complex was carried out at different potentials from 0.0 to -1.0 V, followed by cathodic stripping up to -1.5 V. The peak current was found to be maximum for an accumulation potential of -0.2 V. Hence, this potential was selected for further studies. The variation in the peak current with the accumulation potential is shown in Fig. 5.

An adsorptive accumulation of the complex was carried out for different periods from 20 s to 240 s. Initially, there was an increase in the peak current with the accumulation time; however, equilibrium was reached in about 180 s (Fig. 6). An accumulation period of 60 s was selected for further studies.

With an increase in the surface area of the mercury drop, a linear increase in the peak current was observed and a drop size of 1.4 mm^2 was maintained for all the studies. An increase in the scan rate and the pulse amplitude showed an increase in the peak current. A scan rate of 30 mV/s and a pulse amplitude of 30 mV were selected. At higher pulse amplitudes, the signals were not reproducible.

Under the optimum conditions, the coefficient of correlation was found to be 0.9995. The equation of regression line is $y(\mu\text{A}) = 14.37x(\text{ppb}) + 1.23$. The detection limit calculated as 3-times the standard deviation of the blank, was found to be 0.02 ppb.

The effect of various ions on the peak current was determined at 0.2 ppb concentration. It was observed that Mn(II), Fe(II), Fe(III), Zn(II), Cu(II), Pb(II), Cr(III), Ni(II) and Co(II) did not interfere, even when present in 100-times excess of Cr(VI). Ni(II) and Co(II) gave separate peaks with peak potentials of -1.02 V and -1.10 V, respectively, which are well-resolved from that of Cr-bipyridine peak.

Table 1 Analysis of effluent samples

Sample	Concentration of chromium, ppb	
	Present method ^a	AAS method
1	35	36
2	187	196
3	6	5
4	6	5
5	15	16
6	6	5

a. (Avg $\pm$ SD) of 4 observations.

Table 2 Analysis of ore samples

Sample	Concentration of chromium, ppm	
	Present method ^a	AAS method
1	5.32	5.192
2	10.46	10.319
3	3.20	3.225

a. (Avg $\pm$ SD) of 4 observations.

Applications of the method

Spiked water samples. The above-developed method was applied to the determination of Cr(VI) in spiked water samples. Tap water samples (100 ml) were spiked with 0.010 μg and 0.02 μg of chromium. To them, 1 ml conc. HNO_3 and 1 ml H_2O_2 were added and evaporated to almost dryness. The residue obtained was dissolved in 10 ml of double-distilled water. NH_4Cl , NaNO_2 and 2,2'-bipyridine solutions were added in appropriate amounts, as discussed previously. The pH was adjusted to 6.0 with diluted ammonia, and voltammograms were recorded. A blank recording was made and necessary corrections were performed. Results were obtained using the standard addition method. The values, obtained as an average of 3 experiments, were 0.010 and 0.0202 μg , respectively.

Effluent samples. Four effluent samples were collected from an industrial area of Hingna near Nagpur. A 100-ml volume of each filtered sample was taken in a beaker. A 2-ml volume of conc. HNO_3 was added and evaporated to about 10 ml in order to destroy any organic matter. About 2 ml of H_2O_2 was added and heated to about dryness to remove excess of peroxide. It was neutralized with an ammonia solution, and the volume was made up to 50 ml. Suitable aliquots were taken and analyzed using the standard addition method. The obtained results were checked by the AAS method (Table 1).

Ore sample. Three ore samples were obtained from Indian Bureau of Mines (IBM), Nagpur. About 2 g of each of the samples was accurately weighed and digested with 20 ml of conc. HCl on a hot plate for half an hour. To it, 5 ml of conc. HNO_3 was added and heated to reduce the volume to about half; 5 ml of 1:1 H_2SO_4 was added, followed by 2 ml of H_2O_2 and heated to almost dryness. It was cooled and the residue was dissolved in diluted HCl . A 2 ml H_2O_2 solution was added and evaporated to dryness. The residue was dissolved in distilled water. The solution was filtered through a Whatman filter paper and the volume was made up to 50 ml. Suitable aliquots were taken and voltammograms were recorded after following the above-developed procedure. The results obtained using the standard addition method and further checked by the AAS method were found to be comparable (Table 2).

Conclusion

A simple and rapid method has been developed for the determination of Cr(VI) at the trace level. The method was found to be reproducible, reliable and accurate. An important advantage of the method is that 60 s of the accumulation period is sufficient to achieve a sensitivity of 0.02 ppb. The standard deviation, relative mean deviation and coefficient of variation at 0.1 ppb were found to be 0.007, 2.1% and 4.0%, respectively.

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