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ELECTROCHEMISTRY

Determination of Chromium(VI) by Batch Injection Analysis and Adsorptive Stripping Voltammetry

Christopher M. A. Brett,[1],* Olga M. S. Filipe,[2] and C. Susanna Neves[1]

[1]Departamento de Química, Universidade de
Coimbra, Coimbra, Portugal
[2]Escola Superior Agrária de Coimbra,
Bencanta, Coimbra, Portugal

ABSTRACT

A new sensitive voltammetric method is presented for the determination of trace levels of Cr(VI). The method is based on square wave adsorptive stripping voltammetry (AdSV) in conjunction with the electrochemical batch injection analysis technique at mercury thin-film electrodes. The determination of chromium is made in the presence of cupferron as ligand. Relevant experimental parameters are explored and optimized, such as injection mode, cupferron

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*Correspondence: Christopher M. A. Brett, Departamento de Química, Universidade de Coimbra, 3004-535 Coimbra, Portugal; Fax: +351-239-835295; E-mail: brett@ci.uc.pt.

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concentration, accumulation potential and time, and square wave parameters. A preconcentration time of 20 s at −0.8 V vs. SCE results in a detection limit of 32 nM. The relative standard deviation for 12 measurements of 0.12 μM was 6.5%. Possible interferences by other trace metals are considered.

Key Words: Chromium; Trace metals; Batch injection analysis; Adsorptive stripping voltammetry; Cupferron.

1. INTRODUCTION

The toxicity of chromium(VI) in the environment is well known. It occurs in various minerals but also accumulates from industrial effluent ion soil and sediment, as well as in surface and groundwaters. Although Cr(III) compounds also exist in nature, Cr(VI) compounds are highly oxidizing and soluble. Speciation of chromium is thus highly important and recent efforts have been addressed towards this end. An excellent summary of the speciation in different industrial materials may be found in Ref.,[1] as well as in soils, sediments, and sludges.

Before analysis, samples are usually subjected to some pretreatment, which may involve complexation, filtration, extraction, acid treatment, oxidation, or reduction etc.[2] Detection methods used have included ultraviolet and visible spectrophotometry,[3–5] atomic absorption spectrometry,[6–9] high pressure liquid chromatography,[10,11] chemiluminescence,[12] mass spectrometry,[13,14] and sample preparation methods include ultrasonic extraction[3,15] and EDTA or acetic acid extraction.[16]

Electrochemical detection is a particularly important type of technique, given its natural tendency to act as a speciation probe. Although, electrochemical reduction of Cr(VI) and Cr(III) has been studied directly at the hanging mercury drop electrode,[17] most strategies have involved adsorptive cathodic stripping voltammetry (AdCSV). AdCSV has found wide application in water analysis for many trace elements.[18] The determination of chromium by AdCSV has used a number of different complexing agents in the accumulation step which have included diethylenetriaminepentacetic acid (DTPA), triethylenetetranitrilohexaacetic acid, 1,5-diphenylcarbazide, 2,2′-bipyridine, and cupferron.[19–34] Most of these investigations have been carried out at the hanging mercury drop electrode with differential pulse scanning in the determination step, but there are also reports using mercury microelectrodes on platinum[27] and iridium[30] substrates as well as a mercury thin film electrode in flowing solution.[25]

The aim is to develop a fast, rapid-response, and simple procedure for the detection and quantification of chromium using electrochemical batch injection analysis with adsorptive stripping voltammetry, a combination of techniques already demonstrated for cobalt and nickel ions.[35] In the batch injection analysis (BIA) technique,[36–38] a sample of between 50 to 100 μL of analyte is injected perpendicularly from an electronically-controlled motorized micropipette directly over the centre of a disc-shaped electrode immersed in electrolyte solution. BIA has been applied to trace metal ion analysis using mercury film electrodes by anodic stripping voltammetry[39] and adsorptive stripping voltammetry,[35] the surface usually being protected by polymer films to prevent contamination of the mercury surface by components of the raw analyte samples.[40–42] Electrolyte does not need to be added, since only a fine jet of analyte solution is injected into the cell; any pretreatment carried out is confined to any desired chemical reactions, e.g., digestion to increase the labile fraction, before injection. Good results have been obtained with anodic stripping voltammetry of copper, lead, cadmium, and zinc ions in real matrices within the cell when the sample is injected.[41]

Thus, an adsorptive stripping voltammetric method for the determination of chromium using batch injection analysis at the mercury thin film electrode has been developed. Two ligands were selected for the study—DTPA and cupferron—the latter leading to superior results.

2. EXPERIMENTAL

The BIA cell was the same as described earlier[37] and is made of Perspex. It contained a working electrode of glassy carbon, diameter 5 mm, a platinum gauze counter electrode, and a saturated calomel electrode as reference. The cell contained approximately 40 cm^3 of inert electrolyte. Injections were done from a programmable, motorized, electronic micropipette (EDP Plus ED-100, Rainin Instrument Co. Inc.); the pipette tip diameter was ~0.47 mm. The glassy carbon electrode was polished with alumina slurry down to 0.3 μm particle size.

Mercury films were prepared by electrodeposition within the BIA cell. A volume of 50 μL of a 0.10 M solution of Hg^{2+} in 0.1 M KNO_3/5 mM HNO_3 was injected directly over the electrode at an applied potential of -1.0 V vs. SCE and dispension rate 22.5 $\mu L\,s^{-1}$, this potential being applied for a total of 60 s.

BIA-SWAdSV experiments were carried out using a computer-controlled CV-50W voltammetric analyzer (Bioanalytical Systems). In the optimized SWAdSV procedure, see below, the square wave parameters were: frequency 100 Hz, potential increment 2 mV, and square wave amplitude 25 mV. Metal ion complexes were accumulated by injection of a 50 μL sample containing chromate ion and ligand at an applied potential of −0.8 V vs. SCE during 20 s. Electrolyte was pH 6, 0.2 M phosphate buffer. Regarding the ligands tested, stock solutions of 0.04 M DTPA were prepared in 0.08 M NaOH solution and 0.1 M cupferron in water.

All reagents were of analytical grade and solutions were made with Millipore Milli-Q water, resistivity >18 MΩ cm, and experiments were carried out at room temperature (25 ± 1°C).

3. RESULTS AND DISCUSSION

The different parameters for square wave adsorptive stripping voltammetry detection of chromium were investigated in the context of combination with BIA, and some differences were found with respect to previous studies on the liquid mercury drop electrode, particularly regarding the effect of ligand identity on response.

3.1. Ligand

Typical SWAdSV data obtained are shown in Fig. 1 and demonstrate that, contrary to the liquid mercury electrode, no visible stripping signal is obtained for the DTPA ligand, despite the addition of a large concentration of nitrate ion to make possible the catalytic cycling of Cr(II) to Cr(III) described previously.[22] This rather surprising finding can be traced to two factors. First, the "mercury film" is probably, in fact, a collection of closely-spaced droplets[43] so that the exposed surface is both glassy carbon and mercury. Secondly, there is no catalytic cycling of Cr(II) to Cr(III). At liquid mercury electrodes, DTPA leads to catalytic cycles in the presence of nitrate ion, such that Cr(II) formed by reduction is once more oxidized to Cr(III), increasing the observed current.[22,27] Similar effects have been observed in other situations, for example in the adsorptive stripping voltammetry of cobalt ions.[44] However, in the batch injection analysis cell, the concentration of nitrate ions in the zone of the electrode surface is less, and almost certainly not sufficient to produce a catalytic effect. Besides signifying that cupferron is a better ligand for chromium detection using BIA, these results are also further evidence that the proposed catalytic effect of the DTPA-nitrate system at SMDEs is, in fact, correct.

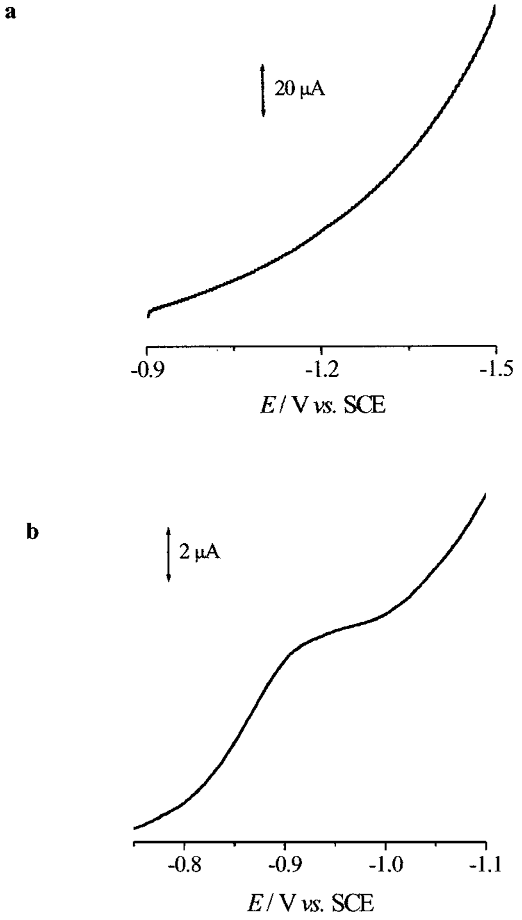

Figure 1. SWAdSV using ligands (a) 0.020 M DTPA and, (b) 0.025 M cupferron: $[CrO_4^{2-}] = 0.119\,\mu M$ in $0.04\,M$ $KCH_3COO + 0.4\,M$ KNO_3, pH 6.1, $E_{ads} = -1.15\,V$, $t_{ads} = 20\,s$, $f = 75\,Hz$, amp $= 25\,mV$, $\Delta E = 2\,mV$.

Thus further studies and optimization employed the cupferron ligand.

3.2. Injection Parameters

Whereas a high injection rate leads to higher currents and hence higher sensitivity in amperometric and direct voltammetric detection, this is not the case in coulometric experiments. A higher percentage electrolysis is achieved at lower flow rates, as demonstrated explicitly for BIA.[37] Additionally, in the type of processes described in this work, the kinetics of the accumulation process can be an important consideration, since the analyte is in constant hydrodynamic movement across the detector electrode. In principle, the accumulation process can take place through direct substitution of the ligand adsorbed at the surface by the chromium(III) complex, or by the metal ion exchanging between non-adsorbed and adsorbed ligand molecules. Both of these can be slow processes and limit the efficiency of the process.

It was found that the signal obtained using the slowest available injection dispension rate was very low, Fig. 2, but, using the "Titration" mode of the micropipette, much larger signals could be obtained. In this pipette mode the sample is ejected in very tiny microdroplets, the speed of which is much lower than in "Dispense" mode, the whole ejection process taking approximately 20 s for a volume of 50 μL. Such an improvement obtained using "Titration" mode would be expected for slow kinetics, and permits a much larger fraction of the analyte sample to be accumulated at the electrode. Even so, and in agreement with previous results for anodic stripping voltammetry,[39] injected volumes above 50 μL did not give any significant increase in reduction peak current obtained.

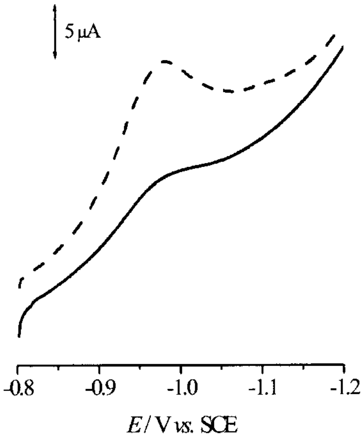

Figure 2. Influence of injection rate: ---- 24.5 μL s^{-1}, — "titration" mode. [CrO_4^{2-}] = 0.296 μM, [CupF] = 0.025 M in 0.2 M phosphate buffer pH 6, $E_{ads} = -0.8$ V, $t_{ads} = 20$ s, $f =$ 75 Hz, amp = 25 mV, $\Delta E = 2$ mV.

3.3. Concentration of Cupferron

As would be expected from the slow kinetics observed, there is some influence from increasing concentrations of the cupferron ligand in increasing the peak current, as demonstrated in Fig. 3. Nevertheless, in order not to use excessive concentrations of cupferron, an expensive ligand, it was decided to employ 0.025 M concentration in further studies.

3.4. Accumulation Potential

Since this study involves accumulation of chromium as Cr(VI) reduced to Cr(III) with complex formation, the efficiency of the process should increase with more negative accumulation potential. Nevertheless, if this potential is made too negative, Cr(III) complex is directly reduced to Cr(II) and accumulation does not occur. This is clearly shown in the SWAdSV results illustrated in Fig. 4.

3.5. Accumulation Time

In Fig. 5 is demonstrated the effect of accumulation time for two different concentrations of chromate ion. Using titration mode,

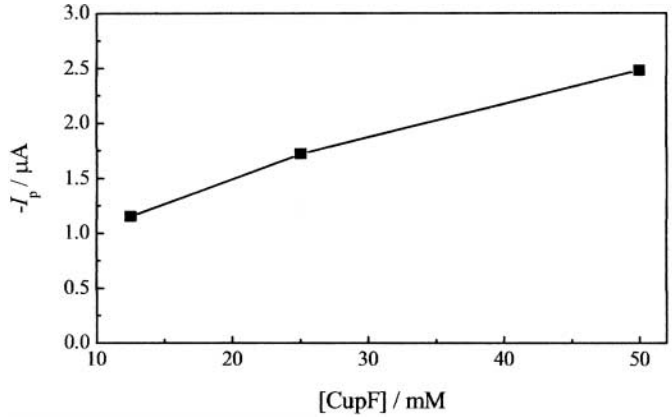

Figure 3. Effect of cupferron concentration on peak current, I_p. $[CrO_4^{2-}] = 0.296\,\mu M$ in 0.2 M pH 6 phosphate buffer, $t_{ads} = 20\,s$, $E_{ads} = -0.8\,V$, $f = 50\,Hz$, amp $= 20\,mV$, $\Delta E = 2\,mV$.

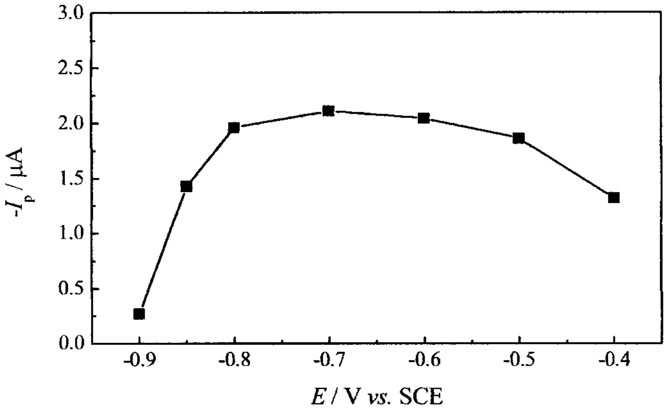

Figure 4. Effect of accumulation potential on peak current. $[\mathrm{CrO_4^{2-}}] = 0.296\,\mu\mathrm{M}$, $[\mathrm{CupF}] = 0.025\,\mathrm{M}$ in 0.2 M pH 6 phosphate buffer, $t_{\mathrm{ads}} = 20\,\mathrm{s}$, $f = 50\,\mathrm{Hz}$, amp = 20 mV, $\Delta E = 2\,\mathrm{mV}$.

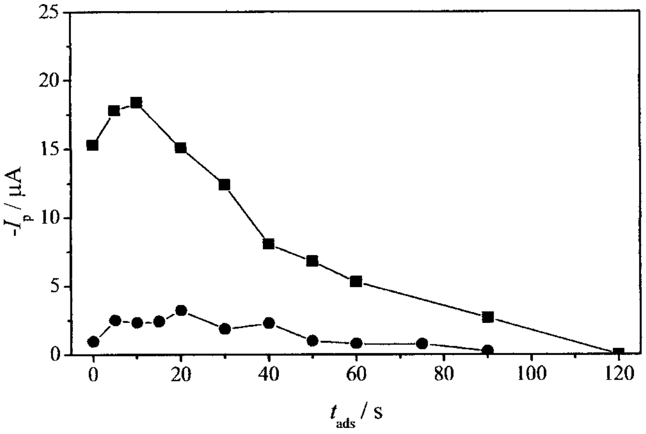

Figure 5. Effect of accumulation time on stripping peak current, I_p, $[\mathrm{CrO_4^{2-}}]$: ■ 5.93 µM, ● 0.593 µM. $[\mathrm{CupF}] = 0.025\,\mathrm{M}$ in 0.2 M pH 6 phosphate buffer; $E_{\mathrm{ads}} = -0.8\,\mathrm{V}$, $t_{\mathrm{ads}} = 20\,\mathrm{s}$, amp = 20 mV, $\Delta E = 2\,\mathrm{mV}$.

injection is complete after approximately 20 s. As discussed above, the results can be explained assuming that adsorption of the complex on the electrode surface is not strong and that there exists a reversible equilibrium between adsorbed and non-adsorbed complex, the result of which is that, as the concentration in solution diminishes with time, there is a slow desorption. It is therefore suggested that the square wave scan be undertaken immediately after injection is complete, after 20 s.

3.6. Square Wave Parameters

The square wave frequency, amplitude, and potential increment were all optimized. There was very little effect of the square wave amplitude over the range 10–50 mV and of the potential increment over the range 2–5 mV. The values chosen were 25 and 2 mV respectively. The effect of square wave frequency for three different chromate ion concentrations is shown in Fig. 6. In all cases there is a decrease with increasing frequency above a particular value, which is expected if there are kinetic limitations (this is another reason for selecting a small potential increment). There is also a small shift in peak potential to more negative values by ~50 mV, again with some dependence on concentration.

3.7. Calibration Plots

A typical calibration plot is shown in Fig. 7. The linear range is between 0.01 and 0.6 μM and the calibration equation is with correlation coefficient 0.999; the limit of detection is calculated to be 32.3 nM (based on the 3σ criterion). Reproducibility was tested for consecutive measurements of chromate and for 12 measurements of 0.12 μM a relative standard deviation of 6.5% was encountered.

3.8 Interferences and Real Samples

Interferences from Pb(II), Cd(II), Cu(II), Mn(II), and Zn(II) were tested at 10 times the concentration of Cr(VI), which was 0.12 M. No visible signs of interference were found. This is agreement with previous reports, where only interference from zinc ions was demonstrated, and then only in very large excess.[28] This is extremely important for the measurement of chromate in real samples, since chromate is usually present together with other metal ions.

Ordinary drinking water was spiked with chromate ion and ligand, without added electrolyte, and injected into the BIA cell containing phosphate buffer electrolyte. No matrix effects were observed. Future application of the technique to industrial effluents is planned where the

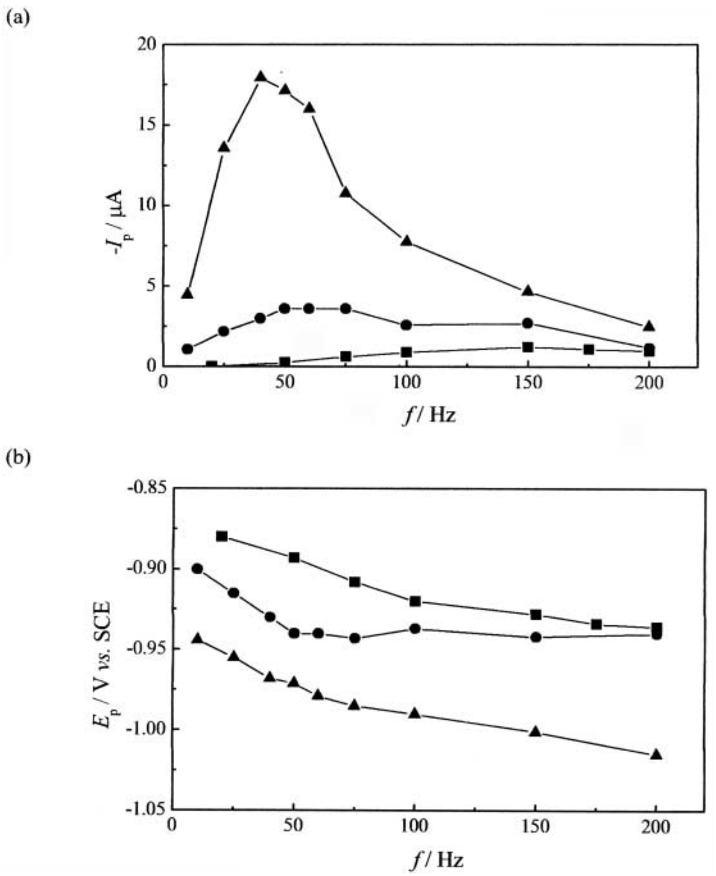

Figure 6. Effect of square wave frequency on (a) peak current and (b) peak potential. $[CrO_4^{2-}]$: ▲ 5.93 μM, ● 0.593 μM, ■ 0.0593 μM, [CupF] = 0.025 M in 0.2 M pH 6 phosphate buffer, $E_{ads} = -0.8$ V, $t_{ads} = 20$ s, amp = 20 mV, $\Delta E = 2$ mV.

small volume of analyte sample employed in BIA is particularly valuable in reducing the influence of the matrix and of electrode contamination.

4. CONCLUSIONS

The present study demonstrates that the coupling of adsorptive accumulation with electrochemical batch injection analysis can constitute the basis of a sensitive stripping procedure for determination of trace

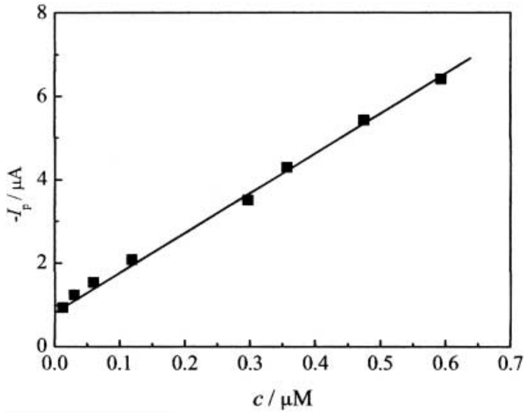

Figure 7. SWAdSV calibration plot for CrO_4^{2-} [CupF] = 0.025 M in 0.2 M pH 6 phosphate buffer, $E_{ads} = -0.8$ V, $t_{ads} = 20$ s, $f = 50$ Hz, amp = 20 mV, $\Delta E = 2$ mV.

levels of chromium through adsorption as cupferron complexes on mercury thin-film electrodes. Under optimized conditions, a detection limit of 32.3 nM was obtained. The method developed provides a simple, fast, and highly sensitive procedure for the determination of trace amounts of chromium. Good selectivity against a number of metal ions is observed.

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