

Cr (VI)/Cr (III) SPECIATION BY *IN SITU* ELECTRODEPOSITION ONTO TUBE PRIOR TO ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Abstract

A new technique of coupled electrodeposition-electrothermal Atomic Absorption Spectrometry (AAS) method has been developed to study chromium speciation. Speciation of Cr (VI)/Cr (III) is carried out by electrodeposition at uncontrolled applied potentials, followed by removal of spent electrolyte and atomisation. At $E_{\text{appl}} = 0.5\text{-}10.0$ V and using codeposition with Hg (and without Pd coating), only Cr (VI) is reduced to Cr (III) and accumulated as Cr (OH)₃ by absorption onto mercury film on the graphite furnace. Total chromium is measured by electrodepositing at 10.0 V without Hg but on the renewable Pd substrate from 0.5 M NaCl and 1% H₂SO₄. It has been demonstrated that chromium speciation can be achieved in samples of 0.5 M NaCl, using acetate buffer to adjust pH to 4.7. The results also will be given for attempted chromium speciation studies by *in situ* deposition onto Pd-coated furnace. At all applied voltages between 2.0-10.0 V in 0.02% H₂SO₄ Cr (III) is reduced to chromium metal and deposited onto the Pd substrate more efficiently than Cr (VI), but the difference is not sufficient for complete discrimination of two chromium forms. The effect of SO₄²⁻ ion concentration and of pH on the yield of deposition were studied for each form of chromium. It was shown that from 1% H₂SO₄ both forms of chromium deposited quantitatively. Apart from achieving speciation, background signal due to high concentration of NaCl in the sample was completely eliminated by the proposed technique. At the same time a two-fold improvement in sensitivity of the determination was achieved with respect to the conventional electrothermal AAS technique.

Keywords: Chromium speciation; Electrothermal atomic absorption spectrometry; Electrodeposition

Introduction

The difference in toxicity and essentiality of hexavalent and trivalent chromium to a biosystem make the researchers to attend the importance of speciation between the species in these two redox states in

environmental and industrial samples [1-4].

Cr (VI) is absorbed by respiratory tract during inhalation and rapidly penetrates to erythrocyte membrane, then is reduced to Cr (III) and binds predominantly to hemoglobin [5] and shows carcinogenicity effect [6]. The toxicity of Cr (VI) on

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plant growth also has been documented as stunted growth, Iron chlorosis and death [6]. In contrast, Cr (III) is essential nutrient for mammals due to its effect on metabolism of glucose, lipid, protein and insulin action [7]. Cr (III) deficiency is a casual factor in atherosclerosis [8]. It has been suggested that diets containing mostly processed foods may be Cr (III) deficient [6,8]. In both serum and urine samples chromium occurs as Cr (III) [5] and in serum, Cr (III) binds to serum proteins especially transferrin and albumin. Therefore, the speciation of these two redox states in serum and urine samples is useless. Thus, for exposure determination of each, it is better to analyse the environmental and industrial sources of chromium [6].

Considerable attempts have been paid to analysis of this element using the ability of techniques to discriminate between two redox states of Cr (VI) and Cr (III) [1-4,9-13]. Inherent in all these procedures is the need to separate the chromium species before analysis. The ability of electrochemical techniques to discriminate between the two redox states of Cr (VI) and Cr (III) is well known and has been explored in electrothermal AAS [1].

Therefore, in this approach a combined technique of electrodeposition with electrothermal atomic absorption spectrometry [14] has been employed to elucidate the ability of this method for speciation of these two forms of chromium in sea water as an environmental sample.

Experimental Section

Instrumentation

A GBC 932AA double beam atomic absorption spectrometer with deuterium lamp background correction equipped with GF3000 furnace and a PAL3000 autosampler were used throughout this work.

The construction of the modified autosampler is similar to an early design [15] in which the last section of PTFE sample delivery tube is replaced with a 6 cm Pt/Ir tube. The furnace and Pt/Ir tube were connected to a D.C. power supply (0-12V) via a multimeter (0-150 mA) indicating the deposition current.

Reagents

Ultrapure water was obtained by passing distilled water through milli-Q ion exchange and membrane filtration system. All acid used, namely HNO₃, HCl, and H₂SO₄ were of Aristar (BDH) quality and were all diluted by milli-Q water.

Sodium chloride solutions were prepared from high purity grade (BDH) Anala R or analytical reagent

(Univar). Stock Pd solution (100 ppm) was made by dissolving PdCl₂ (BDH) in 1-5% Aristar HNO₃ and was diluted to 10 ppm working solution with milli-Q water. All analyte standard solutions were prepared in 1% HNO₃ or 1% HCl by diluting stock solutions of 1000 ppm (BDH) standard solution for AAS. All solutions were stored in high density polyethylene containers previously soaked in 1% HNO₃ for a long time.

Procedure

Experiments involved both conventional sample introduction and *in situ* sample electrodeposition into the pyrolytic graphite furnace pre-coated or not by electrodeposited Pd modifier. In the conventional way a standard autosampler-furnace program was utilized to deposit the sample into the furnace (with electrodeposited Pd modifier), followed by a furnace program. Table 1 shows the autosampler-furnace program for conventional introduction of sample into the furnace pre-coated by electrodepositing from 40 μ l of 10 ppm Pd in 0.5-1% HCl or HNO₃ at 2.0-3.0 V (electrolysis current 2-5 mA). The spent electrolyte is removed by autosampler and the deposited Pd is dried before the normal deposition of the sample follows. Table 2 shows procedure for *in situ* electrodepositing Cr onto furnace pre-coated with electrodeposited Pd (as in Table 1) or without Pd deposition. Following the procedure for Pd deposition and drying the deposit, 25 μ l of 0.01-1% H₂SO₄ or 0.5 M NaCl and 4×10^{-4} M Hg(NO₃)₂ (pH adjusted to 4.7 by using 0.02 M acetate buffer) containing 1-12 ppb of the Cr (VI) or Cr (III) were electrolysed at 0.0-3.0 V or 2.0-10.0 V (0.0-10 mA) for 80-100 s in the furnace pre-coated with or without electrodeposited Pd modifier, the spent electrolyte removed by autosampler and a furnace program initiated.

Results and Discussion

In situ Electrodeposition of Cr (VI)/Cr (III) with Mercury onto Pyrolytic Furnace Tube

The optimisation of electrodeposition potential was made for selection of suitable potential for speciation by studying the *in situ* codeposition with mercury of both Cr (VI) and Cr (III) over a wide potential range.

Figure 1 shows the results for variation of AA signals versus deposition potential for both *in situ* electrodeposition of 10 ppb Cr (VI) and Cr (III) from 0.5 M NaCl and 4×10^{-4} M Hg(NO₃)₂ solutions (buffered by 0.02 M acetate buffer to pH = 4.7) onto pyrolytic furnace tube.

Table 1. Autosampler-furnace program for AAS determinations of Cr by conventional sample introduction into the pyrolytic graphite furnace pre-coated with electrodeposited Pd modifier

Graphite Furnace Parameters						
Step	Final temperature (°C)	Ramp time (s)	Hold time (s)	Gas type	Read	Signal graphics
1	110	20.0	30.0	Inert	Off	Off
2	20	20.0	5.0	None	Off	Off
3	110	20.0	5.0	Inert	Off	Off
4	140	5.0	5.0	Inert	Off	Off
5	1300	8.0	1.0	Inert	Off	Off
6	400	4.0	1.0	Inert	Off	Off
7	400	1.0	1.0	None	Off	Off
8	2500	1.0	2.0	None	On	On
9	2500	1.0	1.5	Inert	Off	Off

Autosampler Parameters						
Solutions	Inject at step	Injection mode	Volume (µl)	Rinse	Current on	Current time (s)
Modifier	1	Electro dep.	40	No	Yes	40.0
Sample	3	Normal	25	No	No	1.0

Table 2. Autosampler-furnace program for AAS determinations of electrodeposited Cr in the pyrolytic graphite furnace with or without electrodeposited Pd Modifier

Graphite Furnace Parameters						
Step	Final temperature (°C)	Ramp time (s)	Hold time (s)	Gas type	Read	Signal graphics
1	110	20.0	30.0	Inert	Off	Off
2	20	20.0	5.0	None	Off	Off
3	110	20.0	30.0	Inert	Off	Off
4	140	5.0	5.0	Inert	Off	Off
5	1300	8.0	1.0	Inert	Off	Off
6	400	4.0	1.0	Inert	Off	Off
7	400	1.0	1.0	None	Off	Off
8	2500	1.0	2.0	None	On	On
9	2500	1.0	1.5	Inert	Off	Off

Autosampler Parameters						
Solutions	Inject at step	Injection mode	Volume (µl)	Rinse	Current on	Current time (s)
Modifier	1	Electro dep.	40	No	Yes	40.0
Sample	3	Electro dep.	25	No	Yes	80.0

* These steps were used for pre-coated furnace by Pd electrodeposition.

At deposition potential higher than 3.0 V, both Cr (VI) and Cr (III) are reduced and accumulated onto the furnace by forming an amalgam with mercury [2]. The results show a higher quantitative deposition for Cr (VI) than that for Cr (III) at deposition potential higher than 2.5 V which could be due to the difference in the diffusion coefficients of two species as is discussed by Batley and Matousek [1]. However, at applied potential between 0.5-1.0 V the principal mode of mass transfer to the electrodes is diffusion. The results show and the literature also indicates [16] that Cr (VI) ions have higher diffusion coefficients and diffuse faster than Cr (III) ions to the cathod. Therefore, only Cr (VI) is reduced to Cr (III) and accumulated as Cr(OH)₃ by adsorption onto mercury film on the graphite furnace. Cr (III) would remain in the bulk of solution and is withdrawn before thermal program initiated. The calibration curves for electrodeposited Cr (VI) and Cr (III) from the 0.5 M NaCl and 4×10^{-4} M Hg(NO₃)₂ solutions (buffered by 0.02 M acetate buffer to pH=4.7) were performed at 0.5 V applied deposition voltage. The results are shown in Figure 2. The selective determination and speciation of Cr (VI)/Cr (III) is confirmed by these results as Cr (VI) gives an AA signal increasing with concentration, but Cr (III) does not show considerable increase in the AA signal in higher concentrations of this species in the solution. This means that it is not deposited in any concentration at this deposition voltage and electrolyte. However, some errors are introduced due to a small contribution from Cr (III). These results are in agreement with those obtained by Batley and Matousek [1] and Vidal *et al.* [2].

Electrodeposition of both Cr (VI) and Cr (III) Quantitatively onto Pd-Coated Furnace

Avoiding the limitations [1,2] in using the mercury amalgam for accumulation of total chromium at higher deposition potentials experiments were carried out for electrodeposition of both Cr (VI) and Cr (III) onto Pd-coated furnace.

As one of important parameters other than the composition of the supporting electrolyte for electrodeposition step on the resulting AA response as peak area and peak height, for the same amount of electrodeposited Cr (III) and Cr (VI), is shown in Figure 3. A constant maximum absorbance value is achieved for Cr (III) deposition in the applied voltage range of 6-10 V, as it is shown in Figure 3. However, for electrodeposition of Cr (VI) in this range of voltage, the yield of deposition still varies slightly with applied voltage and reaches a maximum at 10 V (Fig. 3). The

probable explanation for this difference in the yield of deposition for these two forms of the element could be that, the process for reduction of Cr (VI) to Cr metal involves an additional electrochemical step (Cr (VI) to Cr (III) in relation to the reduction of Cr (III) to elemental form. There is an indication in the literature [16] that dichromate is mainly reduced to Cr (III) in H₂SO₄ electrolyte and Cr (OH)₃ is formed on the graphite electrode at lower voltages. Thus vaporisation and atomisation of Cr (OH)₃ show different characteristics in ET process in comparison to Cr metal. However, at higher voltages this Cr(OH)₃ might be reduced to chromium metal and show a better deposition that reaches a maximum at 10 V, as is shown in Figure 3.

The difference between reduction mechanisms of these two forms of chromium ions may be responsible for the difference in yields of electrodeposition for Cr (VI) and Cr (III) in H₂SO₄ electrolyte, as it is seen in Figure 3. However, this difference is not sufficient for complete discrimination of the two chromium forms.

The effect of SO₄²⁻ ion concentration and of pH on the yield of deposition were studied for each form of chromium. The results are shown in Figure 4. It was shown that from 1% H₂SO₄ both forms of chromium deposited quantitatively.

By using a 0.5 M NaCl and 1% H₂SO₄ as supporting electrolyte, the deposition of both Cr (VI) and Cr (III) are quantitatively comparable to that of conventional deposition in 1% H₂SO₄. The results are shown in calibration curves in Figures 5 and 6 for conventional ETAAS and ED-ETAAS or the same range of concentration for redox states of chromium respectively. Therefore the total chromium [(Cr (VI) + Cr (III))] could be measured by electrodeposition at 10.0 V without using mercury but on the renewable Pd substrate as is shown in Figure 6.

Apart from achieving speciation, another interesting finding is that the background signal due to high concentration of NaCl in the sample (0.5 M) was completely eliminated by the proposed technique. At the same time a two-fold improvement in sensitivity of the determination was achieved with respect to the conventional electrothermal AAS technique as is shown in Figure 7. Figure 7a shows the AA and background signals for a 0.5 M NaCl and 1% H₂SO₄ containing 8 ppb Cr (III) which was analysed by the conventional ETAAS technique. Although an optimised ashing program is used for removing the interfering matrix before the atomisation step, the AA signal is overlapped a very high background signal from the matrix. Apparently, the loss of analyte due to molecular compound formation takes place in this step. However, the ED-ETAAS technique for the same sample was quite successful in removing the

highly concentrated interfering matrix and separating traces of Cr from the bulk of sample. Thus, background signal was removed completely and two-fold improvement in Cr AA signal was obtained as is shown in Figure 7b.

Conclusion

The previous results and discussion demonstrated the feasibility of *in situ* electrodeposition-ETAAS

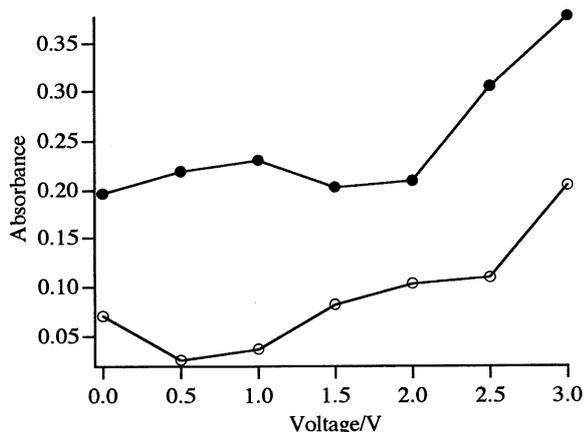


Figure 1. Plots of AA signals vs. the applied voltage for 10 ppb Cr⁶⁺ (●) and Cr³⁺ (○) electrodeposited from 0.5 M NaCl and 4 × 10⁻⁴ M Hg(NO₃)₂ (pH adjusted to 4.7 by acetate buffer) onto pyrolytic graphite furnace.

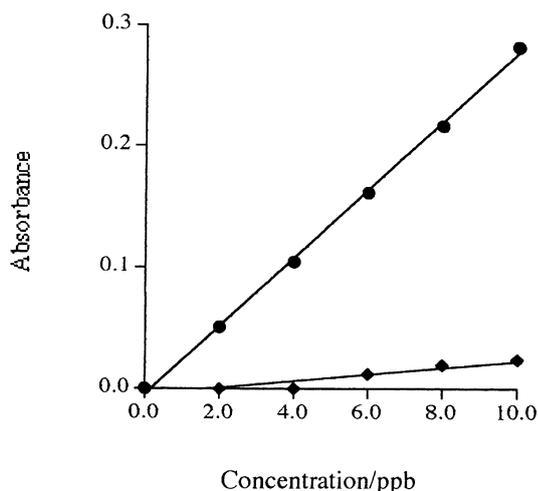


Figure 2. Calibration curves for Cr⁶⁺ (●) and Cr³⁺ (◆) codeposited with mercury from 0.5 M NaCl solutions, (buffered by 0.02M acetate buffer to pH=4.7), at E_{appl}=0.5V.

technique for speciation of Cr (VI)/Cr (III) in high concentration of NaCl (0.5 M). On basis of the deposition potential, the method permits the selective electrodeposition of only Cr (VI) with mercury codeposition onto pyrolytic graphite furnace tube. The total Cr also was electrodeposited with using mercury onto the Pd-coated graphite furnace tube in higher deposition potential which both AA measurements could be used for speciation of Cr (VI)/Cr (III) in salt waters.

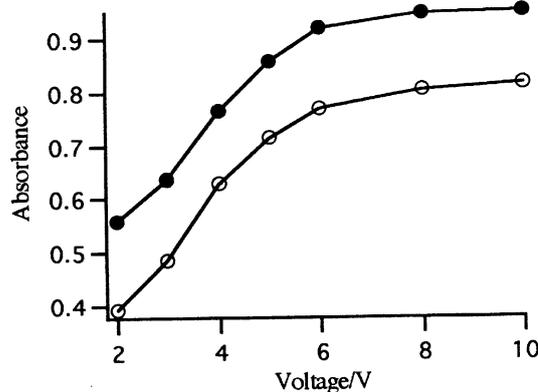


Figure 3. Plots of AA signals vs. the applied voltage, for 12 ppb Cr⁶⁺ (○) and Cr³⁺ (●) electrodeposited from 0.02% H₂SO₄ onto Pd substrate.

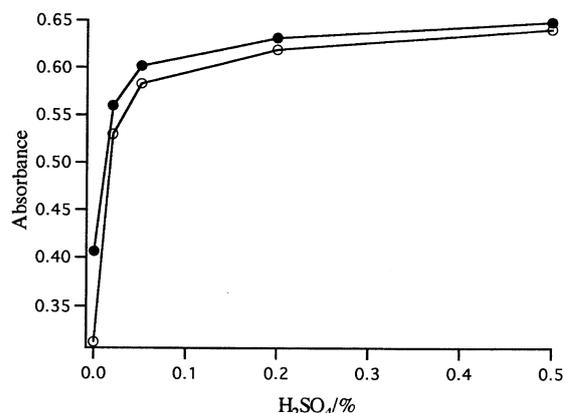


Figure 4. Plots of AA signals vs. H₂SO₄ concentration for 10 ppb Cr⁶⁺ (○) and Cr³⁺ (●) electrodeposited onto Pd-coated furnace.

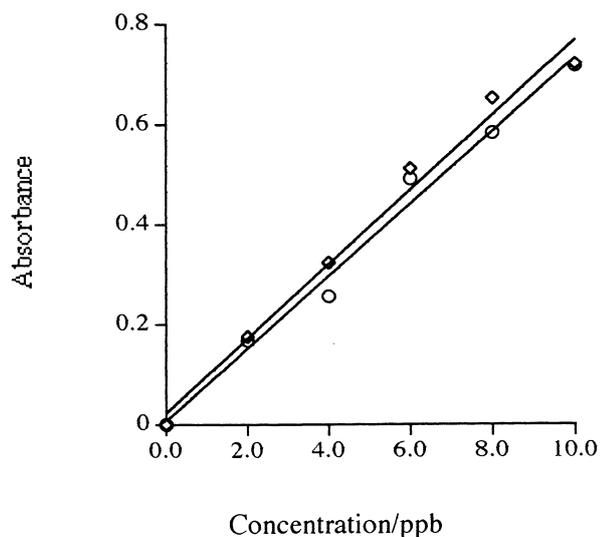


Figure 5. Calibration curves for Cr^{6+} (○) and Cr^{3+} (◇) conventionally deposited in 1% H_2SO_4 on the Pd-coated furnace.

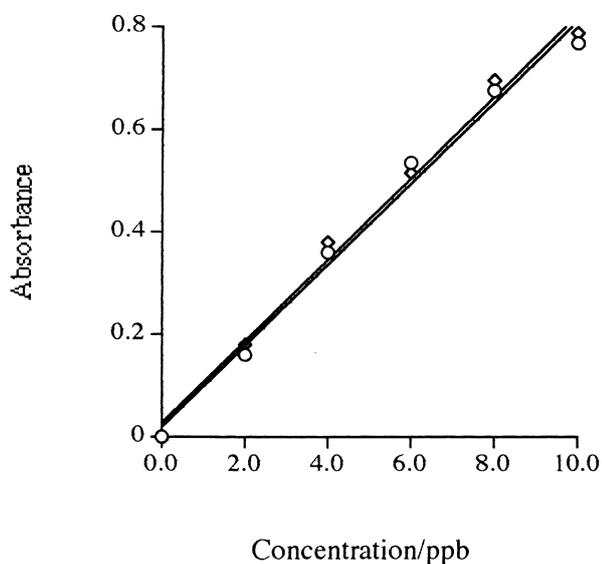


Figure 6. Calibration curves for Cr^{6+} (○) and Cr^{3+} (◇) electrodeposited from 0.5 M NaCl in 1% H_2SO_4 onto Pd-coated furnace at 10.0 V.

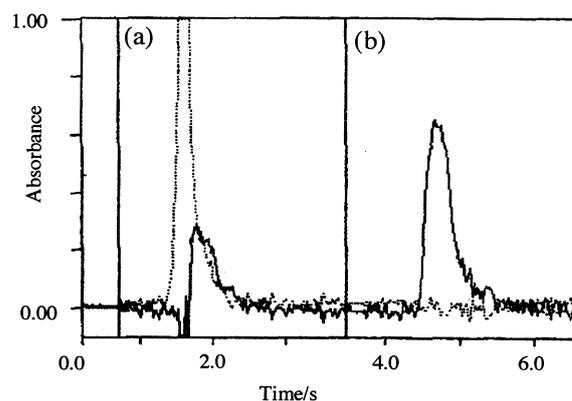


Figure 7. Typical AA signals (—) and background (...) measured at Cr 357.9 nm, for 0.5 M NaCl solution by: a) conventional ETAAS technique, b) ED-ETAAS technique.

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