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RESEARCH ARTICLE

Chemical Speciation of Chromium in Various Matrices in South African Terrestrial Water Using an Optimised Adsorptive Stripping Voltammetric Procedure

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Received 15 November 2000; Revised 2 April 2001;
Accepted 20 June 2001

Abstract

Optimization of analytical procedure for the determination of chromium (III)/(VI) speciation is described. A very sensitive adsorptive-catalytic stripping voltammetry method in the presence of diethylenetriaminepentaacetic acid (DTPA) is used for chromium speciation study in surface and ground water with in very different matrices.

The effects of various parameters (pH, ligand concentration, potential, collection time, equilibration time,) on the response are optimized. Concentration ratio of chromium (III)/(VI), and interferences from other metals and anions, typical for South African waters, are considered. Results for total chromium determination are compared with atomic absorption spectrometry (AAS) measurements.

Keywords Chromium speciation, waters, adsorptive stripping voltammetry.

1. Introduction

In South Africa main chromium waste materials are generated during the mining and production of chromium metal and ferroalloys, in the use of chromate solutions for electroplating and in the production of chromium pigments and dyes. Waste materials from these industries have been designated as hazardous due to their toxicity and leaching potential. Ground water contamination by chromium is a major problem in industrial areas. Typically chromium-containing wastes have been disposed of by discharging them into surface dams or lagoons and leakage from these into groundwater has been relatively common. All reported incidences of chromium-related groundwater contamination are of industrial origin.

The mobility of chromium in surface and groundwater depends on its solubility and its tendency to be absorbed by soils and aquatic species[1]. A number of different chromium species exist in water environments and the concentration and mobility of chromium depends strongly on its speciation characteristics.

In natural waters chromium species exist mainly in two different oxidation states, Cr (III) and Cr (VI). Its toxicity is a function of the oxidation state and aqueous concentration of species. Trivalent chromium is an essential element to mammals as it maintains glucose, lipid and protein metabolisms. In contrast, hexavalent chromium is carcinogenic and can diffuse as CrO_4^{2-} or $HCrO_4^-$ through cell membranes [1-4]. The chemistry of oxidation state change depends on pH and oxidation-reduction potential in natural waters [3.] For these reasons a considerable interest has been developed in the determination of chromium in environmental, industrial and clinical samples.
Reported analytical procedures involved separation[5-8], spectrophotometric[9-11] and electrochemical [12-44] methods.

Electroanalytical techniques, particularly adsorptive stripping voltammetry (AdSV), have been developed for measuring chromium sub-ppb concentration level. In addition to their sensitivity and selectivity, these methods have a great potential to be used *in situ* for chromium analysis in rich matrices of environmental water samples[45].

In AdSV a chelate of chromium with an organic ligand is adsorbed on a hanging mercury drop electrode under appropriate conditions. The reduction current of accumulated Cr(III)-L complex to Cr(II) is recorded. Cr(VI), which is reduced electrochemically to Cr(III) on the electrode when the potential is more negative than –0.05V (vs Ag/AgCl ref.electrode), gives rise to the peak current. The catalytic effect

caused by the nitrate ions enhances the measured signal. The mechanism of the reactions involved in the accumulation and stripping processes was studied previously [46-47]. The ligands used for complexing of chromium were: ethylenediaminetetraacetic acid (EDTA), diaminocyclohexanetetraacetic acid (DCTA), diethylenetriaminepentaacetic acid (DTPA)[41], bipyridine (BPY)[15, 34], diphenylcarbazide (DPCI) [25], cupferron (PIPES) [22, 24], ethylenediamine [26]. Cupferron and 2,2 bipyridine have been used for total chromium determination because both Cr(VI) and Cr(III) have identical stripping responses. EDTA, DPTA, Diphenylcarbazide, and ethylenediamine in acetate buffer have been employed in chromium redox speciation in water systems. Ethylenediamine has the lowest Cr (VI) detection range (0.035 µg/ml – 0.001 mg/ml) while the other three ligands have higher detection limits. The DPCI ligand is reported[25] to be unstable therefore requires daily preparation and is subject to Cl^- interferences with more than 0.020 mg/ml chloride causing complete disappearance of the signal. The highest sensitivity of determination both Cr (VI) and Cr (III) can be achieved by using of DPTA or EDTA as a complexing agents in nitrate supporting electrolyte in a mode of catalytic adsorptive stripping voltammetry. The broader and more distorted signals from EDTA make DPTA more sensitive and therefore preferred.

An electrochemical technique can selectively detect Cr (VI) with minimal disturbance to the natural equilibrium of the water matrix.The analytical procedure involving DTPA was previously optimised mainly for seawater samples[16, 19, 28, 36] and water samples with known described matrices[34, 38, 41]. In our laboratory we optimised the method and applied for the study of chromium speciation in industrial discharge waters, surface and ground water samples in different very rich matrices (high values of TDS – total dissolved solids) and different environmental conditions. AAS was used as a verification method for determination of total chromium concentration.

2. Experimental

2.1. Apparatus

Adsorptive stripping voltammetric measurements were performed using a Metrohm potentiostat/galvanostat PGSTAT 12 with General Purpose Electrochemical System software and a model 663VA stand (Metrohm). A multimode electrode (Metrohm, cat. No 6.1246.020) was employed as the working electrode in the hanging mercury electrode mode with the drop size 3. A silver/silver chloride (3M) electrode and

platinum electrode (both Metrohm) were used as reference and auxiliary electrodes, respectively. The stripping steps were recorded as a differential pulse voltammograms. All measurements were performed in a Metrohm jacketed glass vessel, equipped with a magnetic stirrer, and thermostatted at 298K from a constant temperature water bath. The pH of solutions was measured to +/- 0.001-pH unit with pHI 72-pH meter and combination glass electrode (cat. No 39536) both Beckman. High purity nitrogen was used for deaeration of the sample solutions.

A 500W high pressure UV mercury lamp with cooling water system was used for oxidation of chromium (III) to chromium (VI) in water samples. UV-irradiation was carried out for 3 hours.

AA Spectrophotometer with hydrides generation system (SpectrAA-10 with VGA-10 (Varian)) was used for the determination of total concentration of chromium. The WTW MultiLine SET-3 equipment for water analysis was used to record field measurements: pH, temperature, conductivity, oxidation-reduction potential (ORP) with platinum – Ag/AgCl (in 3M KCl) electrodes system, and dissolved oxygen (DO).

2.2. Reagents

All solutions were prepared using deionised water obtained by passing distilled water through a Milli-Q-water purification system.

All chemicals used were of analytical grade obtained from Aldrich and Merck.

2.3. Environmental Water Samples Collection and Treatment

The surface and ground water samples were collected from few sampling sites with different environmental conditions. They include samples from waters with small industrial pollution: depth profile samples from Emmarentia Dam in Johannesburg, samples from areas heavily affected by industry: surface and ground waters from Germiston wetland, and industrial waste water and discharge water samples from and around Brits chromium smelters.

The field measurements were performed for every sampling point during samples collection and included measurements of: pH, temperature, conductivity, redox potential and total dissolved oxygen.

All samples were collected into washed and conditioned PVC bottles according to commonly accepted sampling procedures [5, 48-50].

Samples for speciation analysis of chromium were not acidified. Collected samples were filtered immediately after coming back to laboratory (after maximum 1hour) and stored in a refrigerator at temperature $+4^0$C. Half of each sample was acidified and stored at the same temperature for analysis of total chromium concentration by AA-VGA spectrophotometry.

The determination of chromium (VI) concentration by AdSV was performed the same day or no later than the next day. AdSV was used to determine total concentration of chromium (as Cr (VI)) after oxidation of samples by exposure to UV radiation during 3 hours for each sample at neutral pH.

2.4. Procedure

For every sample or blank (deionised water) analysis a 10ml of sample and 2.5ml of supporting electrolyte solution and ligand solution were added into a water-jacketed (25^0C) voltammetric cell to maintain the final concentration of 0.2M acetate buffer, 0.45mM DTPA and 2.5M $NaNO_3$. The pH of solution in the voltammetric cell was adjusted to the optimized value using 40% w/v NaOH solution. The solution was then purged with nitrogen for 300s to remove dissolved oxygen and stood for an additional 600s to allow decay of peak of Cr(III)-DTPA complexes present in solution[36-38] . For Cr (VI) concentrations less than 0.0005 mg/l, an enrichment potential of –1.0 V was applied to a fresh mercury drop while the solution was still stirred. Following, usually, 30s preconcentration period and 10 s equilibration time the voltammogram was recorded by applying a negative differential pulse scan from –1.0 V to –1.4 V with a scan rate of 30 $mVs^{-1,}$ frequency 50Hz and pulse amplitude of 50 mV. The determination of Cr (VI) in each sample was achieved by three standards addition method. All measurements for the same sample were repeated at least three times. Samples with higher chromium concentration were diluted to maintain concentration in the linearity region (max.5 µg/l).

3. Results and discussion

The stable signals, highest sensitivity coupled with best analytical shape (reversibility 100-110 mV) of voltammograms were achieved when several experimental parameters were optimised. These parameters include the ligand concentration, deposition potential, deposition time, pH of the solution, the peak evolution time and nitrate concentration. The concentration of the nitrate, which amplifies the measured

signal, was taken as earlier reported [40, 41]. It is well known that in the presence of nitrate ions the response of Cr (III)-chelates shows noticeable enhanced in classical polarography as well as in differential pulse voltammetry [41, 42]. The assumption is that at sufficiently high positive potentials the Cr (II)-chelates formed by reduction are chemically oxidised in the presence of nitrates resulting in a catalytic current.

Effect of Ligand Concentration on a Catalytic Current

The dependence of the peak current on the DPTA concentration is presented in Fig. 1.

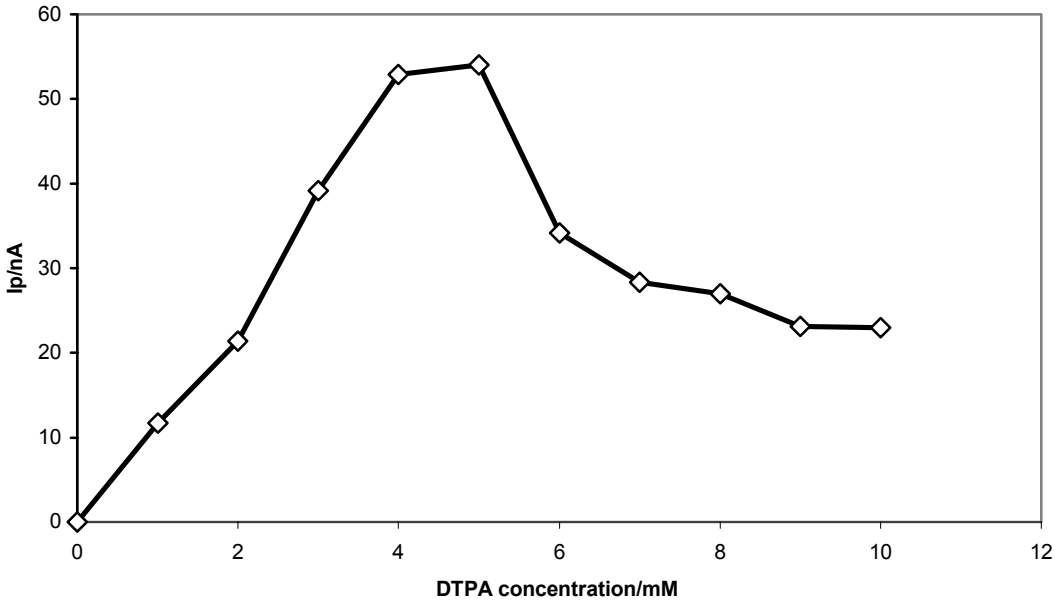

Figure 1 The dependence of peak current as a function of DTPA concentration for 5nM of Cr(VI) following a deposition of 30 s.

Variation of DPTA concentrations showed that the peak current of chromium(III), resulted from reduction of Cr(VI) on the working electrode surface, increased proportionally and attained relatively stable maximum value between 4.0 mM and 5.0 mM DPTA concentrations. The concentration value of 4.5 mM DPTA was chosen as the optimum value. The decrease of the peak height for chromium at higher concentrations of DPTA may be due to the formation of higher order complexes such as Cr (III)-$DPTA_2$ [16].

Dependence of Peak Current on Deposition Potential

The peak of the Cr-DPTA reduction at the HMDE in the presence of nitrate ions exhibits a remarkable dependence on the accumulation potential. (Fig. 2). The peak height increases with the negative increase of the adsorption potential until it reaches stable maximum value between –1.0 V and –1.2 V. The peak then decreases sharply afterwards.

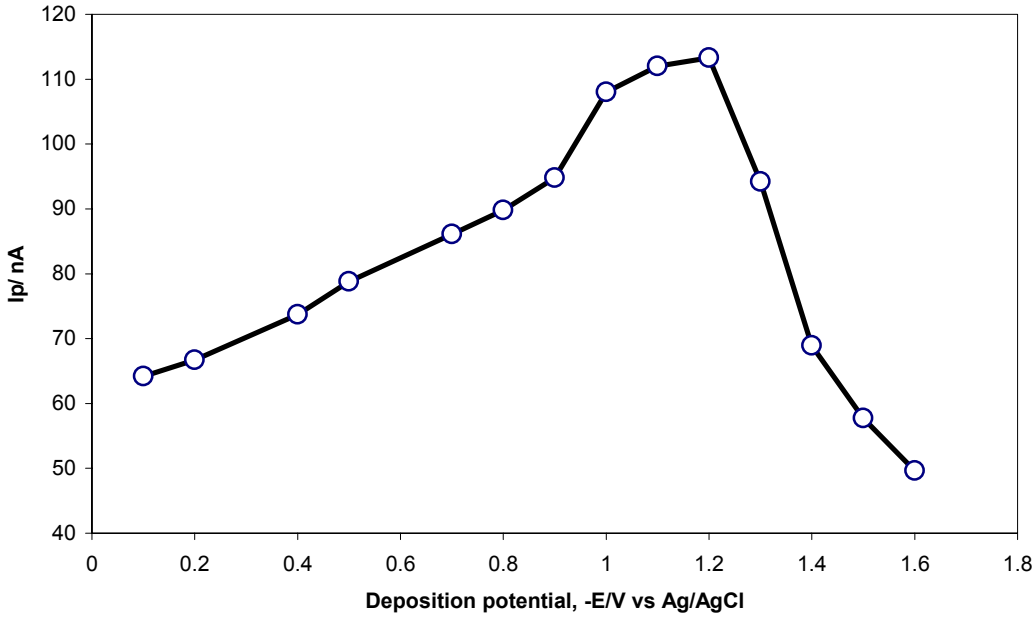

Figure 2 Effect of the deposition potential on Cr-DTPA complex peak current response. Cr(VI) concentration: 4nM, deposition time: 30s, scan rate: 30 mVs^{-1}, pulse amplitude of 50 mV, frequency: 50Hz. Stripping current recorded between –1.0 V and –1.4 V.

The respective reversibility also depends on deposition potential (Fig. 3). The literature has reported that the best reversibility of the electrochemical reaction involved in the Cr(III)-DPTA system is with a peak width in the range 92 mV to 110 mV [16, 19, 24]. The deposition potential of –1.2 V resulted in the highest current peak but with worse reversibility. The best stability and reproducibility (~110 mV) of the peak was achieved at –1.0 V. Therefore, this deposition potential was chosen as the optimum condition.

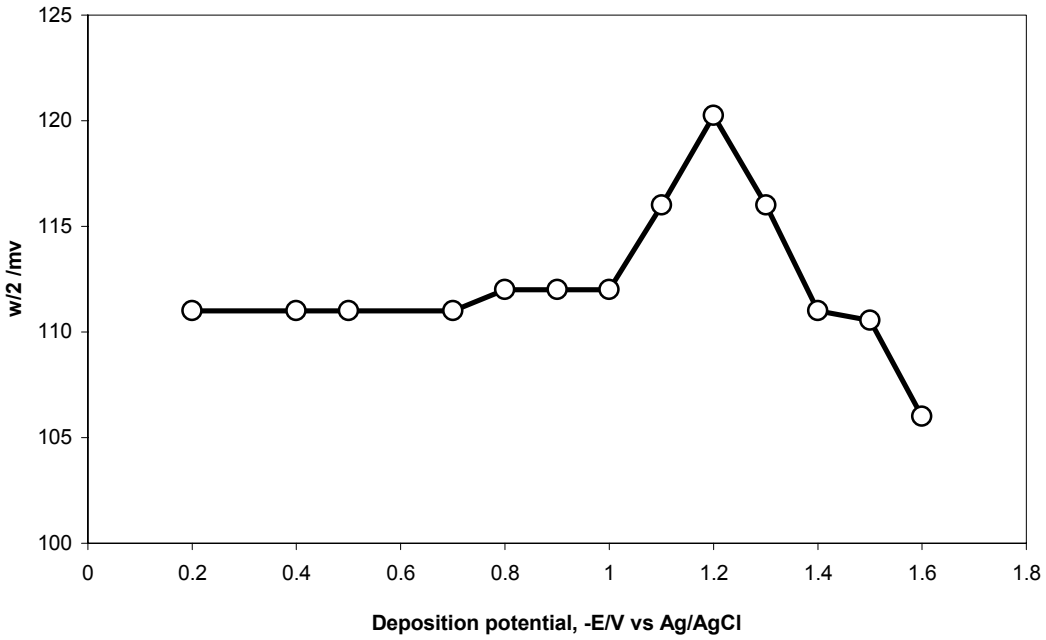

Figure 3 Dependence of reversibility (as a peak half width, w/2) on deposition potential. Deposition time: 30 s, Cr(VI) concentration: 4 nM.

Effect of pH on the Peak Current

The pH dependence of the peak height of the Cr(III)-chelate has been studied before[19, 42, 43]. Maximum of peak height reported was attained in the pH range 6.0 – 6.4.

In this work the reduction of Cr(III)-complexes at the HMDE achieved maximum peak height at pH 5.75 – 6.25. Below pH 4.60 and above pH 7.50 the reduction peak practically disappeared. Boussemart M. et al. [16] reported that the concentrations of H_2DPTA species from the calculated chemical speciation as function of pH in fresh waters reached a maximum at pH 6.45. This pH value agrees very well with the optimal sensitivities obtained in Fig. 4, suggesting that the H_2Y species of DPTA (H_2DPTA) is indeed responsible for the formation of the adsorptive complex with Cr(III) on the mercury drop. The amount of preconcentrated chromium, the electrochemistry of the Cr(VI)/Cr(III) couple and the general electron transfer rate strongly depends on the pH.

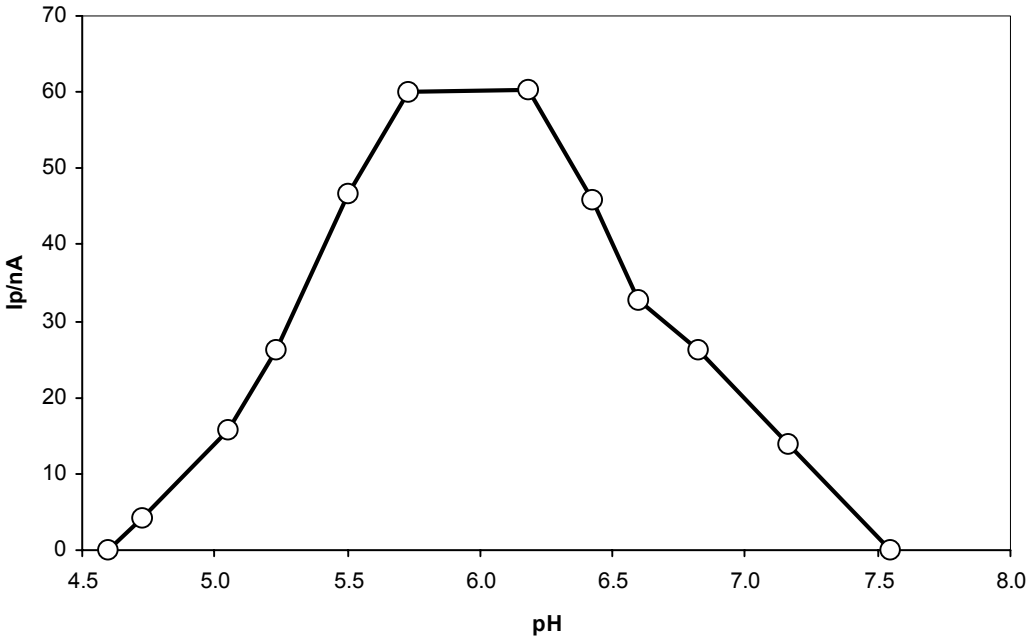

Figure 4 Dependence of pH on peak current. Solution: 5nM Cr(VI), 0.45mM DTPA.

Effect of Deposition Time on Peak Current

The effect of the accumulation time on peak height is presented in Fig. 5.

It was found that a 30 s preconcentration time is satisfactory for routine Cr(VI) determination at low concentrations (ppb). Increasing the preconcentration times to 120 s increases the overall sensitivity but the linearity of current response to concentration is compromised (Fig. 5). This is because increased accumulation times imply that increased surfactants concentrations are accumulated on the HMDE drop surface suppressing the current peak response to chromium concentration[19].

Peak Current Evolution with Time for a Solution of Cr(III) and Cr(VI)

The optimal equilibration time of at least 12 minutes with all other experimental parameters optimised is recommended as showed in Fig. 6. This time allows to selectively detect Cr(VI) in the presence of Cr(III) after the introduction of the ligand, DPTA. The Cr(VI)/Cr(III) ratios up to 1 : 10 were also investigated and no significant change was observed.

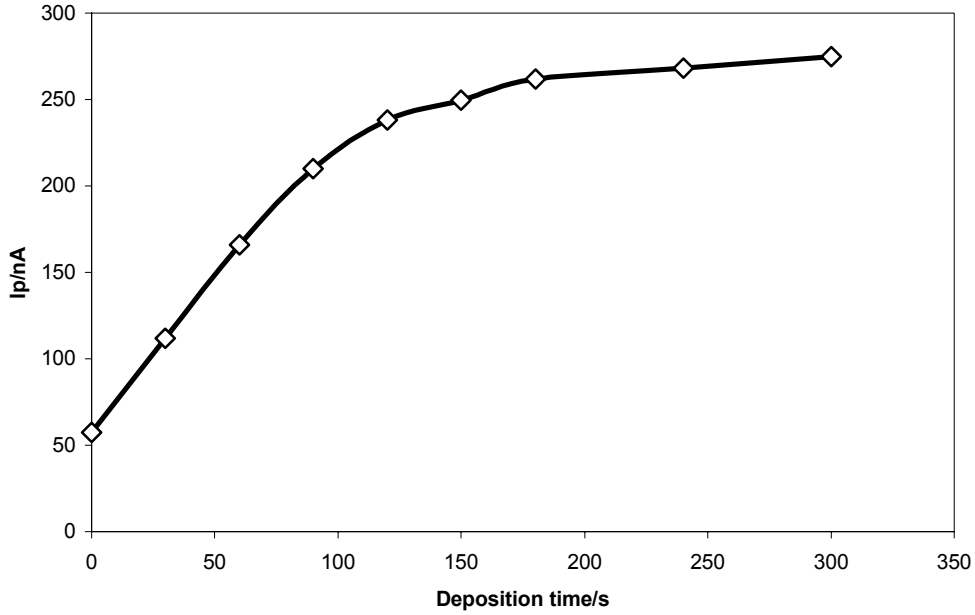

Figure 5 Dependence of peak current on deposition time. Cr(VI) conc.: 4nM, deposition potential: -1.0 V).

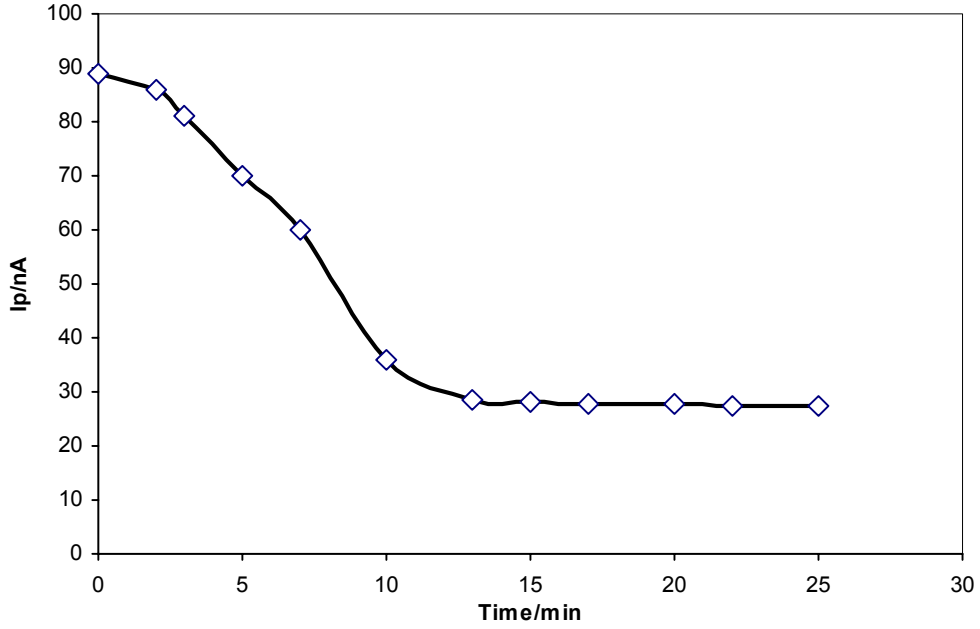

Figure 6 Peak current evolution with time for the solution of 2nM Cr(VI) and 6nM Cr(III) – (1:3 ratio).

Interferences

The interferences in adsorptive cathodic stripping voltammetry include competitive adsorption of surface-active compounds or other metal complexes on to the mercury drop electrode. Typically, natural waters contain 0.2 - 2.0 mg/l of compounds with surface-active effects similar to that of Triton X-100[44]. The inference effect by natural surface-active compounds may be minimized by lowering the deposition times and sample dilution when possible. This effect can also be eliminated by UV-radiation of the sample if total chromium is being determined. Metals can interfere if they form adsorptive electroactive complexes with a reduction peak near that of chromium. Boussemart M. et al.[16] observed no effect, by addition of cobalt (50 mM), nickel (50 mM), zinc (100 mM), titanium (100 mM), manganese (100 mM), iron (10 mM). Pereira et al. [35] report no interferences from iron (90 mM) and calcium (50 mM). We also determined that these concentrations did not suppress the chromium peak. The interfering effect of common anions was determined in our laboratory (Table 1). The concentrations of SO_4^{2-} (up to 5.0 g/l) and Cl^- (up to 1.0 g/l) showed no interfering effect on the recovery percentage of chromium.

Table 1 Recovery of Cr (VI) in the presence of sulphates and chlorides.

Anion conc. in the sample [g/l]	Cr(VI) added	Cr(VI) recovered	Recovery [%]	Ip [nA]
SO_4^{2-}				
0.0	1.00	0.99	99.4	65.1
0.5	1.00	0.99	99.1	64.8
1.0	1.00	1.00	100.0	65.4
4.0	1.00	0.99	98.8	64.6
5.0	1.00	1.00	99.8	65.3
Cl^-				
0.0	1.00	0.99	98.9	62.8
0.3	1.00	0.99	99.3	62.6
1.0	1.00	0.98	98.2	63.3

Further elimination of interferences is achieved due to the requirement of measurements in very diluted samples, in order to work in the linear range established, (Figure 7a,b).

The working concentration range of the optimized procedure is up to 10 µg/l Cr(VI). Under the optimized experimental conditions the Cr(III)-DPTA complex has a reduction potential at -1.22 V and a detection limit of 0.2 nM Cr(VI) was achieved in natural water samples.

The environmental water samples were analyzed through the standard addition method. When samples were spiked with Cr(VI), a mean recovery of about 99.0 % was achieved (Table 2). The optimized procedure is reproducible with mean relative standard deviations of current peak height less than 5 % (Table 3).

Table 2 Spike recoveries in environmental water samples.

Sample	Concentration of Cr(VI) [µg/l]					Recovery
	detected in sample	added	RSD [%]	recovered after spike	RSD [%]	[%]
Emmarentia dam						
(surface water)	7.558	0.500	0.93	8.058	0.97	100.0
(8.0m depth)	1.196	0.500	1.02	1.698	1.04	100.1
Germiston-wetland	0.000	0.500	0.86	0.478	1.12	95.6
Brits smelters area	0.729	0.500	1.06	1.218	1.08	99.1

NB . Presented data are averages from at least three experiments.

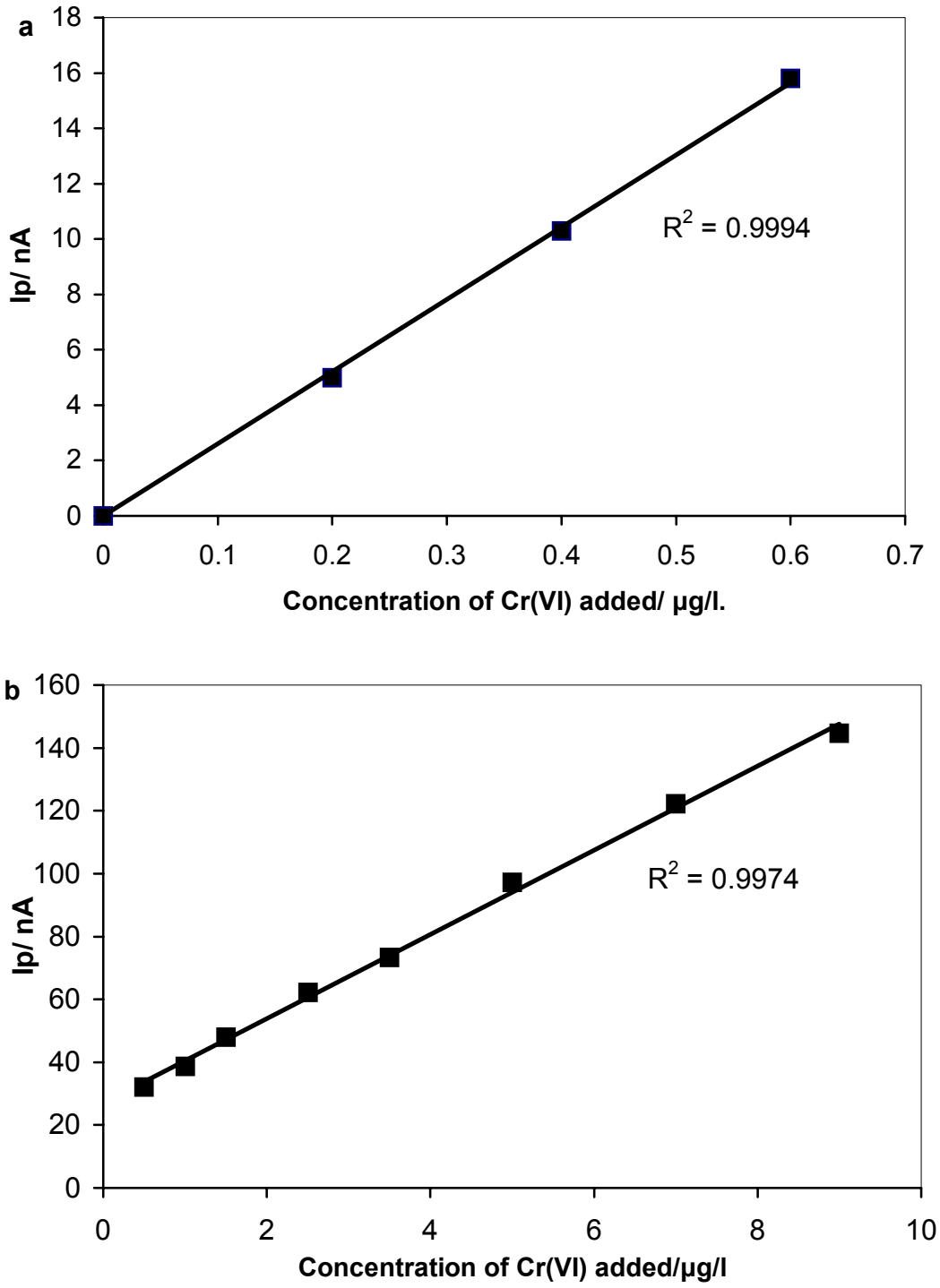

Figure 7 Linearity in the region of 0.2 – 9.0 µg/l. Cr(VI) standard addition to natural water samples: a). Ground water from Germiston wetland, b). Surface water from Emmarentia dam.

Table 3 Reproducibility of concentration measurements for the same sample.

Number of measurement replicates	Cr(VI) concentration	Ip	RSD
[n]	[ug/l]	[nA]	[%]
4	0.10	8.45 8.50 8.67 8.54	1.10
6	0.25	21.88 22.34 21.88 21.68 22.01 21.94	0.99
4	0.50	47.61 47.43 46.86 46.70	0.93

Application of Optimized Procedure for Chromium Speciation Analysis in Different Matrices of South African Waters

The results for the determination of chromium chemical speciation in environmental samples with different matrices are presented in Table 4. The field measurements including pH, temperature, conductivity, redox potential and dissolved oxygen are added for comparison of matrices.

The total chromium concentrations obtained from the optimized procedure are very comparative to respective total chromium concentration values from AAS. The field measurements reveal that the three sampling sites are, very varied in their matrices composition.

Table 4 The results for the determination of chromium chemical speciation in environmental samples with different matrices (Field measurements included for comparison of matrices).

Sample	pH	Temp.	ORP (vs. SHE)	Cond.	DO	Cr (VI) by AdSV	Cr (III) by AdSV	Cr tot. by AdSV	Cr tot. by AAS	d_i	t-paired test for 95% confidence level
		[^{0}C]	[mV]	[mS/cm]	[mg/l]						
A: Emmarentia Dam, depth profile [m] *(samples collected: 12.12.1999)*											
						[µg/l]	[µg/l]	[µg/l]	[µg/l]		
	8.20	23.2	605	0.306	5.59	0.07	9.19	9.26	9.30	-0.04	
1	8.12	23.0	606	0.309	5.52	1.31	7.56	8.87	8.93	-0.06	
2	8.04	22.5	603	0.310	5.40	1.88	4.82	6.70	6.71	- 0.01	
3	7.93	21.9	604	0.309	5.27	1.55	5.44	6.99	7.10	-0.11	$d_{ave.}$=-0.03$_5$ s_d= 0.05$_5$ $t_{calc.}$=2.02 $t_{tab.}$= 2.262
4	7.79	21.6	604	0.309	4.48	0.04	7.45	7.49	7.55	-0.06	
5	7.62	21.4	605	0.310	3.20	n d	7.48	7.48	7.49	-0.01	
6	7.16	20.5	336	0.327	0.84	n d	8.17	8.17	8.23	-0.06	
7	7.12	19.8	263	0.350	0.42	n d	9.29	9.29	9.20	0.09	
8	7.07	19.5	245	0.376	0.26	n d	10.98	10.98	10.99	-0.01	
8.5	6.92	19.1	205	0.402	0.18	n d	10.95	10.95	11.03	-0.08	
B: Germiston wetland *(samples collected: 14.01.2000)*											
Surface water											
1s	3.20	16.3	551	6.64	4.35	n d	100.57	100.57	101.66	-1.09	
1	6.26	15.3	230	0.37	5.31	n d	57.62	57.62	57.18	0.44	d_{ave}=-0.09$_7$ s_d= 0.05$_1$ $t_{calc.}$= 0.51 $t_{tab..}$= 2.447
2s	3.14	16.5	540	4.62	4.51	n d	89.03	89.03	89.34	-0.31	
2	4.63	15.1	466	0.53	5.40	n d	59.12	59.12	58.82	0.30	
3	4.61	15.2	441	0.58	5.11	n d	59.68	59.68	59.81	-0.13	
4	4.57	15.0	466	0.62	5.12	n d	58.21	58.21	58.23	-0.02	
5	4.53	15.0	463	0.60	5.16	n d	58.58	58.58	58.45	0.13	
											NB: 1s, 2s - seepage water
B: Germiston wetland *(samples collected: 14.01.2000)* (cont.)											
Ground water *(1 m depth)*											
1a	3.40	17.6	500	6.33	2.06	n d	67.15	67.15	67.14	0.01	d_{ave}=-0.00$_5$ s_d= 0.14$_2$ $t_{calc.}$= 0.07 $t_{tab..}$= 3.182
1b	3.38	18.3	516	5.70	2.78	n d	45.65	45.65	45.75	-0.10	
2a	3.76	17.6	490	3.69	1.87	n d	83.57	83.57	83.69	-0.12	
2b	3.32	18.3	568	4.16	2.85	n d	67.14	67.32	67.13	0.19	
											NB: a - lower ground level, b - higher ground level from surface water table.

Table 4 (cont.) The results for the determination of chromium chemical speciation in environmental samples with different matrices (Field measurements included for comparison of matrices).

Sample	pH	Temp.	ORP (vs. SHE)	Cond.	DO	Cr (VI) by AdSV	Cr (III) by AdSV	Cr tot. by AdSV	Cr tot. by AAS	d_i	t-paired test for 95% confidence level
		[^{0}C]	[mV]	[mS/cm]	[mg/l]						
C: Brits area; chromium smelters *(samples collected:15.03.2000)*											
						mg/l	mg/l	mg/l	mg/l		
slimes	8.74	27.30	225	13.36	5.40	0.73	32.46	33.19	33.49	-0.30	
water	9.03	27.30	234	0.40	5.10	0.41	5.23	5.65	5.35	0.30	d_{ave}=-0.00$_8$
overflow	8.05	29.40	225	3.12	5.10	0.82	0.94	1.76	1.79	-0.03	s_d=0.19$_0$
dam	8.13	28.20	250	0.87	6.30	0.33	1.54	1.88	1.89	-0.01	$t_{calc.}$= 0.14
dam	8.47	29.30	264	1.16	5.50	0.64	0.31	0.95	0.96	-0.01	$t_{tab..}$= 2.571
drinking	7.61	28.50	315	0.43	5.60	0.00	0.12	0.12	0.12	0	

n d - not detectable

d_i - individual differences between results for Cr tot. measured by AdSV and AAS for each sample, $d_{ave.}$ -average difference between results for Cr tot. measured by AdSV and AAS, n - number of pairs of data

$s_d = [\sum(d_i - d_{ave})^2 / _{n-1}]^{1/2}$, $t_{calc.} = (d_{ave.} / s_d)\, n^{1/2}$

4. Conclusions

The optimized catalytic adsorptive cathodic stripping voltammetric method has been applied successfully for the study of chromium speciation in industrial discharge waters, surface and ground water samples with different, very rich, matrices and in different environmental conditions. It proofs to be a very sensitive and very selective method for study of chromium speciation. The method is very resistant to many interferences from high concentration of cations and anions, especially typical for industrially polluted waters like acid mine drainage waters with very high concentration of iron, calcium and sulphate. AdSV can be successfully used for direct measurements without samples special treatment, like cost effective and time-consuming separation, extraction or preconcentration which make it much quicker and cheaper. The direct measurement minimizes also changes in chromium speciation, which is often the case while using other more disturbing methods. The optimized method was successfully applied for analysis of chromium speciation in South African natural waters and wastewater in extreme conditions.

Acknowledgements

Financial support by University of the Witwatersrand and the National Research Foundation is gratefully acknowledged.

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