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Determination of Chromium(VI) at Trace Level by Adsorptive Stripping Voltammetric

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A new method is proposed for the determination of Cr(VI) by differential pulse adsorptive stripping voltammetry using 4-(2-pyridylazo)resorcinol 100 nM and diethylenetriammine pentaacetic acid as complexing agents. The base electrolyte contains 100 nM 4-(2-pyridylazo)resorcinol and 0.625 M of $NaNO_3$ and 0.025 M of CH_3COONH_4 and 0.0125 M of diethylenetriammine pentaacetic acid, at pH = 6.2; under the optimum conditions. The peak current (Ip) is proportional to the concentration of Cr(VI) over the range 0.0288-6.00 nM. The lowest detected was 0.0481 nM. The relative standard deviation did not exceed ± 4.5 %. The method is highly selective and sensitive and has been applied to the determination of Cr(VI) in some vegetables.

Key Words: Chromium(VI), Differential pulse adsorptive stripping voltammetry.

INTRODUCTION

Chromium exists in +3 and +6 oxidation states. The major toxic effects of Cr(VI) are chronic ulcers, dermatitis, corrosive reaction in nasal septum and local effects in lungs[1].

Tanaka and Ito[2] 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. There are some methods which use of nitrate ions as catalytic agents like cupferron[3], diphenylcarbazide[4] and polyamino acids, like diethylenetriamine pentaacetic acid[5] and TTHA[6]. Cr(VI) is reduced at the surface of the electrode to Cr(III), which immediately forms a complex with TTHA and then it gets reduced at the surface of the electrode to Cr(II) during a cathodic scan[7]. The reduction product is reoxidized by nitrate ions to enhance the peak current by catalytic action[8]. Another study has made a comparative account of square wave *versus* the differential pulse voltammetric behavior of Cr(VI)-TTHA. Another study has reported the use of diethylenetriamine pentaacetic acid for speciation studies of chromium[9], where the addition of Cr(VI) or Cr(III) to a solution containing diethylenetriamine pentaacetic acid in acetic-acetate medium (pH 6.2) gave a rise to the appearance of a single reduction peak at -1.22 V. This peak corresponds to the electrochemical reduction of the Cr(III)-diethylenetriamine pentaacetic acid complex formed by the Cr(III) arising from the electrochemical reduction of the Cr(VI) during the accumulation stage. The fact that the single reduction peak leads to the conclusion that under these experimental conditions no complex is formed between the Cr(VI) and the diethylenetriamine pentaacetic acid or if it is formed, it is not electrochemically active. The reduction current of the diethylenetriamine pentaacetic acid complex formed from Cr(III) aquo complexes were not stable and gradually diminished in height. However, Cr(III)-diethylenetriamine pentaacetic acid complexes formed from Cr^{3+} ions obtained by electrochemical reduction of Cr(VI) gave stable and well-defined reduction peaks[10-13].

In the present study, the reaction of Cr(VI) at trace levels, by differential pulse adsorptive stripping voltammetry and using a mixture of 4-(2-pyridylazo)resorcinol (PAR) and diethylenetriamine pentaacetic acid (DTPA) as complexing agents was studied and this method was applied to determine Cr(VI) in some vegetables.

EXPERIMENTAL

Differential pulse adsorptive stripping voltammetric (DPAdSV) studies were carried out using Metrohm 757 VA. A Metrohm 757 VA stands with a multi-mode electrode (MME) operating in the hanging mercury drop electrode (HMDE) as a working electrode, an auxiliary platinum electrode and a reference electrode, double junction type, Ag/AgCl saturated with a 3.0 M KCl solution and the three-electrode cell were used (Germany). Very pure nitrogen gas (99.999 %) was used for de-oxygenation. pH meter from radiometer company model ion check was used to study and monitor the pH effects.

All of the chemicals were used from the AR grade. The solutions were prepared in double-distilled water. A stock

standard solutions of Cr(VI) were prepared by dissolving the adequate amount of CrO_3 in water. Solution of the chelating agents were prepared by dissolving the appropriate quantities of 4-(2-pyridylazo)resorcinol (PAR) and diethylenetriamine pentaacetic acid (DTPA) in water.

General procedure: The base solution is used for analytical determination of chromium with 4-(2-pyridylazo)resorcinol. This solution contains 0.5 mL of 0.1 mol L^{-1} ammonium-acetate (the pH was adjusted to pH 6.0 ± 0.2 with 0.1 M CH_3COOH solution,100 µL of 10^{-5} mol/L^{-1} of 4-(2-pyridylazo)-resorcinol[14]. Another base solution with diethylenetriamine pentaacetic acid contains (0.1 mol L^{-1} of ammonium acetate, 0.05 mol L^{-1} of diethylenetriamine pentaacetic acid and 2.5 mol L^{-1} of sodium nitrate, the pH was adjusted to 6.2 ± 0.1, using NaOH). But when using a mixture of 4-(2-pyridylazo)resorcinol and diethylenetriamine pentaacetic acid contains 100 µL of 10^{-5} mol/L^{-1} of 4-(2-pyridylazo)-resorcinol and 2.5 mL of solution 0.1 mol L^{-1} of ammonium acetate, 0.05 mol L^{-1} of diethylenetriamine pentaacetic acid and 2.5 mol L^{-1} of sodium nitrate, the pH was adjusted to 6.0 ± 0.2, using NaOH. Then it was diluted to a total volume of 10 mL. When using 4-(2-pyridylazo)resorcinol, a waiting time of 7 min is required after each addition of chromium(VI) to the solution. The solution was deaerated with nitrogen for 5 min before actual recording. In all cases, blank recordings were performed and necessary corrections were made in the calculations (Fig. 1).

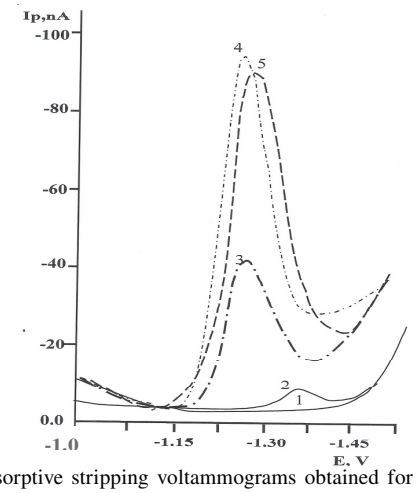

Fig. 1. Adsorptive stripping voltammograms obtained for Cr(VI) in the presence of: (1) 0.625 mol/L $NaNO_3$ + 0.025 M CH_3COONH_4, (2) 5 mMCH_3COONH_4 + 10^{-7} M 4-(2-pyridylazo)resorcinol; 4nM Cr(VI), (3 and 4) 1 + 0.0125 M diethylenetriamine pentaacetic acid + 4nM Cr(VI), (5) 1 + 10^{-7} M 4-(2-pyridylazo)resorcinol + 0.0125 M diethylenetriamine pentaacetic acid + 0.4 nM Cr(VI), (E_{dep}, -1.1 V; t_{dep}, 120 s), T = 45 ºC curves (1, 2, 4, 5), T = 30 ºC (curve 3)

RESULTS AND DISCUSSION

Effect of concentration of the electrolyte: CH_3COONH_4 was selected as a base electrolyte that gives a smooth baseline for the entire potential range of studies. The concentration of CH_3COONH_4 was varied from 0.5-10 mM while other parameters were kept constant. 5 mM of CH_3COONH_4 was selected as a supporting electrolyte.

Effect of concentration of 4-(2-pyridylazo)resorcinol: To a solution containing 5 mM of CH_3COONH_4 and 480.7 nM of Cr(VI) solution with pH 6.0, varying concentrations of 4-(2-pyridylazo)resorcinol were added in the range 20-200 nM (Fig. 2). The peak current increased up to a ligand concentration of 100 nM and remained constant above this value.

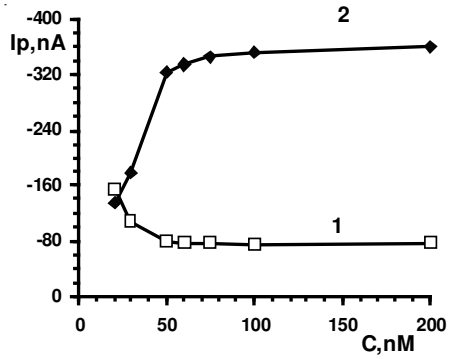

Fig. 2. Effect of the concentration of 4-(2-pyridylazo)resorcinol on the Ip in 5 mM CH_3COONH_4 solution (pH 6.0), with 480.7 nM Cr(VI). 1-Ip, 4-(2-pyridylazo)resorcinol, 2-Ip, Cr(VI)

Effect of time: The effect of time for formation complex was studied from 0-10 min the time was selected at 7 min which had been the best time.

Effect of pH: The pH was varied from 4.5-6.5 using diluted ammonia and diluted CH_3COOH (0.1 M) solutions. The dependence of peak current (Ip) on pH is shown in Fig. 3. The best results with respect to enhancement, shape and reproducibility of the peak current were obtained in 5 mM of ammonuim acetate buffer solution in pH = 6 by using DPAdSV method.

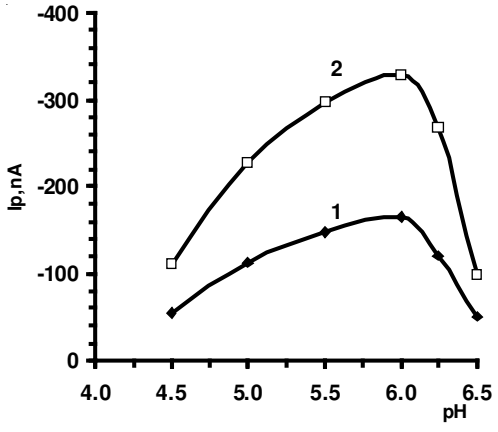

Fig. 3. Effect of the pH on Ip in the presence of 5 mM CH_3COONH_4, 0.1 µM 4-(2-pyridylazo)resorcinol, with Cr(VI) (1) 240.3 nM, (2) 480.7 nM

Effect of accumulation potential: An adsorptive accumulation of the complex was carried out at different potentials from -0.2 to -1.4 V. The peak current was found to be maximum for an accumulation potential of -1.1 V. Hence, this potential was selected for further analysis. The variation of the peak current with the accumulation potential is shown in Fig. 4.

Effect of the accumulation time: An adsorptive accumulation of the complex was carried out for different periods from 0-160 s. Initially, there was an increase in the peak current with the accumulation time. However, equilibrium was reached in about 120-160 s (Fig. 5).

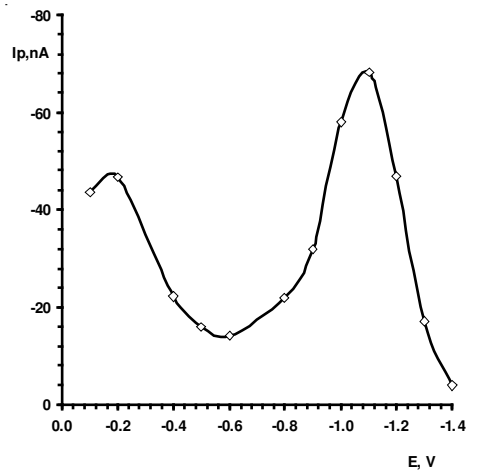

Fig. 4. Effect of the accumulation potential on the Ip in the presence of 5 mM CH_3COONH_4, 0.1 μM 4-(2-pyridylazo)resorcinol, at (pH 6.0), $C_{Cr(VI)}$ 480.7 nM

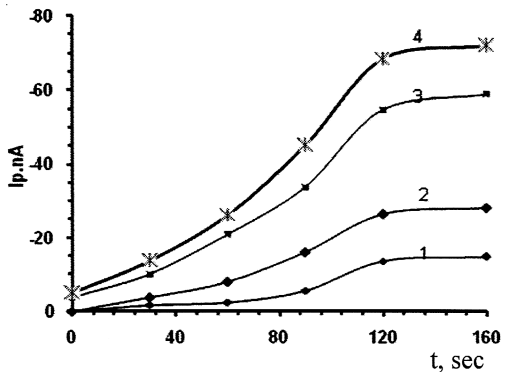

Fig. 5. Effect of the accumulation time (t) on the Ip in 05 mM CH_3COONH_4, 0.1 μM 4-(2-pyridylazo)resorcinol solution (pH 6.0) with Cr(VI): (1) 96.15 nM, (2) 192.3 nM, (3) 384.6 nM, (4) 480.7 nM

Effect of pulse amplitude: The effect of pulse amplitude on DPP polarograms using HMDE for Cr(VI) in ammonium acetate solution pH = 6 was studied. The peak current Ip increases proportionally to the increasing of pulse amplitude up to the value 100 mV. Therefore the value of pulse amplitude 100 mV was chosen for the highest and sharp peak.

Effect of temperature studies: The effect of temperature was studied on Ip for the adsorptive of Cr(VI) on HMDE, in the range between 25-50 ºC. It is noticed that the Ip was being increased with the elevation of temperature up to 45 ºC and then it was being decreased. It is also noticed that the peak potential Ep was being decreased from (-1.43. to -1.36 V) with the elevation of temperature from 25-35 ºC, then the Ep was being stable with the elevation from 35-45 ºC and finally the Ep was being decreased (Fig. 6). So, the 45 ºC was the best temperature, because it has a high sensitivity Ip and stable Ep.

Effect of diethylenetriamine pentaacetic acid and 4-(2-pyridylazo)resorcinol for determination of Cr(VI): Each complexing agent, 4-(2-pyridylazo)resorcinol and diethylenetriamine pentaacetic acid with Cr(VI) 4 nM was studied alone and a mixture of them with Cr(VI) 0.4 nM was studied. As a result, only one reduction peak was observed at -1.36 and -1.228 V for both 4-(2-pyridylazo)resorcinol and diethylenetriamine pentaacetic acid, respectively and at -1.284 V for the mixture. The current peak of Cr(VI) with

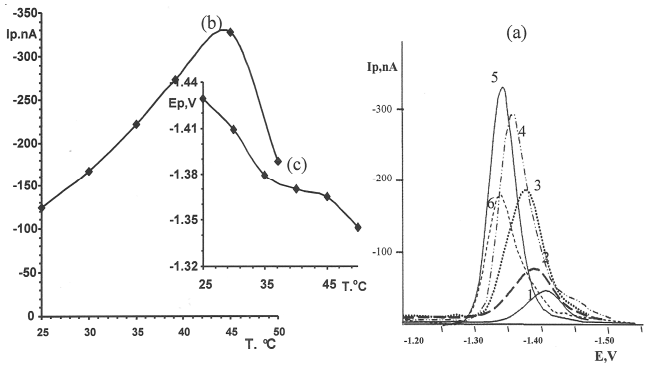

Fig. 6. Effect of temperature on the Ip in 0.05 mM CH_3COONH_4 + 0.1 μM 4-(2-pyridylazo)resorcinol solution at pH 6.0, $C_{Cr(VI)}$ = 480.7 nM, t = 120 s, Ep = -1.1 V (a): (1) 25 ºC, (2) 30 ºC, (3) 35 ºC, (4) 40 ºC, (5) 45 ºC, (6) 50 ºC, (b) Ip = f(T), (c) Ep = f(T)

diethylenetriamine pentaacetic acid was being increased as the temperature was raised from 30-45 ºC. However the current peak of diethylenetriamine pentaacetic acid and 4-(2-pyridylazo)resorcinol mixture with Cr(VI) was increased more than using each agent alone at 45 ºC.

Description: By a chemical reaction, 4-(2-pyridylazo)-resorcinol formed complex with Cr(VI) after 7 min of adding, then the resulting complex was transformed to analytical cell. The adsorbed Cr(VI)-4-(2-pyridylazo)resorcinol was reduced electrochemically to Cr(III) during the accumulation potential stage. In the presence of diethylenetriamine pentaacetic acid, these free Cr(III) formed a complex with diethylenetriamine pentaacetic acid on HMDE. A highly sensitive and sharp peak was appeared as a result of the reduction of Cr(VI) in the complex 4-(2-pyridylazo)resorcinol-Cr(VI) and the formation of a complex between Cr(III) and diethylenetriamine pentaacetic acid.

Calibration curves: Calibration curves for the determination of Cr(VI) by DPAdSV using 4-(2-pyridylazo)resorcinol, diethylenetriamine pentaacetic acid and 4-(2-pyridylazo)-resorcinol + diethylenetriamine pentaacetic acid as complexing agent at pH = 6.2 were studied. Only one peak was observed, the peak current (Ip) is proportional to the concentration of Cr(VI) over the ranges 0.96-288.5 nM using 4-(2-pyridylazo)-resorcinol ($y = 1.151x - 0.233$, $R^2 = 0.9996$); 0.192 to 30 nM using diethylenetriamine pentaacetic acid ($y = 23.12X - 2.555$, $R^2 = 0.9996$) and 0.023-6.000 nM using 4-(2-pyridylazo)resorcinol + diethylenetriamine pentaacetic acid ($y = 198.1X + 5.474$, $R^2 = 0.9994$), y: Ip, nA and X: $C_{Cr(VI)}$, nM). Table-1. The limits of quantifying Cr(VI) were 0.961, 0.481 and 0.0481 nM with the relative standard deviation (RSD) of ±4.6, ±5.2 and ±4.5 % using 4-(2-pyridylazo)-resorcinol, diethylenetriamine pentaacetic acid and 4-(2-pyridylazo)resorcinol + diethylenetriamine pentaacetic acid, respectively.

Applications: Determination of chromium, in some vegetables (cauliflower, radish and cabbage) by using differential pulse adsorptive stripping voltammetry with 4-(2-pyridylazo)-resorcinol and diethylenetriamine pentaacetic acid as complexing agents in presentacetate buffer of pH 6.2 and hanging dropping mercury electrode (HMDE) were proceeded. The results of quantitative analysis for chromium were calculated by standard addition methods, Table-2.

TABLE-1
EVALUATION OF ACCURACY AND PRECISION FOR DETERMINATION OF THE Cr(VI) WITH 4-(2-PYRIDYLAZO)RESORCINOL, DIETHYLENETRIAMMINE PENTAACTIC ACID AND MIXTURE OF 4-(2-PYRIDYLAZO)RESORCINOL AND DIETHYLENETRIAMMINE PENTAACTIC ACID ON HMDE BY DPADSV

Complexing agents	$C_{Cr(VI)}$ taken (nM)	$C_{Cr(VI)}$ found, $\bar{x}$ (nM)	SD (nM)	Anal. standard error, $\frac{SD}{\sqrt{n}}$ (nM)	Confidence limits $\bar{x} \pm \frac{SD}{\sqrt{n}} t$ (nM)	RSD (%)
4-(2-Pyridylazo)-resorcinol	0.9610	0.9650	0.04440	0.01990	0.9650 ± 0.05500	4.6
	1.9250	1.9250	0.07890	0.03530	1.9250 ± 0.09800	4.1
	4.8070	4.8300	0.19320	0.08640	4.8300 ± 0.23980	4.0
	9.6150	9.6260	0.33690	0.15070	9.6260 ± 0.41830	3.5
	19.2500	19.2500	0.61600	0.27500	19.2500 ± 0.76500	3.2
	48.0700	48.1800	1.25300	0.56000	48.1800 ± 1.55600	2.6
	96.1500	96.2200	2.21300	0.99000	96.2200 ± 2.74800	2.3
	192.3000	192.3000	3.84600	1.72000	192.3000 ± 4.77500	2.0
	288.5000	289.3300	5.20800	2.32900	289.3300 ± 6.46600	1.8
Diethylenetriammine pentaactic acid	0.1950	0.1880	0.01090	0.00490	0.1880 ± 0.01350	5.9
	0.4810	0.4780	0.02490	0.01130	0.4780 ± 0.03090	5.2
	0.9610	0.9610	0.04320	0.01930	0.9610 ± 0.05360	4.5
	1.9250	1.9200	0.07680	0.03430	1.9200 ± 0.09530	4.0
	4.8070	4.7850	0.16870	0.07540	4.7850 ± 0.20940	3.6
	9.6150	9.6200	0.37840	0.16920	9.6200 ± 0.46980	3.2
	19.2500	19.3200	0.54100	0.24190	19.3200 ± 0.67170	2.8
	48.6700	48.2200	1.20600	0.53940	48.2200 ± 1.49720	2.5
	96.1500	96.2000	2.20900	0.98790	96.2000 ± 2.74240	2.4
	192.3000	192.000	4.42300	1.97810	192.0000 ± 5.49120	2.3
	288.5000	288.3500	5.76700	2.57920	288.3500 ± 7.15980	2.0
	307.7500	308.8000	5.55800	2.48570	306.5600 ± 6.90030	1.8
4-(2-Pyridylazo)resorcinol + Diethylenetriammine pentaactic acid	0.0288	0.0300	0.00016	0.00007	0.0300 ± 0.00020	5.4
	0.0481	0.0485	0.00218	0.00097	0.0485 ± 0.00269	4.5
	0.0961	0.0950	0.00399	0.00178	0.0950 ± 0.00495	4.2
	0.1950	0.1940	0.00740	0.00340	0.1940 ± 0.00920	3.8
	0.4810	0.4810	0.01640	0.00730	0.4810 ± 0.02040	3.4
	0.9610	0.9640	0.02890	0.01290	0.9640 ± 0.03590	3.0
	1.9250	1.9200	0.05380	0.02410	1.9200 ± 0.06680	2.8
	2.8840	2.8600	0.07150	0.03200	2.8690 ± 0.08880	2.5
	3.8460	3.8400	0.08830	0.03950	3.8400 ± 0.10960	2.3
	4.8070	4.7850	0.09570	0.04280	4.7850 ± 0.11880	2.0
	6.0000	5.9800	0.10760	0.04810	5.9800 ± 0.13360	1.8
	7.6920	7.6680	0.19170	0.08580	7.6680 ± 0.23800	2.5

n = 5, t = 2.776.

TABLE-2
DETERMINATION OF CHROMIUM IN CAULIFLOWER, RADISH AND CABBAGE BY USING DPADSV METHODS ON HMDE AT pH = 6.2

Vegetable	$\bar{x}$ (ppm)	RSD (%)
Cauliflower	0.660-0.800	2.4-1.8
Radish	0.680-0.834	2.5-2.0
Cabbage	0.480-0.520	2.6-2.2

Conclusion

Differential pulse adsorptive stripping voltammetry for determination of Cr(VI), with 4-(2-pyridylazo)resorcinol and diethylenetriamine pentaacetic acid as complexing agents in present of acetate buffer of pH = 6.2 were studied. Only one peak was observed at -1.284 V, the peak current (Ip) is proportional to the concentration of Cr(VI) over the ranges from 0.96-289.33 nM by using 4-(2-pyridylazo)resorcinol, 0.1923-306.560 nM by using diethylenetriamine pentaacetic acid and 0.023-6.000 nM by using 4-(2-pyridylazo)resorcinol + diethylenetriamine pentaacetic acid. The limits of Cr(VI) quantifying were 0.961, 0.481 and 0.0481 nM, respectively, with the relative standard deviation (RSD) of ±4.6, ±5.2 and ±4.5 % by using 4-(2-pyridylazo)resorcinol, diethylenetriamine pentaacetic acid and 4-(2-pyridylazo)resorcinol + diethylenetriamine pentaacetic acid, respectively. Therefore the proposed methods can be used for applied to the determination of Cr(VI) in some vegetables.

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