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Determination of Chromium(VI) by Differential-Pulse Polarography with a Sodium Borate Supporting Electrolyte

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A suitable choice of supporting electrolyte medium for trace level determinations of chromium(VI) by differential pulse polarography is described. A comparative study suggests that sodium borate buffer is superior to ammonium acetate, ammonium tartrate, and especially to NaF which was recently known to be one of the most proper medium for the purpose. With 0.01 M borate, the best combination of high sensitivity, well-defined base line, and freedom from common interferents was attained. With 5.0×10^{-7}M Cr(VI), tenfold excesses of Cu(II) and Fe(III), and a five hundred-fold excess of Cl^- do not change the peak current by more than about 1%. And the detection limit was 5.0×10^{-8}M Cr(VI).

Introduction

The development of an analytical method suitable for the trace level Cr(VI) species is a continuing problem. Because Cr(VI) has a significantly higher toxicity than Cr(III),[1] it is desirable to perform trace level determinations, which yield directly the former species. Atomic absorption spectrometry has the required sensitivity, but it does not distinguish between the oxidation states unless it is coupled with a separation step.[2]

Polarographic techniques, however, can determine directly Cr(VI) in the presence of Cr(III). Most of the recent work on this subject has focused on the differential-pulse

polarography (DPP) in a suitable supporting electrolyte.[3,4] A variety of neutral and basic buffers have been suggested as supporting electrolytes for the polarographic reduction of Cr(VI), involving ammonium chloride/ammonia buffer, ammonium tartrate, and sodium hydroxide solutions[5]; ammonium acetate/acetic acid buffer[6], sodium hydrogen carbonate solution[7], sodium sulfate[8], sodium fluoride solution[3] and phosphate buffered solution.[4] Two common concerns which these suggestions share are to improve analytical detection limits and to avoid or alleviate interferences from the various metal ions, especially copper, a common substance in a diversity of analytical samples, whose reduction wave coincides with or appear near that of Cr(VI) in
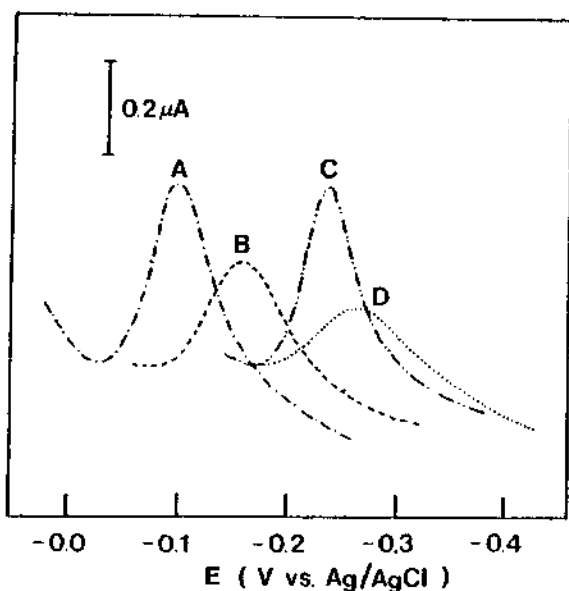
Figure 1. Representative differential pulse polarograms for the reduction of 2.0 × 10⁻⁶M Cr(VI) in A, 0.1M ammonium acetate; B, 0.2M sodium fluoride; C, 0.01M sodium borate; D, 0.1M ammonium tartrate. The pH values are given in Table 1.

most electrolytes.

In this work, we describe a superior supporting electrolyte medium suituable for the very purpose.

Experimental

Apparatus. A PAR Model 174A polarographic analyzer with a PAR Model 303 static mercury drop electrode was used. The DP polarograms were recorded on a PAR Model RE0089 X-Y recorder.

Materials. All purchased reagent-grade chemicals were used without further purification. The mercury as triply distilled. The water used for dilution and for the standard was deionized and double distilled in quartz material. Nitrogen purified by passing through a vanadous chloride solution and saturated with water vapor was used for purging.

A stock solution of 0.01M chromium (VI) was prepared from K₂CrO₄. Other standard solutions were prepared by serial diluting this solution as required. A stock solution of 0.1M sodium borate was prepared from borax.

Procedure. A 10m*l* sample solution, with appropriate concentrations of chromium (VI) and supporting electrolyte, and pH adjusted by nitric acid and/or sodium hydroxide was deaerated for at least 12 min prior to polarographic measurement. A nitrogen atmosphere was maintained over the solution at all times.

River water samples were obtained from Tdook-Sum area at Han River and used within 24hrs. As they did not contain Cr(VI), they were spiked with known amounts just prior to the measurements. In all instances the river water matrix was diluted less than two-fold.

Polarography was performed in the differential pulse mode with a 25-mV pulse being applied to a middle-size mercury drop of drop time 0.5 sec. Scan rate was 10mV/sec. The peak currents were measured from extrapolated base lines.

Table 1. Characteristics of Differential Pulse Polarograms of 1.0 × 10⁻⁶M Cr(VI) in Various Electrolyte Media

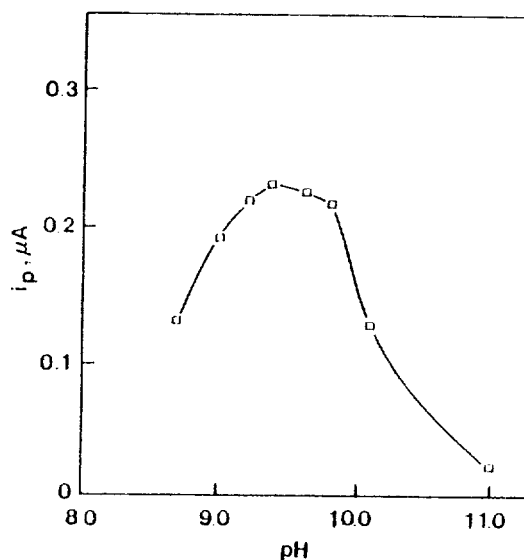| Electrolyte	pH	Sensitivity ($\mu A/\mu M$)	b½* (mV)	E_p (V vs Ag/AgCl)
0.10 M NH₄OAc	7.00	0.243	50	-0.102
0.20M NaF	8.00	0.126	80	-0.165
0.01M Na₂B₄O₇	9.40	0.230	50	-0.240
0.10M NH₄Tar	9.50	0.100	105	-0.270

*The peak width at half-peak height.

Figure 2. Effect of pH on the peak current for 1.0 × 10⁻⁶M Cr(VI) in 0.01 M sodium borate.

Experiments were conducted at room temperature (22 ± 2°C).

Results and Discussion

Characteristics of DP polarograms. The differential-pulse polarograms of Cr(VI) in various electrolyte solutions at their best sensitivities are shown in Fig. 1. Only ammonium acetate ammonium tartrate, and NaF, which are commonly used,[3,6] were included in the comparative study. The characteristics of these DP polarograms are summarized in Table 1. The polarogram in borate medium is characterized by a narrower peak, approaches the ideal shape more closely, at -2.240 V, relatively more negative than other two. This shift in peak potential may offer the great advantages over the ones that appear at more positive potential by improving in the background behavior. Only ammonium tartrate shifts the Cr(VI) reduction peak to -0.270 V, more negative than in borate, giving a broad peak. The polarogram obtained in sodium fluoride shows also a broad peak. These results suggest that the inclusion of a strongly coordinating ligand in the supporting electrolyte may result the peak broadening. Obviously this peak broadening is a disadvantage that brings a peak current reduction, i.e., low sensitivity and a poor resolution with a adjacent interfering peak. Fluoride ion has been known as one of the strongly coordinating ions with the reduction products of Cr(VI),[9] therefore, using this medium it was expected to minimize the surface passivation.[3] The above con-
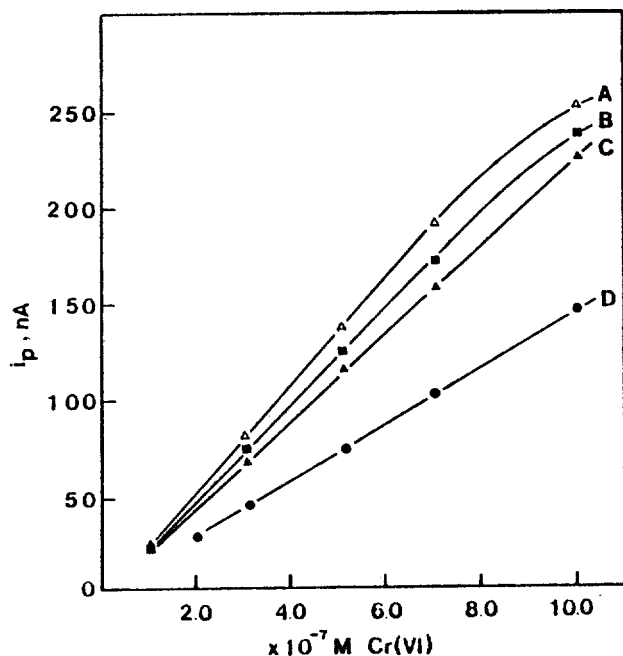
Figure 3. Calibration graphs obtained in various concentrations of sodium borate: (A) 0.005M; (B) 0.008M; (C) 0.01M; (D) 0.05 M.

Table 2. Effect of Chloride on Differential Pulse Polarographic Peak Current for 5.0 × 10^{x7}M Chromium (VI) in Various Supporting Electrolytes

Concentration of chloride (M)	Δi_p, %			
	0.1M NH$_4$OAc	0.1M NH$_4$ Tar	0.2M NaF	0.01M Na$_2$B$_4$O$_7$
1.0 × 10^{-5}	−14	− 5	·	0
1.0 × 10^{-4}	−20	− 9	− 3	− 1
1.0 × 10^{13}	−3	−41	−16	−24
1.0 × 10^{-2}	58	−52	−41	−56

Figure 4. Effect of fluoride on the peak current for 5.0 × 10^{-7}M Cr(VI) reduction in 0.01M sodium borate.

Table 3. Effect of Cu(II) and Fe(III) on Peak Current for Cr(VI) Reduction in Various Electrolytes

Concentration of Cr(VI)/M	Supporting electrolyte	Interferent	Δi_p(%)
2.0 × 10^{-6}	0.1M NH$_4$ Tar	1.0 × 10^{-1}M Cu(II)	−64
2.0 × 10^{-6}	0.1M NH$_4$OAc	1.0 × 10^{-6}M Cu (II)	37
		1.0 × 10^{-6}M Cu(II)+ 0.002M en	−54
5.0 × 10^{-7}	0.2M NaF	5.0 × 10^{-6}M Cu(II)	−1.4
		5.4 × 10^{-6}M Fe(III)	−0.7
5.0 × 10^{-7}	0.01M Na$_2$B$_4$O$_7$	5.0 × 10^{-6}M Cu(II)	−1.1
		5.4 × 10^{-6}M Fe(III)	−1.1

siderations indicate, however, electrode surface passivation problem is insignificant for a very low level of Cr(VI), as is the our case. Instead, fluoride ion brings about some difficulties as we shall see in the subsequent results.

Effect of variation of the pH and borate concentration. DPP measurements were made at various pHs and concentrations of sodium borate to determine the optimum conditions for analytical purposes. Figure 2 shows the effect of pH on the peak current for 1.0 × 10^{-6}M Cr(VI) in 0.01M sodium borate. The maximum sensitivity was obtained at pH 9.4 and peak potential at −0.24V. The peak potentials were shifted ±73mV/pH with respect to this potential, negative with higher pH.

Figure 3 shows the calibration graphs at the optimum pH 9.4 in various concentration of sodium borate. The peak potential was independent of borate concentration. With 0.01M Na$_2$B$_4$O$_7$, the best combination of a moderate sensitivity, linearity, reproducibility, and a well-defined base line was obtained. With borate concentration less than 0.01, the sensitivity is high but reproducibility was poor, probably due to the low buffer capacity.
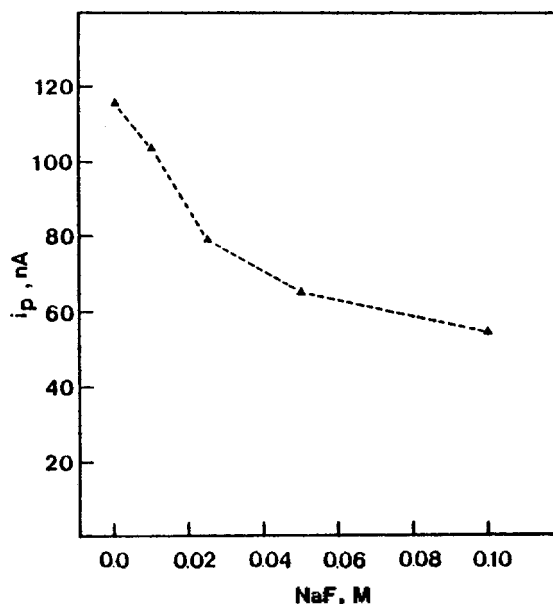
Interference study. Because the Cr(VI) reduction poten-

tial is near to that of the oxidation of mercury, anions that form sparingly soluble salts with the mercury(I) ion are candidates as interferents in DPP procedures. The most important ion in this category is chloride because it is ubiquitous in natural samples. Table 2 shows the effect of Cl$^-$ on the DPP peak height in various electrolytes. It is apparent that high concentrations of Cl$^-$ decrease the peak currents; with 0.1 mM Cl,$^-$ the interference is most severe with ammonium acetate, the least or not significant with 0.01M sodium borate. This result may be due to the greater separation of the analytical peak from the sloping portion of the background current, i.e., less coordinating or precipitating property of borate, which results less shift in the potential of mercury oxidation.

Fluoride (0.2M) medium, strongly coordinating ion, has been suggested as a superior medium for trace level determinations of Cr(VI).[3] As we have already seen, however, the strongly coordinating power of F$^-$ with the reduction products of Cr(VI) may give rise to a loss in so-called replating gain, a great advantage of DPP mode, that would result a reduction in the sensitivity by accompanying with a peak broadening. Figure 4 demonstrates this behavior; with a 0.05 M NaF in 0.01 M sodium borate, Cr(VI) reduction peak cur-
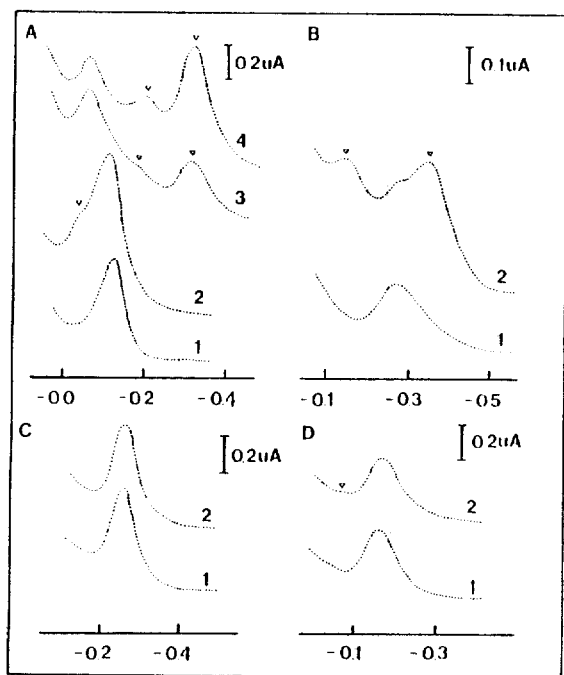
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Figure 5. Differential pulse polarograms of 2.0 × 10^{-6}M Cr(VI) in different electrolytes showing the effect of Cu(II) interferent. A, 0.1M, ammonium acetate; B, 0.1M ammonium tartrate; C, 0.01M sodium borate; D, 0.2M sodium fluoride: (1), No Cu added; (2), 1μM Cu added; (3), (2)+0.002M en: (4), (3)+1.0μM Cu. Other conditions as in Fig. 1. Inverted triangles (▽) indicate the locations of Cu(II) peaks.

rent decreases to the half.

Interference can also be expected from metals that are electroactive near 0 V. The test ions in this category are two common ions found in natural waters, copper (II) and iron (III). Table 3 shows the effect of these ions. It was found that added 5-fold excess of Fe(III) in 0.1M NH_4Tar, and 10-fold excess in NH_4OAc and 0.2M NaF cause 29% increase, 11% decrease and 4% increase, respectively in Cr(VI) peaks.[3] According to Table 3, however, 10-fold excess of Fe(III) showed no effect (less than 2%) on the Cr(VI) reduction peak in both NaF and $Na_2B_4O_7$.

Another important feature of the DP polarograms of Cr(VI) in the 0.01M sodium borate supporting electrolyte is its independence on the Cu(II) interferent which is evident acetate, overlap of the Cu(II) and Cr(VI) reduction peaks (2 in Figure 5A) could be avoided by shifting negatively the Cu(II) peak by the addition of small amounts of ethylenediamine (en),[6] thus eliminating copper as an interferent. The polarograms, 3 and 4 in Figure 5A indicate that this procedure is not satisfactory, showing the significant reduction in Cr(VI) peak height. This effect is mainly due to the base line modifications in both sides and to the positive shift of Cr(VI) reduction peak. Ammonium tartrate that shifts the Cr(VI) peak to he most negative potential (Table 1) did also accompany the shift of the Cu(II) peaks which correspond to stepwise reductions of $Cu(NH_3)_2$ (Tart) complex.[10] With a 0.2M NaF, a ten-fold excess of Cu(II) shows no significant effect (Table 3). The polarogram 2 in D indicates, however, that fluoride

shifts the copper peak that will modify the starting base line of Cr(VI) peak when a sample solution contains larger amounts of copper. From these results and Figure 5. C, it is apparent that only with 0.01 M sodium barate even larger amounts of copper could be tolerated.

The borate-containing electrolyte was tested on a river water sample. The sample did not contain Cr(VI) at a level that could be detected by DPP in any of the tested supporting electrolytes. It was, therefore, spiked to a known amount of 5.0 × 10^{-7}M Cr(VI). With 0.01M sodium borate, the peak current in the river water matrix was 43% lower relative to a value in simple laboratory standard. The peak height, however, was proportional to the Cr(VI) concentration. The detection limit, defined as twice the noise level, was 5.0 × 10^{-8} M Cr(VI) in river waters estimated by standard addition method.

In conclusion, sodium borate is a new superior medium for the DPP determination of Cr(VI) to any of the electrolytes those are commonly used, namely sodium hydroxide, ammonium tartrate, ammonium acetate, and especially sodium fluoride. With 0.01M sodium borate a combination of high sensitivity, good separation of the analytical peak from the sloping portion of the base line(negative shift of chromium peak), and freedom from common cation interferences (no shifting in copper wave) is attained. This outstanding feature of borate medium as a supporting electrolyte may be interpreted in terms of coordinating power of borate ion. Borate ion shifts the Cr(VI) reduction wave to a relatively negative potential, which results in less interference from Cl⁻ and in improvement in background behavior. Very weak coordinating power of borate ion with the reduction products of Cr(VI) and with common cations may be the cause for the narrowness and freedom from cation interferences, respectively. Determination of Cr(VI) in river water can be easily performed by the standard addition method at the 10^{-8}M Cr(VI) level with 0.01M sodium borate supporting electrolyte.

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