

Differential Pulse Cathodic Stripping Voltammetric Investigation of CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^-

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The differential pulse cathodic stripping voltammetric behaviour of CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^- has been investigated and applied to the determination of trace concentrations of these oxyanions. Detection limits of 5.6×10^{-7} , 6.1×10^{-8} , 1.1×10^{-7} and 8×10^{-8} M and quantitation limits of 1.87×10^{-6} , 2.03×10^{-7} , 1.1×10^{-6} and 2.7×10^{-7} M have been calculated for the cathodic stripping voltammetric determination of CrO_4^{2-} , WO_4^{2-} , MoO_4^{2-} and VO_3^- , respectively. The effects of equimolar and lower concentrations of selected cationic and anionic interferents on their differential pulse cathodic stripping voltammetric behaviour have also been examined. These reveal that certain heavy metal cations such as Pb^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Ag^I can compete with Hg^I for the appropriate oxyanions and that anions such as S^{2-} and I^- , which form partially insoluble mercury salts, can compete for sites around the mercury drop.

Keywords: Differential pulse cathodic stripping voltammetry; oxyanions

The polarographic behaviour of CrO_4^{2-} and MoO_4^{2-} has been described in detail elsewhere, with the reduction of Mo^{VI} receiving the most attention.¹⁻¹⁸ These studies were usually conducted in hydrochloric and sulphuric acid solutions and showed multi-step reductions. The catalytic effect of Mo^{VI} in the concentration range 4×10^{-7} – 4×10^{-4} M on the reduction of nitrate can be used quantitatively for the determination of the former.⁵

The stripping voltammetric behaviour of CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^- has received some attention in recent years. Vydra *et al.*¹⁹ summarised the literature in this field. The d.c. cathodic stripping of these ions in 0.05 M potassium nitrate at a hanging mercury drop electrode, after the formation of the corresponding Hg_2^{2+} compounds at a positive potential, has yielded quantitative methods for the determination of MoO_4^{2-} , WO_4^{2-} and VO_3^- in the range 3×10^{-6} – 10^{-5} M.²⁰

The reaction $\text{MoO}_4^{2-} \longrightarrow \text{MoO}_2 \cdot 2\text{H}_2\text{O}$, carried out on a mercury electrode, has been proposed for the determination of MoO_4^{2-} in 3 M sodium chloride down to a concentration of 5×10^{-6} M by chronopotentiometric stripping.²¹ The selective adsorption of WO_4^{2-} on the hanging mercury drop electrode in the zero current state has been recommended for the stripping determination of this anion in the concentration range 1×10^{-7} – 2×10^{-6} M, using a plating potential of +0.2 V and a solution buffered at pH 3.6.²²

Owing to the importance of these anions in environmental chemistry, this study was carried out to develop more sensitive voltammetric methods by which the oxyanions could be determined. The differential pulse mode was chosen for the stripping investigations. The selectivity of these methods was also evaluated with respect to the determination of the oxyanions in the presence of other cations and anions.

Experimental

Apparatus

All experiments were performed using a Princeton Applied Research (PAR) Model 174 A polarograph with a PAR Model 303 hanging mercury drop electrode (HMDE). Voltammograms were recorded on a PAR Model RE 0074 X-Y recorder. The electrode system was constructed with a platinum wire auxiliary electrode and a saturated calomel

electrode as a reference electrode, together with the hanging mercury drop electrode. Oxygen-free nitrogen was used for de-gassing the system and a Kent Model EIL 7055 pH meter was used for the pH measurements.

Reagents

All solutions were diluted with de-ionised water unless stated otherwise. All glassware was washed with Decon 90 and thoroughly rinsed with de-ionised water.

Solution preparation

Standard stock solutions and interfering cation and anion solutions were prepared using the method reported earlier.²³

Procedure

Solutions (10^{-5} M) of oxyanions were prepared in a 0.05 M potassium nitrate supporting electrolyte, and 10 ml of this solution were taken for the sample cell. The solution was de-gassed by bubbling oxygen-free nitrogen through the solution for 4 min, after which a flow of nitrogen was maintained over the solution throughout the analysis. After bubbling the nitrogen through the solution and a 30 s quiescent time, the solution was electrolysed at an appropriate positive potential (+0.15–0.20 V) for 1–5 min and was then scanned in a negative potential direction at 10 mV s⁻¹ to obtain the DP stripping peak using a medium-sized hanging mercury drop. The interfering ions were injected through the side orifice in the cell using a 100 μ l micropipette. Limits of detection (LOD) and quantitation (LOQ) were determined and calculated by the method of Morrison.²⁴

Results

Optimisation of DPCSV Parameters for the Determination of CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^-

The effect of initial potential, E_{el} , plating time and pH on the DPCSV behaviour of CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^- were studied. The conditions that gave rise to the most sensitive determination of the oxyanions in 0.05 M potassium nitrate supporting electrolyte were then selected and are presented in Table 1.

Effect of Concentration on the DPCSV Behaviour of CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^-

The effect of concentration on the DPCSV behaviour of the oxyanions was studied under optimised conditions. For

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CrO_4^{2-} at 10^{-5} M and lower concentrations, only one peak, at a peak potential of $E_p = 0$ V, is observed. At concentrations greater than 10^{-5} M more than one peak is observed, showing multi-layer formation phenomena. The optimum concentration range for the determination of CrO_4^{2-} by this method is 10^{-5} – 1.8×10^{-6} M in 0.05 M potassium nitrate (pH 6) supporting electrolyte.

For MoO_4^{2-} at 10^{-5} M concentration and higher, two peaks are observed, showing multi-layer formation. One peak is observed at -0.04 V and the other at -0.28 V. At concentrations of 10^{-6} M and lower only one peak is observed for MoO_4^{2-} , at -0.08 V. This peak is of analytical importance at concentrations lower than 10^{-5} M.

At a concentration of 10^{-5} M, VO_3^- also shows the multi-layer formation phenomena. At pH 4, 5 and 6, VO_3^- gives a two-peak pattern, one peak with a peak potential of -0.03 V and the other at -0.1 V. The peaks are independent of pH at pH 4–6. The effect of plating time on the VO_3^- signal was studied. Only the first peak shows a proportional increase with plating time. This increase suggests that there is an outer multi-layer formed by HgVO_3 and $\text{Hg}(\text{VO}_3)_2$ around the mercury drop. The monolayer is strongly bound to the mercury drop and is stripped at more negative potentials. At lower concentrations only one peak is observed for the DPCSV of VO_3^- . Also, the peak potential (E_p) varies with concentration. As the concentration increases, the peak potential moves towards more negative potentials.

Multi-layer formation at higher concentrations is also observed for the DPCSV behaviour of WO_4^{2-} . At pH 6, WO_4^{2-} shows two peaks, one at $E_p -0.07$ V and the other at $E_p = -0.235$ V. The latter peak shows no increase with plating time. The first peak is of analytical importance and was chosen for the study. At lower concentrations only the first peak is observed.

Effect of Interfering Ions on the DPCSV Behaviour of CrO_4^{2-} and MoO_4^{2-}

CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^- all stripped at the same potential and so inevitably interfered with each other. The effects of cationic and anionic interferences of equimolar and sub-equimolar concentrations were studied for each oxyanion in turn. These studies are illustrated for CrO_4^{2-} in Table 2.

Among the cations studied, equimolar concentrations of Pb^{II} , Zn^{II} and Ag^I interfere with the DPCSV signal of 10^{-5} M CrO_4^{2-} , with recoveries of 86.8, 89.7 and 90.3%, respectively. This decrease is due to the competitive complexation of CrO_4^{2-} with these heavy metals, thus reducing a certain percentage of the CrO_4^{2-} available for determination by DPCSV. At a concentration of 10^{-6} M these cations do not interfere. Equimolar concentrations of Na^I , Ca^{II} and F^- also interfere, with recoveries of 116, 117 and 119%, respectively. At a concentration one order of magnitude lower, this effect starts to decrease. Equimolar concentrations of Br^- and S^{2-} do not affect the CrO_4^{2-} peak recovery, but the DPCSV of CrO_4^{2-} in the presence of S^{2-} shows an interfering peak at approximately 0 V and a residual HgS stripping peak at -0.7 V (Fig. 1). This shows a competition between Hg_2CrO_4

(or HgCrO_4) and HgS for sites around the mercury drop and seriously impairs the usefulness of the DPCSV determination of CrO_4^{2-} in the presence of equimolar concentration of S^{2-} . I^- is also a serious interferent in that it strips at a slightly more negative potential, *i.e.*, -0.15 V, when it is present on its own. When it is added as an interferent to CrO_4^{2-} no separate peak is observed for I^- and it adds to the CrO_4^{2-} peak with a resulting recovery of 172.2%.

The effect of equimolar and lower concentrations of selected cations and anions on the DPCSV behaviour of 10^{-5} M MoO_4^{2-} is given in summarised form in Table 3. Among the cations studied, only Pb^{II} significantly interferes at equimolar concentrations, reducing the MoO_4^{2-} peak by

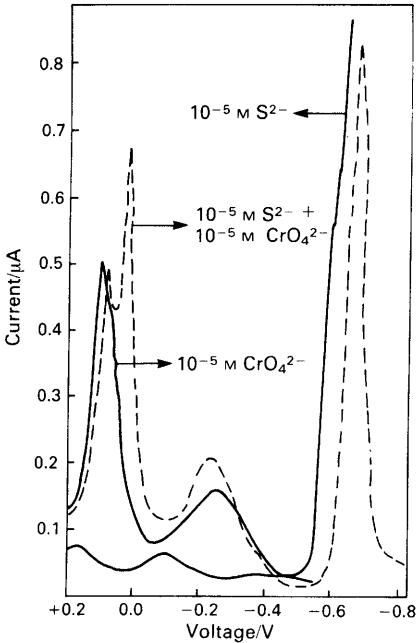


Fig. 1. Effect of equimolar concentrations of S^{2-} on the DPCSV behaviour of CrO_4^{2-} . Scan rate, 20 mV s^{-1} ; modulation, 25 mV

Table 2. Effect of equimolar and lower concentrations of selected cations and anions on the DPCSV behaviour of 10^{-5} M CrO_4^{2-} in 0.05 M KNO_3 supporting electrolyte (pH 6)

Interferent added				Concentration of interferent/M	Recovery, %
Cu^{II}	10^{-5}	100
Cd^{II}	10^{-5}	100
Ni^{II}	10^{-5}	100
Pb^{II}	10^{-5}	86.8
Pb^{II}	10^{-6}	100
Ca^{II}	10^{-5}	117
Ca^{II}	10^{-6}	114.3
Ca^{II}	10^{-7}	100
Na^I	10^{-5}	116
Na^I	10^{-6}	116
Na^I	10^{-7}	115.1
Na^I	10^{-8}	114.8
Na^I	10^{-9}	101.7
Zn^{II}	10^{-5}	89.7
Zn^{II}	10^{-6}	100
Ag^I	10^{-5}	90.3
Ag^I	10^{-6}	100
Cl^-	10^{-5}	100
F^-	10^{-5}	119
F^-	10^{-6}	100
I^-	10^{-5}	172.2
I^-	10^{-6}	136.4
I^-	10^{-7}	100
S^{2-}	10^{-5}	100
Br^-	10^{-5}	100

Table 1. Optimum DPCSV conditions for the determination of CrO_4^{2-} , MoO_4^{2-} , WO_4^{2-} and VO_3^-

Oxyanion	Initial potential, $E_{el}/\text{V vs. SCE}$	Plating time/ min	Optimum pH using 0.05 M KNO_3 as supporting electrolyte
CrO_4^{2-}	..	5	6
MoO_4^{2-}	..	5	6
WO_4^{2-}	..	2	6
VO_3^-	..	5	6

15.5%. This could be due to competitive complexation of MoO_4^{2-} with Pb^{II} . I^- is the main anionic interference at an equimolar concentration, as it cathodically strips at the same potential. An equimolar concentration of S^{2-} reduces the MoO_4^{2-} peak by 13%. This is presumably due to the competition of S^{2-} and MoO_4^{2-} for sites around the mercury drop. S^{2-} strips at a more negative potential (-0.7 V). The same effect was observed for the DPCSV behaviour of mixtures of S^{2-} and CrO_4^{2-} . Equimolar concentrations of F^- and Cl^- reduce the MoO_4^{2-} peak by 4 and 19%, respectively.

Effect of Interferences on the DPCSV Behaviour of VO_3^-

The effect of equimolar concentrations of various cations and anions on the DPCSV behaviour of 10^{-5} M VO_3^- was studied under optimum analytical conditions and the results are summarised in Table 4.

Equimolar concentrations of Ca^{II} , Ag^{I} , Cl^- , F^- and Br^- have no effect on the recovery of the VO_3^- peak. An equimolar concentration of Pb^{II} gives a serious interference. In the presence of an equimolar concentration of Pb^{II} , the first peak of VO_3^- is observed with a 40% recovery, whereas the

second totally disappears. The disappearance of the second and the decrease of the first peak are presumably due to the formation of lead vanadate $[\text{Pb}(\text{VO}_3)_2]$ after the successful competition with Hg_2^{2+} or Hg^{2+} for complexation with the VO_3^- anion. The total disappearance of the second peak and partial disappearance of the first suggest that the Pb^{II} competes successfully for VO_3^- in the monolayer state and is partly successful on the multi-layer. The effect of Pb^{II} on the DPCSV behaviour of VO_3^- is shown in Fig. 2. The interference effect of Pb^{II} is no longer observed when it is present one order of magnitude lower than VO_3^- . Equimolar concentrations of Cu^{II} , Zn^{II} , Ni^{II} and Cd^{II} decrease the VO_3^- peaks with peak recoveries of 72.7, 85.7% (peak 1 and peak 2); 82.8, 86.01; 91.1, 91.8; 73.7, 78.0%, respectively, owing to the complexation of VO_3^- with these heavy metal cations, affecting both the multi-layer and monolayer states of $\text{HgVO}_3 - \text{Hg}(\text{VO}_3)_2$. In the presence of these cations the first peak is generally more affected than the second and this can be explained by the cations preferring the multi-layer of $\text{HgVO}_3 - \text{Hg}(\text{VO}_3)_2$ around the mercury drop to the monolayer.

The anions S^{2-} and I^- interfere with the $\text{HgVO}_3 - \text{Hg}(\text{VO}_3)_2$ stripping peak at equimolar concentrations. VO_3^- and S^{2-} compete for sites around the mercury drop to form their respective salts, resulting in a decrease in the $\text{HgVO}_3 - \text{Hg}(\text{VO}_3)_2$ stripping peak. In the presence of an equimolar concentration of I^- (Fig. 3), the second peak of VO_3^- totally disappears, with the appearance of a reduced I^- peak at the expected potential of approximately -0.1 to -0.2 V . I^- in this instance effectively disrupts the monolayer of $\text{HgVO}_3 - \text{Hg}(\text{VO}_3)_2$ around the mercury drop as compared with S^{2-} . To determine VO_3^- by this method the concentration of Pb^{II} and I^- should be at least one order of magnitude lower than the concentration of VO_3^- .

Effect of Interferences on the DPCSV Behaviour of WO_4^{2-}

The effect of equimolar and lower concentrations of selected cations and anions on the DPCSV behaviour of $10^{-5}\text{ M WO}_4^{2-}$ was studied and is given in summarised form in Table 5.

Equimolar concentrations of Cu^{II} , Pb^{II} , Na^{I} , Zn^{II} , Ag^{I} , Cl^- and F^- have no effect on the peak recovery of WO_4^{2-} .

Table 3. Effect of equimolar and lower concentrations of selected cations and anions on the DPCSV behaviour of $10^{-5}\text{ M MoO}_4^{2-}$ in 0.05 M KNO_3 supporting electrolyte (pH 6)

Interferent added	Concentration of interferent/M	Recovery, %
Cd^{II}	10^{-5}	100
Pb^{II}	10^{-5}	84.5
Pb^{II}	10^{-6}	100
Cu^{II}	10^{-5}	100
Zn^{II}	10^{-5}	100
Na^{I}	10^{-5}	99.0
Ag^{I}	10^{-5}	100
Ca^{II}	10^{-5}	100
I^-	10^{-5}	350
I^-	10^{-6}	100
F^-	10^{-5}	95.9
F^-	10^{-6}	100
Br^-	10^{-5}	100
Cl^-	10^{-5}	81.0
Cl^-	10^{-6}	100
S^{2-}	10^{-5}	87.0
S^{2-}	10^{-6}	100

Table 4. Effect of equimolar and lower concentrations of selected cations and anions on the DPCSV behaviour of 10^{-5} M VO_3^- in 0.05 M KNO_3 supporting electrolyte (pH 6)

Interferent added	Concentration of interferent/M	Recovery, %	
		$E_p = -0.03\text{ V}$	$E_p = -0.1\text{ V}$
Cu^{II}	10^{-5}	72.7	85.1
Cu^{II}	10^{-6}	100	100
Zn^{II}	10^{-5}	82.8	86.0
Zn^{II}	10^{-6}	100	100
Ni^{II}	10^{-5}	91.1	91.8
Ni^{II}	10^{-6}	100	100
Cd^{II}	10^{-5}	73.7	78.0
Cd^{II}	10^{-6}	98.7	100
Na^{I}	10^{-5}	102.8	100
Ca^{II}	10^{-5}	100	100
Ag^{I}	10^{-5}	100	100
Pb^{I}	10^{-5}	40.0	0.0
Pb^{II}	10^{-6}	100	100
S^{2-}	10^{-5}	80.0	87.2
S^{2-}	10^{-6}	100	100
I^-	10^{-5}	100	0.0
I^-	10^{-6}	100	100
Cl^-	10^{-5}	100	100
Br^-	10^{-5}	100	100
F^-	10^{-5}	100	100

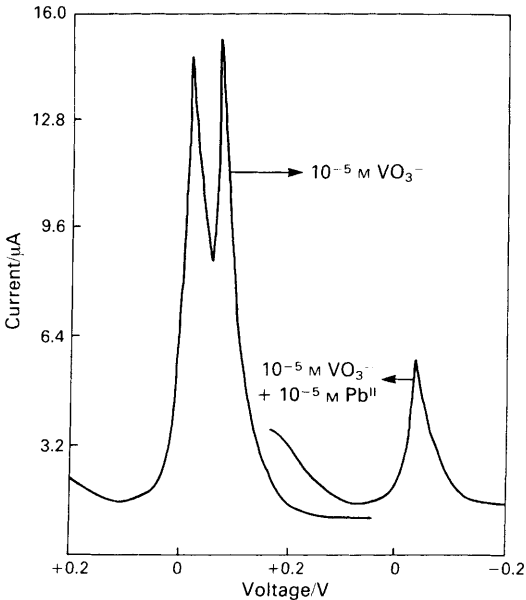


Fig. 2. Effect of equimolar concentrations of Pb^{II} on the DPCSV behaviour of VO_3^- in 0.05 M potassium nitrate supporting electrolyte (pH 6). Scan rate, 10 mV s^{-1} ; modulation amplitude, 25 mV ; plating time, 5 min ; starting potential, $+0.2\text{ V}$

Table 5. Effect of equimolar and lower concentrations of selected cations and anions on the DPCSV behaviour of 10^{-5} M WO_4^{2-} in 0.05 M KNO_3 supporting electrolyte (pH 6)

Interferent added	Concentration of interferent/M	Recovery, %
Cu^{II}	10^{-5}	99
Pb^{II}	10^{-5}	100
Na^I	10^{-5}	100
Cd^{II}	10^{-5}	93
Cd^{II}	10^{-6}	100
Ca^{II}	10^{-5}	97
Ca^{II}	10^{-6}	100
Ni^{II}	10^{-5}	101
Zn^{II}	10^{-5}	99
Ag^I	10^{-5}	100
S^{2-}	10^{-5}	46
S^{2-}	10^{-6}	100
Br^-	10^{-5}	71
Br^-	10^{-6}	100
I^-	10^{-5}	55
I^-	10^{-6}	100
Cl^-	10^{-5}	100
F^-	10^{-5}	100

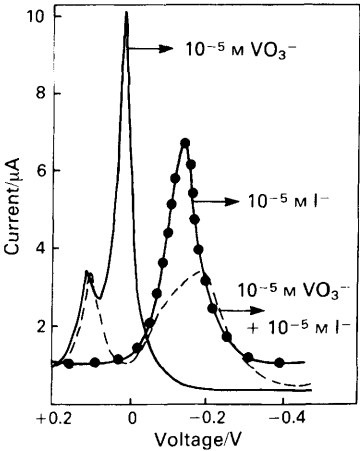


Fig. 3. Effect of equimolar concentrations of I^- on the DPCSV behaviour of 10^{-5} M VO_3^- in potassium nitrate supporting electrolyte (pH 6). Scan rate, 10 mV s^{-1} ; modulation amplitude, 25 mV ; plating time, 2 min

Equimolar concentrations of Cd^{II} and Ca^{II} slightly interfere, reducing the $\text{HgWO}_4 - \text{Hg}_2\text{WO}_4$ stripping peak by 7 and 3%, respectively. Certain anions are the only serious interferences at equimolar concentrations on the DPCSV behaviour of WO_4^{2-} . Equimolar concentrations of Br^- , S^{2-} and I^- reduce the stripping peak with recoveries of 71, 46 and 55%, respectively. The corresponding mercury salts of Br^- , S^{2-} and I^- presumably also adsorb on the mercury drop and compete for sites on the surface with $\text{HgWO}_4 - \text{Hg}_2\text{WO}_4$, hence giving the reduced recoveries.

Analytical Applications

This voltammetric method of determination is very sensitive for the determination of the oxyanions investigated. The limits of detection of these oxyanions were determined and the limit of quantitation and relative standard deviation near the detection limit were calculated and are shown in Table 6. The DPCSV behaviour of VO_3^- at a concentration near the detection limit is shown in Fig. 4. This method could be used for the determination of any of the oxyanions studied in mixtures if the concentration of the interferent anion is one order of magnitude lower in concentration. Some of the cations studied do interfere with the DPCSV behaviour of

Table 6. Limits of detection and quantitation of the oxyanions by DPCSV using the conditions described in Table 1

Oxyanion	Limit of detection/M	Limit of quantitation/M	Relative standard deviation, %
CrO_4^{2-}	5.6×10^{-7}	1.87×10^{-6}	0.93
MoO_4^{2-}	1.1×10^{-7}	1.1×10^{-6}	0.85
VO_3^-	8×10^{-8}	2.7×10^{-7}	0.29
WO_4^{2-}	6.1×10^{-8}	2.03×10^{-7}	1.15

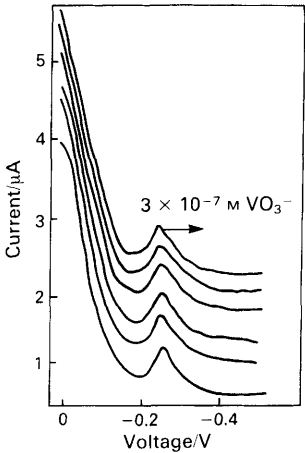


Fig. 4. Repetitive scans at a concentration near the detection limit for VO_3^- by DPCSV in a 0.05 M potassium nitrate supporting electrolyte (pH 6)

these oxyanions, such as Pb^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Ag^I , whereas S^{2-} and I^- are anionic interferents. This method could be utilised for the determination of any of the oxyanions at trace levels in order to monitor them in biological or environmental samples.

Conclusion

The interference effects of the different cations and anions can be classified under the following headings.

Complexation

Certain heavy metal cations such as Pb^{II} , Cu^{II} , Zn^{II} , Cd^{II} and Ag^I can reduce the DPCSV peaks of the oxyanions studied by their competition with $\text{Hg}^{2+} - \text{Hg}_2^{2+}$ for complexation with the oxyanions. VO_3^- is mainly affected by this process.

Competition for Sites

This is generally observed for those anions which also form partially insoluble mercury salts such as S^{2-} and I^- . They compete for sites around the mercury drop and result in decreased peak(s) for the DPCSV signal of the appropriate oxyanions.

Anomalous Effects

The effect of some cations, e.g., Na^I , on the DPCSV behaviour of oxyanions is anomalous. The presence of these cations has enhancement effects on the DPCSV peaks of some of the oxyanions, possibly due to catalysis of the mercury - oxyanion reaction.

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