



## DETERMINATION OF VANADIUM TRACE ON THE MERCURY DROP ELECTRODE BY CATHODIC VOLTAMETRY

Tatiana CAZAC\*, Ludmila KIRIYAK and Igor POVAR

Institute of Chemistry, Academy of Sciences of Moldova, 3 Academiei str., Chisinau MD-2028, R.Moldova

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The influence of bromate-ions on polarographic behavior of the complex of vanadium with 2,3-dihydroxybenzaldehyde in acetate buffer solutions has been studied. In the presence of bromate-ions the analytical signal increases more than one order. The detection limit for the accumulation time of 30 s is  $2 \cdot 10^{-10}$  M. The method has been applied to determination of vanadium in the water of the Prut river.

### INTRODUCTION

Dissolved vanadium is usually present in waters in the form of vanadate and is released in environment objects by combustion of various types of fuel.<sup>1,2</sup> At trace amounts vanadium is useful and toxic when present at higher concentrations. In natural waters the amount of vanadium is at level of  $\text{mkg} \cdot \text{dm}^{-3}$  and for its determination by various methods the preliminary concentration is often used that includes the application of solvents, coprecipitants, adsorbents which significantly complicate the methods of analysis.<sup>3</sup>

The sensitivity of adsorptive methods may be significantly increased by linking electrode reactions with catalytic ones, when the metal reduced form is reoxidized in the initial oxidized one, leading to a substantial growth of analytical signal. Thus, the complexing ligand administers predominantly the adsorption strength, and the efficiency of catalytic reactions depends on used oxidants. The comparison of various oxidants (chlorate, bromate, hydrogen peroxide, hydroxylamine etc.), applied usually for

catalytic determination of some polyvalent metal ions, has shown that bromate is more suitable for the vanadium determination. Other oxidants influence practically insignificantly the analytical signal of vanadium.<sup>2</sup>

The instability as well as the phenomenon of waves overlapping for vanadium and other metal ions in analyzed solution, which are reduced at potentials close to the vanadium reduction potential, explain the lack of methods of vanadium determination by AdCV, as has been reported.<sup>2</sup>

The objective of present paper is studying the influence of bromate-ions on the adsorptive peak of the vanadium complex with 2,3-dihydroxybenzaldehyde (2,3-DHBA) in acetate buffer solutions with pH 5.4 and the use of adsorptive voltametry method for the vanadium determination in the water of the Prut river.

### EXPERIMENTAL

The cyclic voltammograms were registered on the Polarograph POL 150 (France) in the thermostated three

\* Corresponding author: [cazactatiana@gmail.com](mailto:cazactatiana@gmail.com)

electrode cell consisting of the stationary mercury electrode as a working electrode, the saturated calomel electrode (SCE) as a reference electrode and the platinum wire as an auxiliary electrode. The cathodic accumulation of vanadium was carried out in the following conditions: the initial potential  $E_{init}$  -200 mV and the accumulation time  $t_{acc} = 30$  s. During the accumulation of vanadium, the solution was mixed by a magnetic stirrer, after mixing the solution was maintained 2 s and the cyclic voltammogram was registered from -200 mV to -900 mV. Other experimental parameters were the following: the potential of amplitude impulse of -50 mV, the period of drop formation 0.2 s, the period of delay 2 s, the temperature of solutions 20°C. The pH values of solutions were measured by the pH-meter CONSORT C931 (Belgium).

All solutions were prepared with doubly distilled water. Chemicals used were of analytical grade. The initial standard solution of vanadium (V) ( $1 \cdot 10^{-2}$  M) was prepared from sodium meta-vanadate. The solutions of vanadium of smaller concentrations were prepared routinely by dilution of the initial standard solution. The 2,3-DHBA solution was prepared by dissolution of an exact weighted amount in 1–1.5 cm<sup>3</sup> of ethanol in a 100 cm<sup>3</sup> volumetric flask and filled up to the mark by bidistilled water. As a supporting electrolyte was acetate buffer solution (pH 5.4). The working solutions were prepared in the following order: to the neutral solution containing vanadate-ion a certain amount of 2,3-DHBA, acetate buffer and solution of bromate were added, then the pH value was established, the volume was filled up to the mark by bidistilled water and the solution acidity was again verified.

## RESULTS AND DISCUSSION

In the paper it was shown<sup>4</sup> that on a background of the acetate buffer solution with pH 5.2, 2,3-DHBA did not give reduction waves on alternating current polarograms in the range of potentials (-0.3 ÷ 1.0 V). In the presence of V (v) a noticeable peak was registered, the height and potential of which strongly depend on the pH solution. At registration

of alternating current polarograms and cyclic voltammograms the maximal  $I_p$  value is observed in the pH range 4.7-5.5.

Bromate-ions increase the adsorptive peak of the vanadium complex with 2,3-DHBA by more than one order. The adsorptive character of this peak was established in by studying the dependence of the magnitude of oscillopolarographic peak,<sup>4</sup> recognizable under the same conditions, on the voltage scan rate, magnitude of initial potential and delay time.

By increasing the polarizing voltage scan rate, the peak current grows. The value of the rate coefficient (the angle tangent of dependence  $\log I_p - \log v$ ) has been found equal to 0.92, that is characteristic for the adsorption nature of the peak. The current value depends on the initial potential and reaches its maximal value at  $E_{in} = - (0.35-0.45$  V), growing linearly with an increase of the delay time of impulse supply, that also is characteristic for the electrode processes complicated by adsorption.

Under optimal conditions the adsorptive parameters of electrode processes are identified: the attractive constant describing the interaction between depolarizer particles on the electrode surface, the adsorptive equilibrium constant, the maximal superficial concentration of depolarizer on electrode and the adsorption free energy.<sup>4</sup>

The  $I_p$  dependence on the bromate-ions concentration, analogous to a curve with saturation, being characteristic for catalytic processes, is presented in Fig. 1.

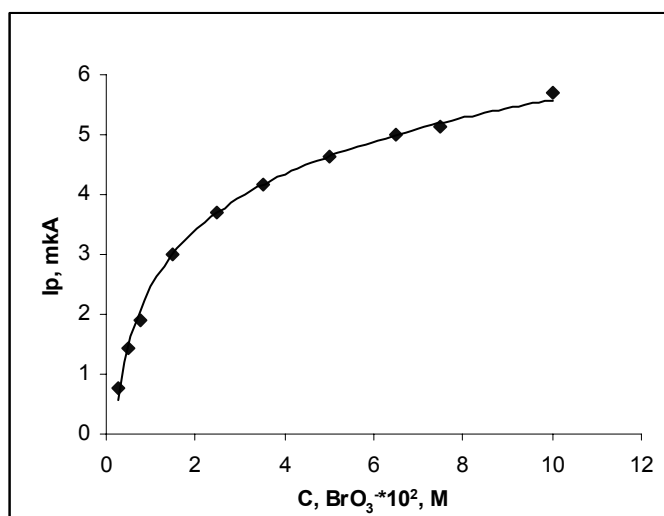


Fig. 1 – Dependence of  $I_p$  of the V complex with 2,3-DHBA on bromate-ion concentrations (0.1M  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} + 5 \cdot 10^{-5}$  M L +  $5 \cdot 10^{-6}$  M V(V) , pH=5.4).

A bend on the curves of such type is explained by formation of a polarographically active complex (PAC) between the metal ion, ligand and oxidant,<sup>5</sup> and the linear dependence of  $I_p$  on  $C_{\text{BrO}_3^-}^{1/2}$  ( $y = 26.385x + 0.3571$ ,  $R^2 = 0.979$ ) specifies that PAC is formed in solution, and then is adsorbed on electrode.

In solutions of 2,3-DHBA on background of the acetate buffer with pH 5.2-5.4 for V (V) one well expressed peak was registered. By the replacement of V (V) on V (IV) ( $\text{VOSO}_4$ ), the adsorptive peaks with the same peak potentials as well as for V (V) were registered on alternating current polarograms and cyclic voltammograms. This specifies that V (V) oxidizes an equivalent quantity of ligand, itself is reduced to V (IV), and on voltammograms a peak of the complex V (IV) with 2,3-DHBA was registered. For the establishment of the composition of complex which was adsorbed on the mercury electrode surface the equation was used:<sup>6</sup>

$$I_p = 1/I_{p_{\text{max}}} + 1/(\beta I_{p_{\text{max}}} \cdot C_{\text{L}}^m),$$

where  $I_p$  is the peak current for a specific ligand concentration;  $I_{p, \text{max}}$  - the peak current when all the metal ions are combined in a complex (50-100-fold excess of ligand);  $C_{\text{L}}$  - ligand concentration;  $m$  - quantity of ligand, combined in complexes with the metal ion. The dependences  $1/I_p - 1/C_{\text{L}}^m$  for the cases, when  $m = 1, 2$  and  $3$  are presented. Only

for the case when  $m = 3$ , a linear dependence  $1/I_p$  on  $1/C_{\text{L}}^m$  is observed. This confirms that on the electrode the complex with a 1:3 composition is discharged, Fig. 2.

The study of the influence of pH solution and ligand concentration on the  $I_p$  value, in the system V (V)-2,3-DHBA-  $\text{BrO}_3^-$ , has shown that the optimal values are following: pH 5-5.5 and  $C_{\text{L}} = 10^{-5}$ - $10^{-4}$ M Fig. 3.

The influence of some metal ions on the value peak current of the vanadium complex with 2,3-DHBA in the presence of bromate-ions has been studied. The 100-fold excess of Zn (II), Mn (II), Pb (II), Fe (II) as well as equal amounts of Cd (II), Co (II), Ni (II), Cu (II) do not interfere to the vanadium determination.

The detection limit of vanadium determination for the accumulation time of 30 s is  $2 \cdot 10^{-10}$  M. The accuracy of vanadium determination has been estimated by the "added-found" method. The vanadium determination was carried out from the calibration curve and by the method of standard addition method in optimal conditions. In Fig. 4. the voltammograms of the complex of vanadium with 2,3-DHBA with and without bromate are presented.

The developed method has been applied to the vanadium determination in the water of the Prut river, Tables 1 and 2.

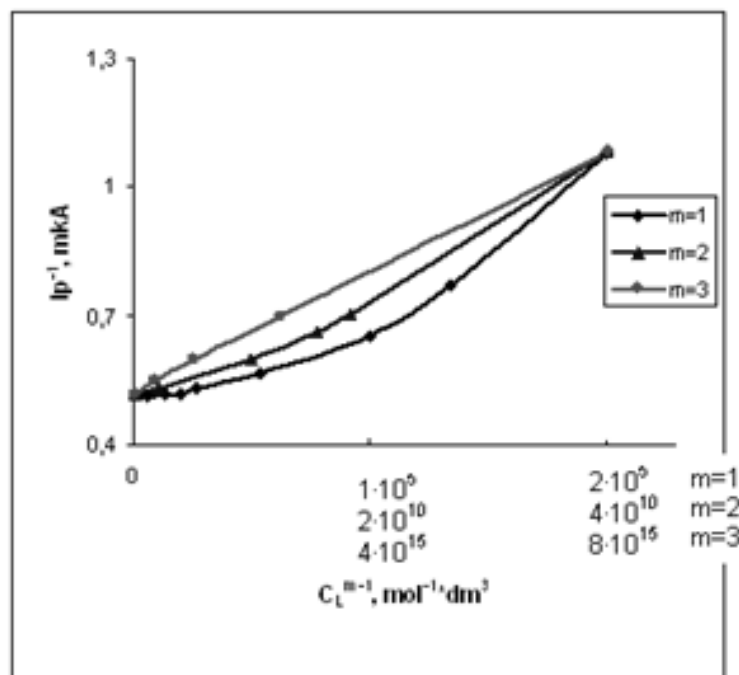


Fig. 2 – Dependence of  $1/I_p$  on  $1/C_{\text{L}}^m$  for the  $m$  various values. The experiment conditions area described in Fig. 1.

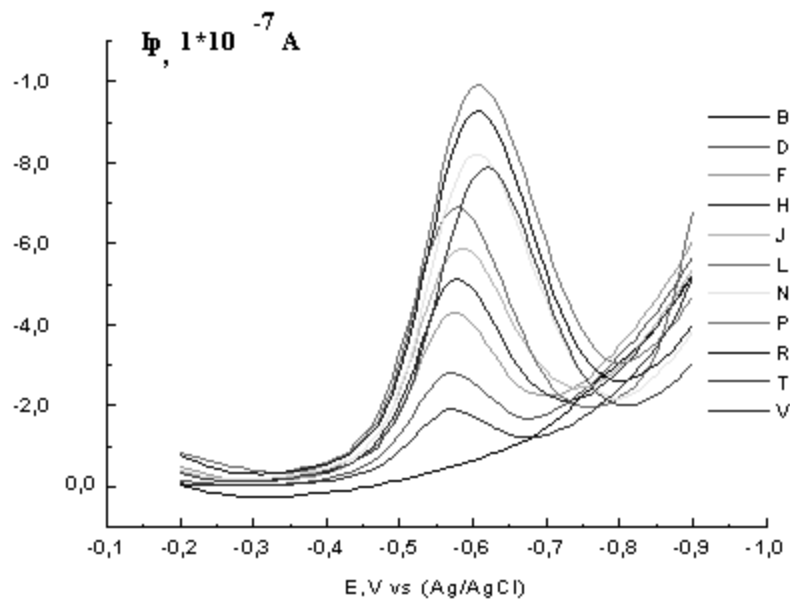


Fig. 3 – Dependence of  $I_p$  of the V on ligands (2,3-DHBA) concentrations (0.1M  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} + 0.03 \text{ M BrO}_3^- + 2 \cdot 10^{-7} \text{ M V(V)}$ , pH=5.4 B-  $C_L- 0$ , V-  $C_L- 5 \cdot 10^{-7} \text{ M}$ , D-  $C_L- 2.5 \cdot 10^{-6} \text{ M}$ , F-  $C_L- 5 \cdot 10^{-6} \text{ M}$ , H-  $C_L- 1 \cdot 10^{-5} \text{ M}$ , J-  $C_L- 2 \cdot 10^{-5} \text{ M}$  L-  $C_L- 4 \cdot 10^{-5} \text{ M}$ , N-  $C_L- 5 \cdot 10^{-5} \text{ M}$ , P-  $C_L- 7.75 \cdot 10^{-5} \text{ M}$ , R-  $C_L- 1 \cdot 10^{-4} \text{ M}$ , T-  $C_L- 1.25 \cdot 10^{-4} \text{ M}$ ).

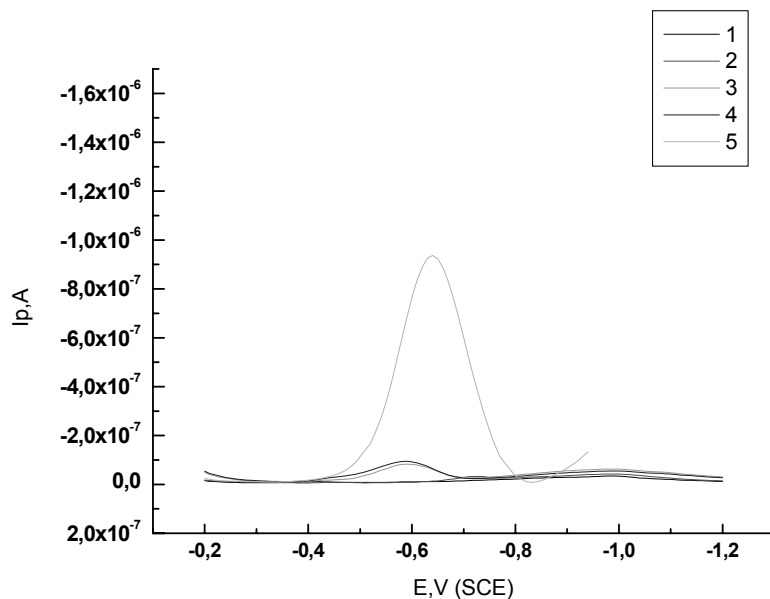


Fig. 4 – Voltammograms (pH=5.4): 1. 0.1M  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} + 5 \cdot 10^{-6} \text{ M L}$ , 2. 0.1M  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} + 5 \cdot 10^{-6} \text{ M L} + 5 \cdot 10^{-7} \text{ M V(v)}$ , 3. 0.1M  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} + 5 \cdot 10^{-5} \text{ M L} + 5 \cdot 10^{-7} \text{ M V(v)}$ , 4. 0.1M  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} + 5 \cdot 10^{-5} \text{ M L} + 1 \cdot 10^{-6} \text{ M V(v)}$ , 5. 0.1M  $\text{CH}_3\text{COONa} + \text{CH}_3\text{COOH} + 5 \cdot 10^{-5} \text{ M L} + 5 \cdot 10^{-7} \text{ M V(v)} + 0.01 \text{ M BrO}_3^-$ .

Table 1

Determination of vanadium in the standard solution with 29 elements (n= 5)

Added, mol/L	Found by the method of standard addition, mol/L, $\bar{X}$	Recovery (%)	Found from the calibration curve, mol/L	Relative standard deviation, RSD (%)
$7.84 \cdot 10^{-7}$	$7.85 \cdot 10^{-7}$	99.87	$7.90 \cdot 10^{-7}$	0.24

Table 2

Vanadium determination in samples of the water in the Prut river (n = 5)

The sampling site	Found, mkg/L	RSD (%)
Well tube in Cotu Morii	11.77	0.22
Cotu Morii	8.24	0.24
Valea Mare	10.05	0.20

## CONCLUSIONS

The influence of bromate ions on the adsorptive peak of the complex of vanadium (IV) with 2,3-dihydroxybenzaldehyde (2,3-DHBA) has been studied. It is shown that in the presence of  $\text{BrO}_3^-$  ions  $I_p$  grows considerably that has allowed to the increase of the sensitivity of vanadium determination by more than one order. The influence of instrumental parameters and the concentrations of 2,3-DHBA, V (V) and  $\text{BrO}_3^-$  ions on the  $I_p$  value have been investigated. The influence of a wide range of metal ions has been studied and the possibility of the adsorptive-catalytic determination of vanadium in the presence of 2,3-DHBA and  $\text{BrO}_3^-$  has been shown. The developed method has been applied to the

vanadium determination in the water of the Prut river.

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