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## Application of Anodic Stripping Voltammetry to Determination of the State of Complexation of Traces of Metal Ions at Low Concentration Levels

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A modified method of anodic stripping voltammetry for determination of the ionic form (state of complexation) of metal ions at very low concentration levels (down to  $10^{-9}$  M) is discussed. The sensitivity and utility of the procedure is compared with that of classical d.c. polarography. The complexation of cadmium at a concentration of  $5 \times 10^{-9}$  M with chloride in the solutions of constant ionic strength  $\mu = 0.7$  ( $\text{NaClO}_4 + \text{NaCl}$ ) was investigated as an illustration of the method. Also the complexation of lead at  $2 \times 10^{-8}$  M with chloride ion at various concentrations was determined under the same conditions.

### INTRODUCTION

Although traces of heavy metals occurring in natural aquatic systems are present at very low concentration levels (below  $10^{-7}$  M), they undoubtedly play an important role in many bio-geo-chemical processes. Therefore, emphasis has been placed in recent years on the analytical determination and characterization of the predominant ionic species (state of complexation) of certain metals in the natural environment<sup>1,2</sup>.

Various polarographic techniques<sup>3</sup> have been employed to determine the ionic form of microconstituents at the low concentration levels at which heavy metals are present under natural conditions. The basis for the determination of the state of complexation of zinc, cadmium and indium in sea-water was the sea-water model system of the same metal ions prepared at higher concentrations<sup>4,5</sup>. Lower concentrations were determined by employing a dropping amalgam electrode. Traces of zinc in sea water samples were also analysed by means of the slowly dropping mercury electrode<sup>6</sup>.

Voltammetric techniques are very sensitive and simple, and enable direct determination of traces of heavy metals in natural waters as well as in electrolyte solutions. Square-wave polarography was used in the investigation of cadmium-EDTA complexation under natural sea water conditions<sup>7</sup>. The concentration range of the metal ion was from  $2 \times 10^{-5}$  M to  $4 \times 10^{-7}$  M. Pulse-polarography was used to determine the concentration of zinc in sea water samples without using pre-electrolysis concentration procedures, at a hanging mercury drop electrode<sup>8</sup>.

\* Taken in part from the M. Sc. thesis of S. B. at the University of Zagreb, 1973

Anodic stripping voltammetry (ASV) with the hanging mercury drop electrode (HMDE)<sup>9</sup> has been employed in the determination of the concentration levels of metals in sea water<sup>10,11,12</sup> and fresh water samples<sup>13</sup>. ASV and differential pulse polarography were used in study of complexation with hydroxide or carbonate ions in natural water applying the shift of the anodic peak potentials. However this procedure is limited with fast complexation reactions, only<sup>14</sup>. In the case when the complexation is slow the method is shown to be unsatisfactory<sup>15</sup>.

The sensitivity of the anodic stripping technique is increased when thin-film mercury electrodes are employed. Thus, a composite mercury-graphite electrode (CMGE)<sup>16</sup> and a rotating glassy carbon electrode (RGCF)<sup>17,18</sup> have been used in investigations on zinc, cadmium, lead and copper species in fresh water samples. The concentration levels of metal ions were from  $10^{-8}$  M to  $10^{-10}$  M. This is a great improvement over all classical d. c. polarographic techniques since the latter enable the detection of the ionic species in electrolyte solutions only up to a concentration of  $10^{-5}$  M and therefore are inappropriate for the study of ions in natural systems.

However, by employing more sophisticated techniques and electrodes, metal ion complexed in the natural environment can be investigated. The stability constants as well as the possible coordination numbers with respect to ligands in metal complexes, can easily be evaluated from the change of half-wave potential with concentration of the complexing agent, as proposed earlier by DeFord and Hume<sup>19,20</sup>.

In the present paper, we describe the application of a modified anodic stripping technique, with a hanging mercury drop electrode, employing the cathodic-reduction process, for characterization of the states of metal ions at low concentration levels in natural waters.

## EXPERIMENTAL

### *Instruments*

Voltammetric measurements were carried out on a Princeton Applied Research Electrochemistry System PAR-170, supplied with a Hewlett Packard digital voltmeter for precise potential readings.

D. c. polarographic measurements were done with a Radiometer P04 Polarograph, supplied with a standard Amel drop trigger.

### *Cells and Electrodes*

Voltammetric runs were carried out in a thermostated glass cell of 40 ml volume. Only 25 ml of oxygen-free solution was used for each run, oxygen being removed by bubbling specially pure nitrogen through the solution for at least 30 min. A three-electrode system was employed: a hanging mercury drop electrode (HMDE) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire was used as the counter electrode. The working area of the hanging mercury drop electrode was  $0.024 \text{ cm}^2$ . The reference and the counter electrodes were separated from the solution in the cell by means of a sintered glass frit. Solutions were stirred with a magnetic stirring bar covered with teflon. D. c. polarographic measurements were carried out in a conventional thermostated polarographic cell 10 ml in volume. In this case, a two electrode system was employed: a standard mercury electrode (DME) and a saturated (NaCl) calomel electrode (SCE). All solutions were deaerated with specially pure nitrogen prior each run. For both types of measurement, the cells were maintained at constant temperature ( $25 \pm 0.1^\circ\text{C}$ ).

### Chemicals and Solutions

All of the chemicals used were analytical reagent grade. Aqueous solutions of sodium perchlorate (Merck Co., Darmstadt,  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ ), sodium chloride (Merck Co., Darmstadt,  $\text{NaCl}$ ) potassium nitrate (Merck Co., Darmstadt,  $\text{KNO}_3$ ) and potassium thiocyanate (Kemika, Zagreb,  $\text{KCNS}$ ) were prepared by dissolving the salts in doubly-distilled water. Traces of heavy metals from the stock solutions were eliminated by means of potentiostatic preelectrolysis on a Hg-pool electrode for 24 h.

Standard solutions of 0.1 M cadmium nitrate  $\text{Cd}(\text{NO}_3)_2$  and lead nitrate  $\text{Pb}(\text{NO}_3)_2$  were prepared by dissolving the required amounts of salts in four times distilled water.

Special purification of »pure« nitrogen was done by passing the gas through the gas line containing a deoxygenating BTS catalyser (BASF, Ludvigshafen).

### Principles of the Method

The traces of heavy metals which are present in natural waters are found to be at concentration levels below  $10^{-7}$  M. Determination of the metal ion by reduction at the electrode surface cannot be directly carried out using samples of natural waters, mainly due to the insensitivity of classical d.c. polarography at such low concen-

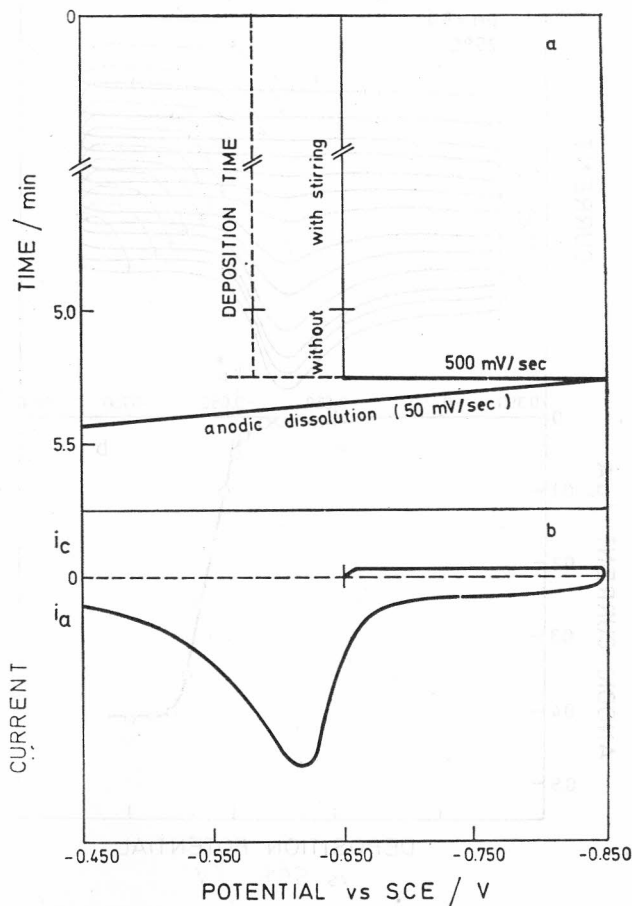


Figure 1. Schematic diagram showing (a) time dependence of the polarizing voltage and (b) typical anodic-current vs. deposition potential curve.

trations. Therefore anodic stripping voltammetry with the hanging mercury drop electrode (HMDE) was applied.

A series of voltammograms was obtained in each run, each carried out at a different but constant deposition potential, with a controlled deposition time (1–5 minutes), followed by fast anodic dissolution in a potential sweep. During the period of the deposition of the metal the solution was continuously stirred and nitrogen was passed above the solution surface. After the deposition, a 15 s period was allowed without any stirring prior to scanning to the reduction potential at the limiting current as shown on the d. c. polarographic wave. The anodic peak-current for metal dissolution from the Hg drop then is obtained. The conditions at which each of the voltammograms was recorded are shown schematically in Figure 1.

From a series of such voltammograms at different metal deposition potentials but for one metal concentration (Figure 2.a), the anodic peak-current vs. deposition potential curve can be obtained. The critical apparent potentials  $E_p^*$ , of such a polarogram-like curves are plotted (Figure 2b) against the anodic peak currents

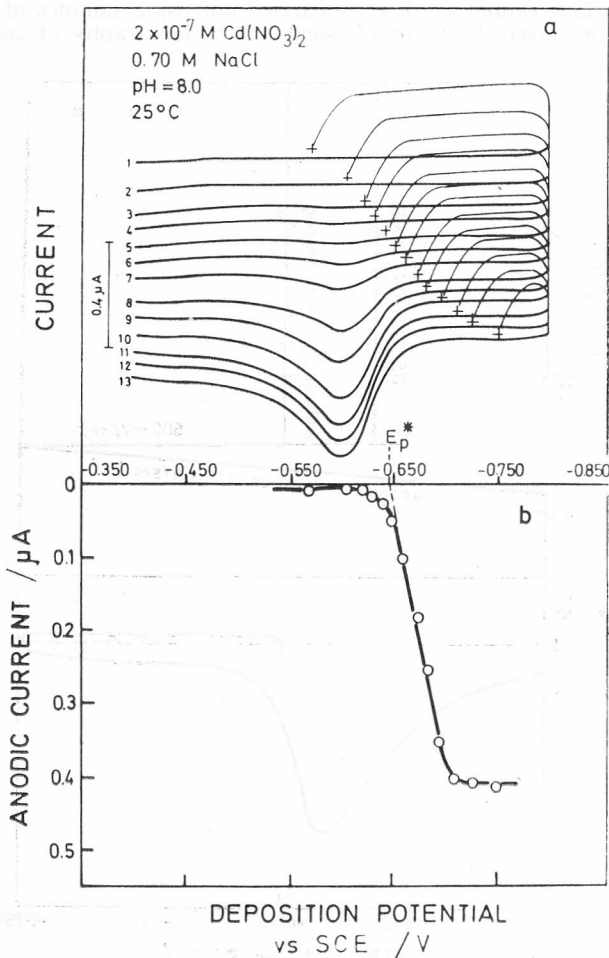


Figure 2. Series of voltammograms recorder for cadmium at concentration  $2 \times 10^{-7} \text{ M}$  in  $0.7 \text{ M}$  sodium chloride solution at  $\text{pH} = 8$ . Voltammograms are obtained at different deposition potentials (a) and the polarogram-like anodic peak-current vs. deposition potential is constructed (b.)

for the anodic stripping experiments equivalent to corresponding half-wave potential  $E_{1/2}$  values for the cathodic polarograms for the same metal (see below).

An experimental and the theoretical correlation between the polarographic half-wave potential  $E_{1/2}$  and the critical apparent potential  $E_p^*$  has been found: for a reversible electrode process  $E_p^*$  is shifted to more negative potentials by up to 100 mV with respect to  $E_{1/2}$ , the corresponding cathodic half-wave potential. Although  $E_p^*$  differs in value from the corresponding cathodic  $E_{1/2}$ , its significance is the same and under invariant experimental conditions,  $E_p^*$  can be used in the evaluation of stability constants of metal complexes as proposed by DeFord and Hume<sup>17-18</sup>.

### Results

The d. c. polarographic waves and the corresponding peak-current vs. metal deposition potential curves obtained for cadmium and lead in 0.7 M sodium chloride solutions are shown in Figure 3. The half-wave potential  $E_{1/2}$  for cadmium is found to be  $-0.615$  V vs. SCE. The corresponding  $E_p^*$  is  $-0.650$  V vs. SCE; hence the difference between  $E_{1/2}$  and  $E_p^*$  is 35 mV (Figure 3). In the case of lead,  $E_{1/2}$  is found to be  $-0.415$  V vs. SCE while the corresponding  $E_p^*$  potential is shifted to  $-0.442$  V vs. SCE so that difference between  $E_{1/2}$  and  $E_p^*$  is 27 mV.

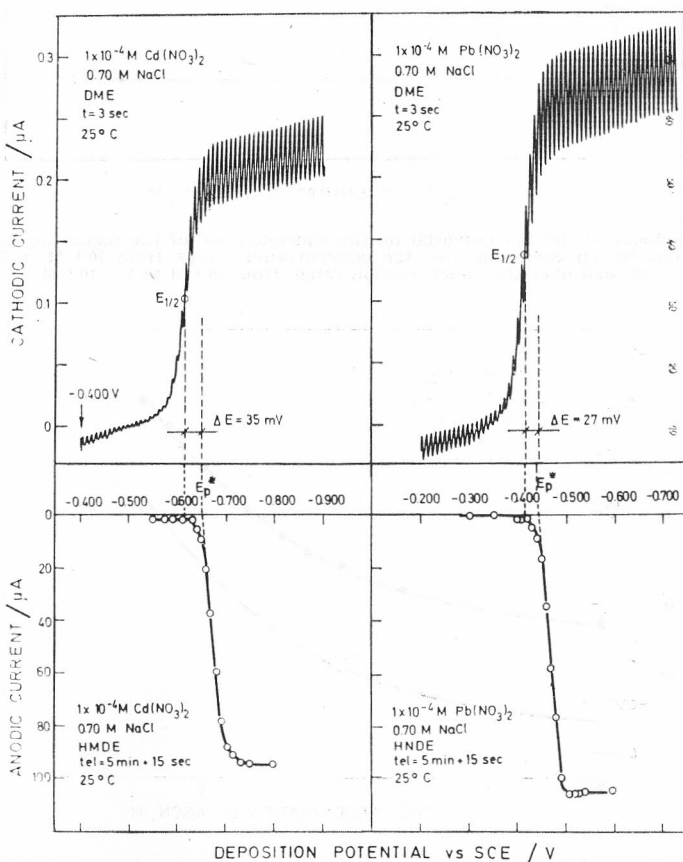


Figure 3. Comparison of the classical d.c. polarographic waves and the polarogram, like anodic-stripping peak current vs. deposition potential curves, obtained for cadmium and lead.

The  $E_p^*$  potential is constant over the wide range of concentration of the metal ion. In Figure 4 is shown the dependence of  $E_p^*$  potential on concentration of cadmium and lead ions in the concentration ranges  $10^{-4}$  M to  $5 \times 10^{-9}$  M and  $10^{-4}$  M to  $2 \times 10^{-8}$  M respectively, in 0.7 M sodium chloride solution as supporting electrolyte.

The method proposed by DeFord and Hume<sup>19,20</sup> enables the determination of the ionic form of the metal ion in the presence of a complexing agent, by taking into the account the change of the half-wave potential,  $E_{1/2}$ , with concentration of the complexing agent. In Figure 5, results are shown for complexation of cadmium with thiocyanate as studied by DeFord and Hume<sup>19,20</sup>; two concentrations of cadmium ion were used: for curve 1, the concentration of cadmium ion is  $10^{-3}$  M and for

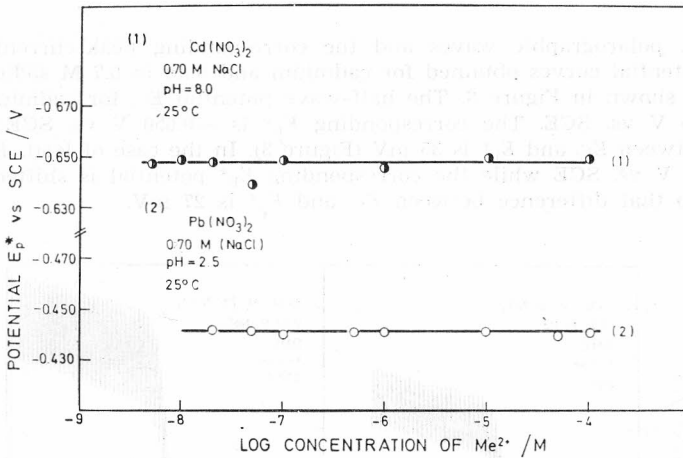


Figure 4. Dependence of the  $E_p^*$  potential on the concentration of the metal ion in 0.7 M sodium chloride solutions for (1) cadmium over the concentration range from  $10^{-4}$  M to  $5 \times 10^{-9}$  M and (2) lead over the concentration range from  $10^{-4}$  M to  $2 \times 10^{-8}$  M.

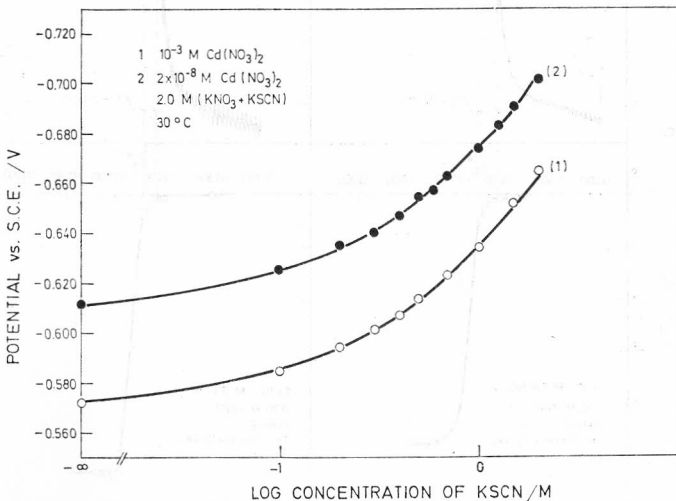


Figure 5. Dependence of the half-wave potentials,  $E_{1/2}$  for  $10^{-3}$  M cadmium on the concentration of KSCN at constant ionic strength,  $\mu = 2.0$  ( $KNO_3 + KSCN$ ), curve (1) and dependence of  $E_p^*$  potential for  $2 \times 10^{-8}$  M cadmium on concentration of KSCN under the same conditions, curve (2).

curve 2,  $10^{-8}$  M. Both curves are similar in shape although a small difference between  $E_{1/2}$  and  $E_p^*$  was observed.

The complexation of cadmium and lead, for concentrations of  $5 \times 10^{-9}$  M and  $2 \times 10^{-8}$  M of metal ion, respectively, at constant ionic strength  $\mu = 0.7$  ( $\text{NaClO}_4 + \text{NaCl}$ ) is shown in Figure 6. In the case of cadmium (Figure 6 curve 1) the  $E_p^*$  potential is constant over a wide concentration range of chloride ion up to  $3 \times 10^{-2}$  M ( $E_p^* = -0.612$  V vs. SCE) but after reaching  $3 \times 10^{-2}$  M of chloride ion,  $E_p^*$  is shifted to more negative values, giving a slope  $\Delta E_p^*/\Delta \log[\text{Cl}^-]$  of 30 mV. This indicated that  $\text{CdCl}^+$  complex is present with a stability constant given by  $\log K_1 = 1.52$  (cf. the calculation given in ref 4).

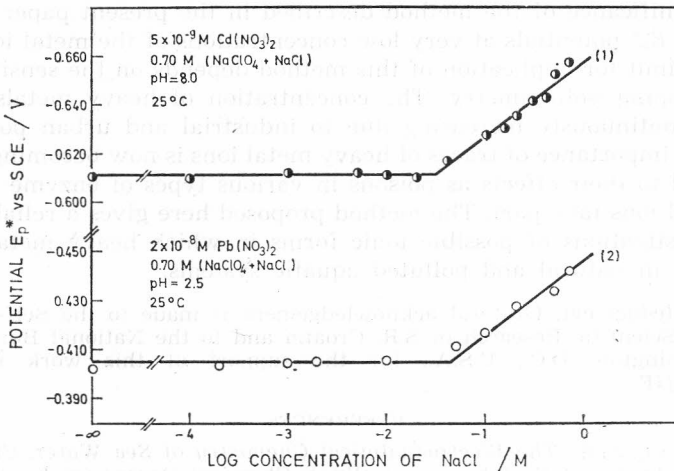


Figure 6. Dependence of  $E_p^*$  potential for cadmium and lead on the concentration of chloride ion at constant ionic strength,  $\mu = 0.7$  ( $\text{NaClO}_4 + \text{NaCl}$ ):

1. for cadmium concentration  $5 \times 10^{-9}$  M, pH = 8.0 and
2. for the lead concentration  $2 \times 10^{-8}$  M at pH = 2.5

Significant complexation of lead with chloride ion was not observed up to a concentration of  $4.3 \times 10^{-2}$  M. The  $E_p^*$  potential is found to be  $-0.405$  V vs. SCE. At higher concentrations of chloride ion, the  $E_p^*$  potential is shifted to more negative values with a slope  $\Delta E_p^*/\Delta \log[\text{Cl}^-]$  of 30 mV. This corresponds to formation of the  $\text{PbCl}^+$  complex with a corresponding stability constant given by  $\log K_1 = 1.43$ .

#### DISCUSSION

In the case of polarographic study of reversible electrode processes, the oxidized form of the metal ion is normally assumed to be in the solution. A varying potential-dependent ratio of the oxidized and reduced forms of the metal ion is established at the electrode surface through the wave. This ratio is greater than 1 at potentials more positive than the half-wave potential  $E_{1/2}$  of the reduction process, or it can be smaller than 1 at potentials more negative than the half-wave potential. This means that when the cathodic deposition of the metal ion is carried out at potentials more positive than that of the half-wave potential  $E_{1/2}$ , the metal deposition does not occur since the equilibrium is shifted in favour of the oxidized form in the solution. On the other hand, metal deposition will occur at potentials slightly more negative than the half-wave potential for reduction. The curves showing the dependence of the anodic peak-current on deposition potential confirm this statement. However, the anodic peak current increases successively for different deposition potentials

at potentials near the half-wave potential (as shown in Figure 2) and therefore it becomes difficult to determine the exact deposition potential.

$E_p^*$  potentials are evaluated by extrapolating the anodic peak-current vs. deposition potential curve to the zero current line as discussed earlier. The  $E_p^*$  values have the same significance as the corresponding  $E_{1/2}$  potentials, although they differ in value.  $E_p^*$  does not depend on concentration of the metal ion in electrolyte solutions of constant composition, as shown in Figure 4., but it does vary with concentration of the complexing agent, as shown in Figures 5 and 6. This is as expected thermodynamically.

The significance of the method described in the present paper is in determination of  $E_p^*$  potentials at very low concentrations of the metal ion. The concentration limit for application of this method depends on the sensitivity of the anodic stripping voltammetry. The concentration of heavy metals in natural waters is continuously increasing due to industrial and urban pollution. The biochemical importance of traces of heavy metal ions is now becoming recognized with regard to their effects as poisons in various types of enzyme processes in which metal ions take part. The method proposed here gives a reliable basis for future investigations of possible ionic forms in which heavy metal and other ions appear in natural and polluted aquatic systems.

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## SAŽETAK

**Primjena voltametrije anodnog otapanja za određivanje stvaranja kompleksa metalnih iona vrlo niskih koncentracija**

*M. Branica, D. M. Novak i S. Bubić*

Predložena je nova primjena voltametrije anodnog otapanja za određivanje ionskih vrsta (i stanja kompleksiranja) metalnih iona pri vrlo niskim koncentracijama tj. sve do  $10^{-9}$  M elektroaktivne vrste. Osjetljivost i nove mogućnosti predloženog postupka uspoređene su sa klasičnom polarografijom istosmjerne struje na primjeru stvaranja kompleksa kadmija ( $2 \cdot 10^{-8}$  i  $10^{-3}$  M) s kalijevim tiocijanatom. Ova metoda je također verificirana na primjeru stvaranja kloridnih kompleksa kadmija ( $5 \cdot 10^{-9}$  M) i olova ( $2 \cdot 10^{-8}$  M) u otopinama stalne ionske jakosti  $\mu = 0.7$  ( $\text{NaClO}_4 + \text{NaCl}$ ).

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