FAST SCAN DIFFERENTIAL PULSE
POLAROGRAPHIC DETERMINATION OF CYANIDE

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The measurement of the catalytic current, caused by the interaction between cyanide and nickel(II)-ethanolamine complex enables the determination with the detection limit $0.4 \, \mu g \, l^{-1}$ with the relative mean deviation 0.90%. Direct fast pulse polarographic determination, based on the measurement of the anodic current has the limit $40 \, \mu g \, l^{-1}$ and the relative mean deviation 0.93%.

The determination of small or trace quantities of cyanide is important in water and food quality control. Among the methods for the determination of cyanide an important role is recently played by pulse polarographic techniques[1]. This is mainly due to high sensitivity of these methods, which can be improved by the measurement of catalytic current caused by the presence of cyanide in the solution measured. Analytically useful catalytic current obtained in solutions containing the nickel(II) complexes with amines (hydroxylamine or ethylenediamine) have been studied in details using the d.c. polarographic technique[2,3]. In the present paper are given the results of the differential pulse polarographic (DPP) examination of the mentioned catalytic currents and compared with the results of the direct DPP determination.

EXPERIMENTAL

Apparatus and Chemicals

The measurements were carried out with the prototype of the Polarographic Analyzer PA3 (Laboratorní přístroje, Prague, Czechoslovakia) with three electrode arrangement (mercury dropping electrode, saturated calomel electrode and platinum electrode). For the base line correction — subtraction of the residual current data from the recorded curve of the sample solution — was applied the prototype of the Recording Polarographic Terminal RPT 1 (Laboratorní přístroje, Prague, Czechoslovakia). The capillaries were prepared according to Novotný[4]; for the DPP the drop time was 3 s, for the fast scan DPP measurements (FSDPP) the drop time was 50 s. FSDPP is one of the operational modes of the Polarographic Analyzer PA3, where the slowly growing mercury drop electrode is polarized by a d.c. voltage ($20 \, mV \, s^{-1}$) with imposed pulses (5 pulses per second) and current sampling is realized before and at the end of each pulse; difference of these data is recorded as in DPP[5].

Dissolved oxygen was removed by purified nitrogen from the measured solutions. All solutions were prepared from r.g. chemicals. Twice distilled water (quartz apparatus) was used throughout the work.

RESULTS

Catalytic Current of Cyanide in Systems Containing Nickel(II)-Amine Complexes

In the solutions containing nickel(II)-hydroxylamine or nickel(II)-ethylenediamine complex, catalytic current can be obtained by d.c. measurement if the solution contains low amount of cyanide[2,3]. Under these conditions (in the case of the hydroxylamine complex at the molar ratio amine : nickel equal to $100-200:1$ and pH $8-10$) DPP yields a peak with the peak potential $E_p = -1.35$ V at pH 9.6; peak current i_p depends on the CN^- ions concentration. The dependence of this current on the concentration of hydroxylamine, pH, temperature and CN^- ions concentration corresponds to these dependences obtained by d.c. measurements. It can be therefore concluded that the DPP current is similarly of catalytic nature and is caused by the regeneration of the active complex which, according to the cited authors[2], is formed on the surface of the electrode by the oxidation of the product of the electroreduction of the nickel(II)-amine–cyanide mixed complex.

The DPP catalytic peak is, however, better separated from the nickel(II)--hydroxylamine peak: while on the d.c. polarogram only an increase of the nickel complex wave can be observed, the DPP technique yields a peak with the E_p value approx. 200 mV more negative than the E_p value corresponding to the reduction of the nickel(II)-hydroxylamine complex. The dependence of the d.c. catalytic current on the concentration of cyanide is linear[2] only in the concentration interval $2 . 10^7$ to $1 . 10^{-6}$ mol l^{-1}. The DPP measurement under identical conditions showed a linear dependence in a wider concentration interval, but with different slopes in the ranges $1 . 10^{-8}-1 . 10^{-7}$ and $1 . 10^{-7}-5 . 10^{-5}$ mol l^{-1}. The change of the slope of the current $vs.$ concentration plot corresponds to the change of the shape of the catalytic peak, on which two poorly separated maxima can be distinguished up from the $1 . 10^{-7}$ mol l^{-1} CN^- ions concentration. This phenomenon illustrates the complex nature of the reaction mechanism resulting in the regeneration of the active nickel complex, for which the mutual rations of nickel, amine and cyanide are important[2,6].

It has been also observed that the height of the catalytic current decreases with time. The rate of the decrease depends on pH and concentration of CN^- ions. At pH 9.5 ten minutes after mixing of the components, 10% decrease of the peak height was observed with the cyanide concentration at the 10^{-7} mol l^- level. The time dependence on the height of the peak was lowered by the application of the FSDPP,

where the recording of the curve takes only about 100 s. The described phenomena show, however, that the described catalytic system cannot be fully recommended for analytical application.

The experiments were further directed to the examination of catalytic current caused by the presence of cyanide in the solutions containing other nickel(II) amine complexes, as e.g. triethanolamine, ethylenediamine, hydrazine etc. The best results have been obtained with nickel(II)-ethanolamine complex. In this case a well developed catalytic peak is obtained at the molar ratio ethanolamine : nickel = 30 : 1. Under these conditions a single peak with E_p value -1.70 V at pH 8·8 is formed over a wide cyanide concentration interval $(10^{-8}-10^{-5} \text{ mol l}^{-1})$. Unfortunately, even in this case the linear dependence of cyanide concentration vs current changes its slope at higher cyanide concentrations.

The determination in the presence of nickel(II)-ethanolamine complex was, however, found more sensitive than that based on the nickel(II)-hydroxylamine complex when the FSDPP was applied. A linear dependence of current on cyanide concentration was verified in the concentration range 0·4 . 10^{-8} to 8·5 . 10^{-8} mol l^{-1}. Because all measured dependences of the current on pH, concentration of ethanolamine, pH and cyanide concentration are of similar nature as in the above described system it has been supposed that the catalytic current is of the same nature as proposed by[2].

In the solutions containing the nickel(II)-ethanolamine complex no measurable decrease of the catalytic peak height was observed when the FSDPP was applied. The technique also increased somewhat the sensitivity of the determination as compared with the DPP.

Direct Determination of Cyanide

For the direct determination of cyanide rapid d.c. polarography[7] or DPP[1] in alkaline medium was recommended. The application of DPP is obviously more advantageous from the point of view of the sensitivity.
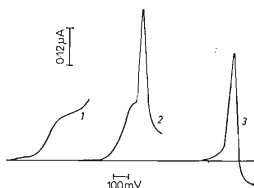

Fig. 1

FSDPP determination of cyanide. 1 Borate buffer pH 8·8, 0·01 mol/l KNO$_3$, 1 . 10^{-3} mol/l Ni^{2+}, 3 . 10^{-2} mol/l ethanolamine; 2 as in 1, 7·5 . 10^{-8} mol/l CN$^-$; 3 automatic subtraction of curve 1 from curve 2.

FSDPP technique yielded a well developed peak $(E_p = -0.22 \text{ V})$ in the borate buffer solution, pH 9·3. Detection limit under these conditions was 40 µg l^{-1}. At the concentration level 10^{-5} mol l^{-1} no change of the peak current was observed in the dependence on time. At the concentration level 10^{-6} mol l^{-1}, a slow decrease of the current values was found; 30 minutes after mixing the decrease was equal to 15% of the original current value. When, on the other hand, the curves were recorded within five minutes after mixing no change of the current was noticed. Reproducibility of the FSDPP determination is very good, in the concentration range 10^{-6} mol l^{-1} the relative mean deviation is 0·93%, at the level 10^{-5} mol l^{-1} it rises to 0·96%

DISCUSSION

The results given above show that the use of the DPP for the determination of cyanide is advantageous. When low cyanide amounts should be determined the application of rapid technique is preferable. This result is in full agreement with the conclusion published by Canterford[7], who suggests that the loss of cyanide by volatilization need not be considered only when a rapid technique of determination is applied. This problem was, however, not discussed in other papers devoted to the DPP (ref.[1]) or d.c. polarographic determination[2,3] of low cyanide concentration.

The use of catalytic current considerably increases the sensitivity of the determination. The method based on the measurement of the catalytic current of cyanide in solutions containing nickel(II)-ethanolamine complex has the detection limit 0·4 µg l^{-1} using the FSDPP technique. This method should be, however, very carefully applied because the slope of the calibration line changes. Therefore, the method of standard addition (with minimum threefold addition of standard solution) must be used for the evaluation of the results. The shape and position of the catalytic peak makes the measurement of the corresponding current rather difficult. A higher accuracy of the measurement can be achieved, when the catalytic peak is recorded with simultaneous subtraction of the curve of the electrolyte containing the nickel(II)-amine complex (Fig. 1). Under these conditions only the catalytic current is read from the polarogram and the relative mean deviation has the value 0·9% at the 10^{-8} mol l^{-1} cyanide concentration level.

The question of interferences is not substantial, because distillation is usually an integral part of the procedure for the determination of cyanide. Sulphides which are not separated by distillation do not interfere with the described determination.

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Translated by the author (M. K.).