Flow-injection analysis with a small cylindrical wire type electrode

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Abstract: An amperometric detector with a small thin mercury film electrode is described. The device demonstrates advantageous operational characteristics such as small dispersion (D<2) and "memory effect" (me < 0.6 %), extensive maximum sample frequency (msf – 200 samples/h), and high sensitivity. It has been proven useful in flow-injection analysis at a constant potential under hydrodynamic conditions.
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1 Introduction

Three basic electrode geometries are preferably used in the voltammetric analysis with flow injection detectors – wall-jet, thin layer and tubular electrodes (a wire fitted into open tubing). For solving various analytical problems an *a priori* prognosis of their applications could be done based on the theoretical descriptions of their behaviors. In the present study, a wire-type electrode (with dimensions 0.12 – 0.16 cm length, diameter 0.06 cm, fitted into open tubing with i.d. = 0.01 cm) has been characterized in flow–injection analysis under constant potential. Some theoretical considerations have been proven applicable for this particular type of electrode under the experimental conditions.

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2 Experimental

2.1 Reagents

Ammonia buffer solutions (1M NH_4OH/NH_4Cl) have been employed as carrier electrolytes. The standard solutions of Cd (II) with concentrations ranging from 2×10^{-4} to 10×10^{-4} g dm^{-3} have been prepared by using standards for atomic–absorption spectrometry (Merck, Germany) with a start concentration of 1 g dm^{-3}. The dilutions of the standards have been done with electrochemically purified 1 M ammonia buffer solution in 100 cm^3 volumetric flasks. All preparations have been made with double distilled water.

The working electrode was prepared as previously described [1], and the flow–injection system ensures that the carrier flows parally to the electrode surface and the electrochemical workstation were set up as illustrated in [2].

2.2 Continuous–flow measurements at potentiostatic regime

The continuous –flow measurements are among the most commonly used techniques in the flow analysis. The limiting current i_{ss} value is normally measured at steady state of the electrochemical reaction, where the diffusion layer thickness δ_N is maintained constant by a laminar flow. The hydrodynamic theory of Levich [3] gives the following common relationship for i_{ss} :

$$i_{ss} = nFAK_iC_0U^\alpha, \tag{1}$$

where: i_{ss} is the limiting steady - state current, μA; n is the number of the electrons exchanged; F is the Faraday constant, C mol^{-1}; A is the electrode surface, cm^2; K_i denotes limiting specific coefficient of mass transfer; U is the fluid flow rate, cm^3 s^{-1}; the power α is a non-integer constant, dependent on the electrode geometry.

When an amperometric cell is in use, equation 1 is frequently applied as a criterion for the laminar character of the flow. In that case the power agree to a constant value, dependent on the cell geometry: $\alpha = 1/2$ for thin-layer cells; 3/4 for wall-jet; and $\alpha = 1/3$ for tubular geometry. According to equation 1 the dependency of log i_{ss} on log U is linear with a slope equal to α. The deviations of α values from the theoretically expected ones could be due either to the flow regime changes or to the alterations in the degree of electrolysis [4].

In the present work is reasonable to consider more extensively equation 1 for the case of tubular electrode. According to M. Elbicki and co-authors [5] equation 1 could be presented as:

$$i_{ss} = 1.61\, nFC_0 \left(\frac{DA}{r}\right)^{\alpha-1} U \quad , \tag{2}$$

where: D is diffusion coefficient, $cm^2 s^{-1}$; r is the wire radius, cm; C_o is the sample initial concentration, g dm^{-3}. The comparison between equation 1 and equation 2 shows that $K_i = \left(\frac{DA}{r}\right)^{\alpha-1}$. A number of publications demonstrate the applicability of equation 2 for

the electrode with open tube geometry [6, 7] as well as for the metal wire in tube type electrode [8].

2.3   Potentiostatic measurements in flow-injection systems (FIS)

The responses of flow-injection measurements are peak-shaped and depend on such factors as the flow rate U, the dispersion coefficient D_m, the electrode geometry, etc. It is obvious that the current measured at the peak i_p differs from the value of i_{ss} measured at continuous flow.

According to P.L. Meschi and D.C. Johansson [9] for the case of open tube electrode the relationship between i_p and i_{ss} in a laminar flow is given by:

$$i\left(t\right) = i_{ss} \frac{C(x,d,t)}{C_0} \tag{3}$$

where: i(t) is time -dependent current, μA; $C(x, d, t)$ is the concentration at any point in the stream (x and d being the axial and radial coordinates).

According to equation 3, which specifies the sample dispersion $D_m = C_m/C_o$ (C_m denotes the concentration at the peak maximum, g dm^{-3}) the following relation is in force for the peak current i_p: $\frac{i_p}{i_{SS}} = \frac{C_m}{C_0}$, where from we obtain:

$$\frac{i_p}{i_{SS}} = \frac{1}{D_m} \tag{4}$$

Dispersion of the bolus of sample can be described by the simple expression [10]:

$$-\ln(1 - C_m/C_o) = k.S_v, \tag{5}$$

where: S_v is the sample volume, mm^3

Provided that the ratio C_m/C_0 is replaced by i_p/i_{ss} [11], equation 5 is transformed into:

$$-\ln(1 - i_p/i_{ss}) = k.S_v \tag{6}$$

that in turn, could be used as the start point for analyzing the data from flow–injection measurements. The plot of the normalized response i_p/i_{ss} vs. lg U is linear and the slope depends on the dispersion: its value is equal to -1/3 at low-, and to -1/6 at high dispersion, respectively. The negative value of the slope indicates a decrease of the ratio i_p/i_{ss} with increasing the flow rate due to the enlarged dispersion, which in turn is caused by a decreased (or descending) concentration gradient.

3   Experimental results and discussion

3.1   The effect of the flow rate on analytical responses

The conditions in the flow-injection analysis, in contrast to continuous flow systems, are non-stationary due to the continuous concentration changes in the sample zone perturbed

by the axial and radial dispersions. The sample dispersion is rather complex problem, which is theoretically solved only for open tube flowing stream [12, 13]. Due to the strong effect of the dispersion on analytical responses in amperometric measurements their description is even more complex problem [14, 15] and rather poorly studied.

Taking into account that the sample dispersion depends mainly upon the volume of the sample injected S_v and tube length L, the introductory experiments were carried out by varying these parameters. Fig. 1. represents the relationship between the normalized response i_p/i_{ss} and the tube length L. It could be seen that the ratio i_p/i_{ss} decreases linearly with L, with a slope of the linear dependency equal to $-3.6 \times 10^{-3} \mu A \cdot cm^{-1}$ and intercept the ordinate at $i_p/i_{ss} = 1$, i.e. i_p approaches i_{ss} for L approaching 0. On the secondary ordinate axis (right side) of Fig. 1., the values of $1/D_m$ as a function of the ratio i_p/i_{ss} are given. It could be seen that for L>15 cm the dispersion strongly increase, which in turn cause a decrease in i_p/i_{ss} value. Additionally, it is obvious that for operating under the conditions of limited dispersion $D_m<2$, the tube length less than 15 cm is required. Fig. 2. illustrates the effect of the injected sample volume S_v on the shape of the analytical response. The superimposing of the elevated parts in all curves is observed that is independent of S_v while the dispersion (given on the right ordinate axis) decreases with S_v ascending. At a volume of approximately 4 mm^3 50 % dilution of the sample zone is reached compared with the initial concentration C_0, which corresponds to $D_m=$ 2. The relation between S_v and the dispersion is illustrated on Fig. 2b. The results falling outside the limits $-\ln(1- i_p/i_{ss}) > 4$ ($i_p/i_{ss} > 0.98$) were not taken into account due to the error amplification, so that their meaning is ambiguous. It could be seen from the presented Figure 2-a that the normalized response decreases proportionally to the injected sample volume due to the increased zone dispersion. The dependency of $-\ln(1- i_p/i_{ss})$ on S_v keeps its linear trend up to 10 mm^3. The deviations from the linearity observed at $S_v = 40$ mm^3 are a result of concentration deficiency due to the electrochemical process [11]. The values of D_m based on the data from the same measurements are presented on the right ordinate axis Fig. 2a. They indicate that a limited dispersion typifies the flow-injection system and an additional expansion of the responses does not take place thus showing that the detector contribution for the enhancement of the dispersion value D_m is negligible.

Aiming at a full description of the proposed cell, the influence of the flow rate U on the amperometric response i_p is investigated. The plot of log i_p vs. log U has been found to be linear with a slope b of 1.02 (Fig. 3.) calculated by using the least-squares method (b = 1.04; r = 0.999, for N = 5; N denotes the number of samples). The direct proportionality between i_p and U might be used as an indirect indicator for the flow turbulence [4]. It is well known from the literature, that for the tubular electrode the increase of U cause a conversion of the laminar flow to turbulent, and the diffusion current becomes proportional to U [3]. The solutions reported in the literature for a cylindrical electrode under laminar flow could not explain all above considered results. Because of the construction reasons, it could be expected that at the electrode top, possessing about 6 % of the entire working area, the electrode will behave like a wall-jet type. Escaping of

the flow from the head part of the electrode will cause turbulence under which, according to the Levich hydrodynamic theory for non-streamline shape corps, the diffusion current increases proportionally to the flow rate U [3].

Concluding this particular discussion, we would like to underline that the amperometric responses measured in the cell proposed, amplifies due to enhanced mass-transport, resulting from the intense convection near the electrode surface. As a result, an improved sensitivity of the analysis could be expected.

The next problems significant from the analytical point of view are the reproducibility of the response, duration and analytical yield (maximum sample frequency). The typical flow-injection peaks of Cd (II) illustrating the calibration curve in the $\mu g \ mL^{-1}$ range are depicted on Fig. 4a. The good reproducibility, the stable baseline as well as their proportionality to the analyte concentration at constant volume of the standard samples injected are seen. The time effect on the analytical response is illustrated on Fig. 4b. At successive injection of two samples differing in their concentrations in position S_1, 5 seconds later, at position S_2 the remaining quantity of the sample in the cell after second injection was found to be below 0.6 %. That means that the "memory effect" does not exceed 0.6 %, since the transfer degree is below that limit. The maximal sample frequency S_{max} of reproductive analytical measurements depends upon the peaks expansion Δt caused by the dispersion, and on the coefficient k, taking into account their overlaying. For $\Delta t = 3$ s calculated from Fig. 4b. and k = 6 the maximum sample frequency found is $S_{max} = 200$ samples per hour. In the context of these data, it must be pointed out that the proposed cell construction permits a high analytical yield at "memory effect" below 0.6 % to be achieved.

4   Conclusions

Based on the experimental results discussed in the present work it could be seen that the proposed electrochemical cell with a small cylindrical electrode has been characterized as follows:

i) it shows dependencies of the analytical responses on the flow rate and on the injected sample volume approaching the theoretically expected ones;

ii) under working regime controlled dispersion is ensured D ≤ 2;

iii) high sample frequency is established $S_{max} = 200$ samples/hour;

iv) the dynamic linear range is found to be within the ppm- range. The high sensitivity and extended linearity of the response observed provide the opportunity for heavy metal ions determination by means of flow – injection analysis (FIA) under constant potential, provided that a method for preliminary components separation is also included in the system.

Notations and symbols

i_{ss} – limiting steady - state current, μA;

n – number of the electrons exchanged;

F – Faraday const, C mol^{-1};

A – electrode surface, cm^2;

K_i – limiting specific coefficient of mass transfer;

U – fluid flow rate, cm$^3 \cdot$s^{-1};

α – a non-integer constant, dependent on the electrode geometry;

D – diffusion coefficient, cm^{2}s^{-1};

r – wire radius, cm;

k – numerical coefficient;

L – tube length, cm;

D_m – dispersion coefficient;

S_v – sample volume, mm^3;

i_p – peak current, μA;

C_o – initial sample concentration, g dm^{-3};

C_m – concentration at the peak maximum, g dm^{-3};

N – number of samples;

δ_N – diffusion layer thickness, cm;

i(t) – time -dependent current, μA;

Acknowledgment

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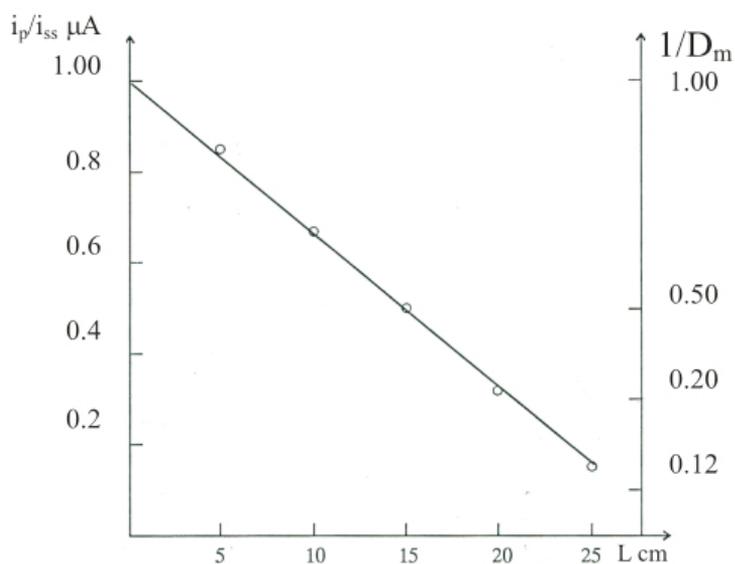
Fig. 1 The dependence of i_p / i_{ss} upon the tube length (L), i.e. the overall length of the tubes in the system, under the following experimental conditions: working potential E_d = -1.2 V (vs. SCE); flow rate U = 0.02 mm^3·s^{-1}; sample volume S_v = 10 mm^3; the analyte concentration $C_{Cd(II)}$ = 0.0126 g·dm^{-3}.
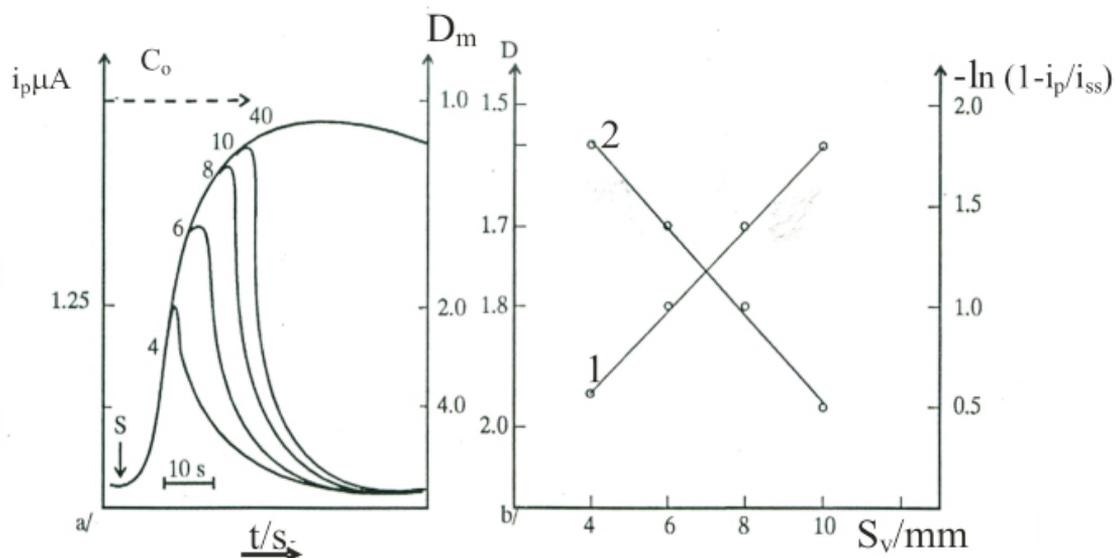
Fig. 2 a) Flow-injection peaks' variatios with the sample volume (marked over the corresponding curve - all curves recorded on the single point S); b) The dependence of the analytical response (1) $-\lg(1 - i_p/i_{ss})$, the right Y-axis and the dispersion (2) (D_m given on the left Y-axis) on the sample volume S_v mm^3 under constant working potential $E_d = -1.2$ V; flow rate U= 0.02 cm$^3\cdot$s^{-1}; analyte concentration $C_{Cd(II)} = 0.1$ g$\cdot$dm^{-3} (N=5).
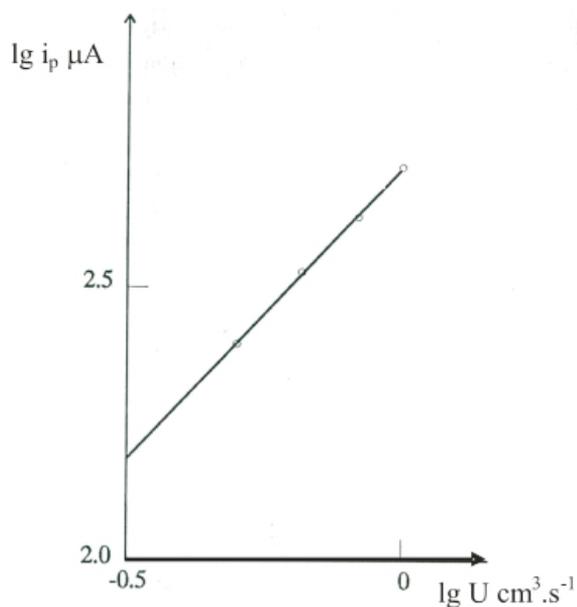
Fig. 3 Dependence of the current ip on the flow rate U in logaritmic co-ordinates at constant analyte concen-tration $C_{Cd(II)} = 0.01$ g·dm^{-3} in 1M am-monium buffer ;working potential E_d = - 1.2 V (vs. SCE); sample volume $S_v = 10$ mm^3 , (N=5).
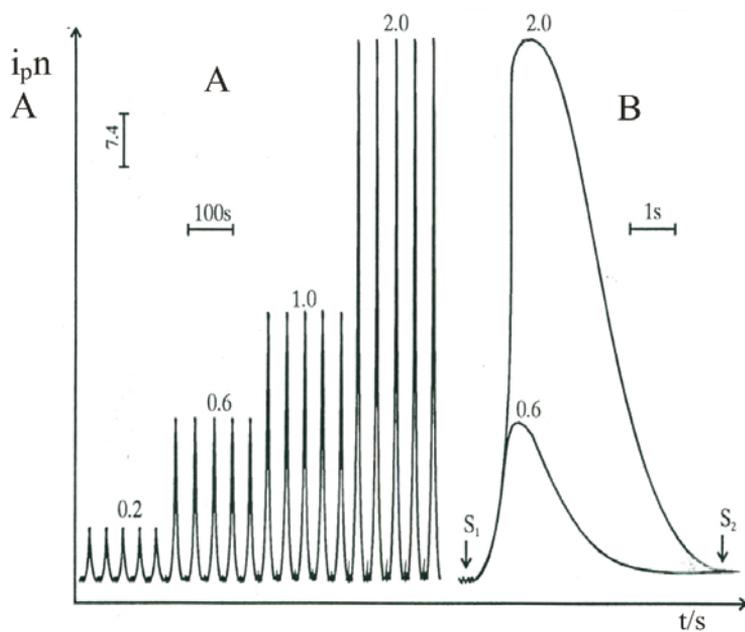
Fig. 4 Flow-injection recordings for the calibration curve of Cd (II) analysis at usual scan rate (A) and at a rapid scanning of the signals (B); $C_{Cd} = 1.10^{-4}$ g·dm^{-3} the analyte concentrations are given over the corresponding FI peaks; flow carrier: 1M ammonium buffer solution.