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Simultaneous determination of species by Differential Alternative Pulses Voltammetry

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Abstract

A new voltammetric technique providing high resolution – Differential Alternative Pulses Voltammetry (DAPV) based on the non-linearity of I/E characteristic of the electrochemical systems was developed, suitable for simultaneous determination of species without their preliminary separation. Superimposition of couples of single rectangular pulses separated by a constant delay time and having same amplitude and opposite polarity, combined with appropriate signal processing yields first derivative of peak shaped curve. The DAPV faradaic current response equation for reversible electrochemical reactions was theoretically derived, graphically presented and experimentally tested. DAPV was applied for determination of species having very near $E_{1/2}$ potentials: Pb^{2+}/Tl^{+} and In^{3+}/Cd^{2+} under increasing concentration ratios. The experimental results compared with those obtained by Differential Pulse Polarography (DPP) and Second Harmonic Alternating Current Polarography show superiority of DAPV resolution power which is combined with high sensitivity, similar to that providing by DPP, employing a simple electronic equipment.

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1. Introduction

The voltammetry (polarography) is among the few analytical methods providing simultaneous species determination in concentrated matrixes providing high sensitivity, low Limit of Detection (LOD) and high resolution power. Additional advantages are the simple procedures of sample pretreatment, as well as the short time and low cost of the determinations. Nevertheless, the application of the voltammetry (polarography) has been restricted recently because of the toxicity of mercury, the most used working electrode material in the past. The mercury electrode can be successfully replaced by solid ones, overcoming their area

reproducibility and working potentials range problems as demonstrated by many authors [1–3].

The simultaneous voltammetric determinations of species couples having very near half-wave potentials $E_{1/2}$ (like Pb^{2+} and Tl^{+} ; In^{3+} and Cd^{2+} ; Co^{2+} and Ni^{2+} ; etc.), as well as species couples with high concentration ratios are problematic however. Even if applying voltammetric techniques providing high resolution power as Differential Pulse Polarography (DPP) [4–8] or Square Wave Polarography (SWP) [9–17] peak overlapping occurs, making the accurate measurement of peak heights complicated, hence the concentration determinations remain unsatisfactory.

The application of some preliminary chemical separation procedures or appropriately optimized supporting electrolytes most often containing specific complexation agents allows limiting or even overcoming the problem, making however the determinations complex, time-con-

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suming or in some cases less precise [18]. Exploiting some mathematical data processing procedures such as FFT [19,20] can be helpful, but unfortunately this approach is also rather complicated and can result in a precision decrease.

A more simple and efficient way providing better peak separation is the application of some of the second-order voltammetric techniques such as Radio-Frequency Polarography (RFP) [21–28], Differential Faradaic Rectification Polarography (DFRP) [29] or Second Harmonic AC Polarography (SHACP) [30–37]. The shape of the voltammogram corresponds to the first-order derivative of peak: the curve involve cathodic peak followed immediately by anodic one, allowing the peaks located at both sides of the zero line to be used for concentration determination in case of overlapping. Many electrochemical reactions however, become irreversible at the high frequencies applied in RFP (0.1 MHz up to 6.4 MHz), thus decreasing the sensitivity of the determinations [38,39]. On the other hand, the sensitivity of some second-order voltammetric techniques (as SHACP) is unsatisfactory [30]. The optimal combination of high sensitivity and instrumental simplicity achieved in DPP and SWP allows their wide application, while the specific noncommercial electronic equipment required by the second-order techniques limits their wider use, in spite of their superior resolution power.

The present paper describes the principles and some applications of a new voltammetric technique called Differential Alternative Pulses Voltammetry (DAPV), providing high resolution power as the second-order voltammetric techniques do, combined with high sensitivity and instrumental simplicity. The sensitivity of DAPV was determined by the common criteria and the resolution power was evaluated comparatively to the other voltammetric techniques under the same conditions, since no ideal ions couples exist providing the properties corresponding to the strict definition of resolution power [40,41].

According to the UPAC definition [42] polarography refers to voltammetry, only applied with mercury or other liquid conductor indicator electrode. The term voltammetry is used in the present paper as a more general one, although most of the results were obtained by the application of Hanged Mercury Drop Electrode (HMDE). Application of DAPV with solid electrodes yields the same results.

2. Experimental

2.1. Reagents

All the reagents used in the experiments were of analytical grade and were purchased from Merck. The solutions were prepared in plastic labware using deionized water purified by Mili Ro and Mili Q water purification systems. The specific electrical resistance of the deionized water was not less than $18 \text{ M}\Omega \text{ cm}^{-1}$.

2.2. Instrumentation

Z-50 (Zenit Lab.), POL-150 (Radiometer) and E 506 (Metrohm) polarographic analyzers were used in combination with their corresponding electrode stands. Hanged Mercury Drop Electrode (HMDE) was applied as working electrode; Ag, AgCl|KCl (3 mol L^{-1}) was the reference electrode and the auxiliary electrode was a Pt wire. A National Instrument Data Acquisition System was used together with E 506 polarograph for real time data transfer to PC. All the measurement data obtained by the three instruments were processed off-line applying SigmaPlot Graphic Software.

2.3. Experimental conditions and measurement procedures

All the curves were recorded using potential scan rate of 10 mV s^{-1} applied with a scan step of 5 mV every 0.5 s. The width of the superimposed rectangular pulses was 60 ms and the pulse amplitude was adjusted in the range from 5 to 50 mV. A Z-50 device was properly modified to perform the potential–time waveform and current signal processing according to DAPV technique requirements.

The volume of the solutions in the electrochemical cell was 20 ml. The desired concentrations were achieved by direct additions of small volumes of appropriately diluted Merck standard solutions into the cell. BIOHIT Proline electronically adjustable pipettes were used for this purpose.

All the solutions were purged with Ar gas for 10 min to remove the oxygen. All the calculated results were obtained averaging 3–5 curves.

3. Results and discussion

3.1. Principles of DAPV

3.1.1. I/E nonlinearity

The current–potential relationship for reversible diffusion controlled electrochemical reactions is described by the following equation, yielding wave-shaped curve having an inflexed point for $E = E_{1/2}$ [43]:

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{I_1 - I_t}{I_t} \quad (1)$$

where E is the potential, $E_{1/2}$ is the half-wave potential, R is the gas constant, T is the absolute temperature, n is the number of transferred electrons, F is the Faraday constant, I_1 is the limiting current and I_t is the instantaneous current. All the voltammetric methods applied recently including DPP, SWP, as well as the second-order ones use this non-linear relationship. The small deviations of the potential superimposed on its main value, shaped as rectangular pulses (DPP and SWP) or sinusoids (second-order techniques) generate current responses which amplitudes follow the slope of this I/E curve, yielding peak shaped plots.

DPP is based on the generation of a pulse faradaic current response dI_p separated along the time from the pulse capacitance current dI_c , the both resulting from a single rectangular pulse dE superimposed on the main dc electrode potential E . The dI_p/E plot has the shape of peak with a height proportional to the analyte concentration, and peak potential corresponding to $E_{1/2}$ shifted with $dE/2$ [4–8,44,45].

The second-order voltammetric (polarographic) techniques are based on the effect of Faradaic rectification, first described by Doss and Agarwal [46–48] as “redox-kinetic effect”, theoretically explained later by Oldham [49], Delahay et al. [50,51] and others [52–59]. One of its manifestation forms is the appearance of a dc current component I_{fr} resulting from the superimposition of a small amplitude ($<RT/nF$) bipolar sinusoidal voltage on the main electrode potential E . The frequency can be very high, up to 6.4 MHz as reported by Barker [21,22], as well as lower than 1 kHz as reported by Saur [29]. As shown by Barker [21], Saur [29] and Chernenko [59,60], the appearance of the effect of the faradaic rectification is due to the nonlinearity of I/E characteristic only and it does not depend on the frequency, which can influence the amplitude of the response only.

Thus, every one period of the superimposed bipolar sinusoidal voltage can be assumed as a pair of successive pulses having the same shapes, duration and amplitudes, but opposite polarities. For the frame of one period, the resulting dc current component I_{fr} can be considered as a deviation of the average of the two corresponding (cathodic and anodic) faradaic current responses. According to the I/E curve shape (Eq. (1)), the I_{fr} has three times zero values: for potential ranges corresponding to “residual” and “diffusion limited” currents, as well as for $E = E_{1/2}$. Thus, the I_{fr}/E plot obtains the shape of first-order peak derivative passing three times through zero with peak

amplitudes depending on the concentration, angular frequency ω and forward electrode process rate constant k_o as shown by Barker [21]. For small electrochemical reaction rate constant k_o and very high frequency, the I_{fr} amplitude should be very small even close to zero. The I_{fr}/E plot is symmetrical only for $\alpha = 0.5$ and $\omega D_o = (k_o)^{1/2}$ [21], where α is the transfer coefficient and D_o is the diffusion coefficient. The asymmetry of the I_{fr}/E plot can be very useful for species determinations using the peaks situated on both sides of the zero line in case of overlapping.

3.1.2. DAPV current response

The voltammetric methods based on the superimpositions of small deviations ($<RT/nF$) of the potential shaped as rectangular pulses (DPV, SWV) or sinusoids (ACV, SHACV, RFP, DFRP) result in “electrochemical differentiation” of the I/E curves and their plots have dI/dE or $\delta^2 I/\delta E^2$ shape in general. The maximal faradaic current response is determined by the amplitude of the potential deviation dE , and the I/E curve slope at this point, as illustrated in Fig. 1C. The shape of the potential deviation dE (rectangular pulse or sinusoid) can only diminish the amplitude of the faradaic current response, according to the electrochemical reaction rate constant and the potential deviation rise time. As it was shown theoretically by Delahay et al. [50], the mean faradaic rectification current and the current response of the voltage step potentiostatic method are equals, thus proving that the origin of both current responses is the same – the nonlinearity of the I/E characteristic of the electrochemical reaction.

Since the appearance of the faradaic rectification dc current component I_{fr} depends on the nonlinearity of the I/E characteristic only, same type of response could be expected if superimposing on the main electrode potential E pairs of single successive rectangular pulses, having equal amplitudes ($<RT/nF$) and durations (from 1 to 100 ms),

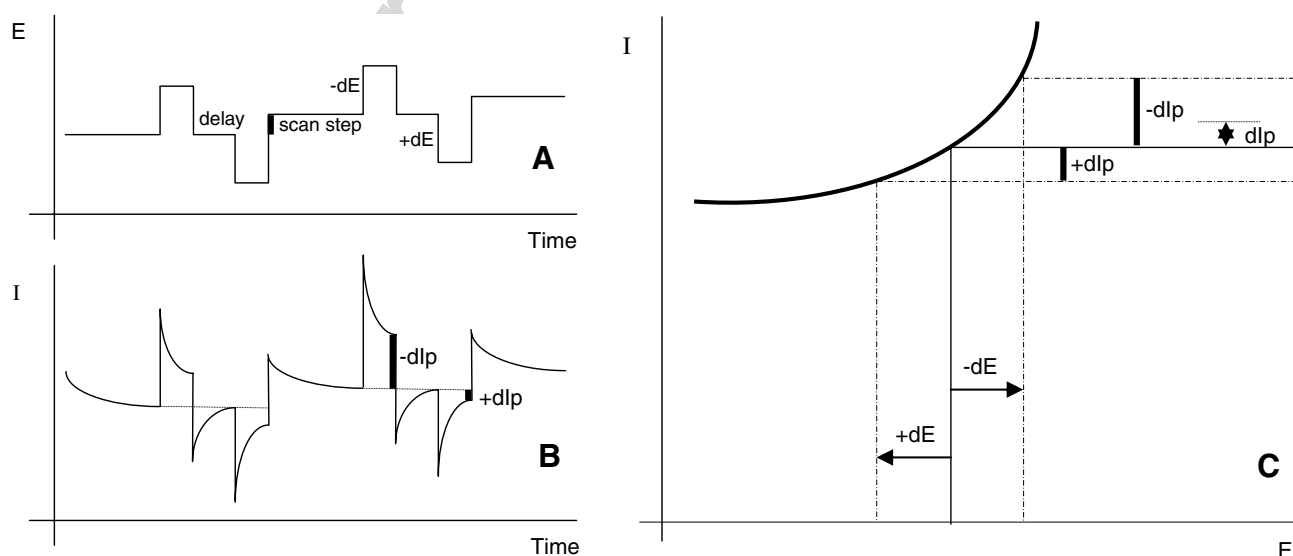


Fig. 1. DAPV base principle: (A) potential/time curve; (B) current/time curve; and (C) DAPV current response.

but opposite polarities (respectively, $+dE$ and $-dE$), with a delay time between them, according to Fig. 1A. The delay between the opposite pulses must be long enough to prevent the influence between them. Practically this condition is fulfilled for delays longer than 350 ms. Combining the described potential/time waveform with an appropriate signal processing extracting the faradaic current response in accordance to Eq. (4), a voltammetric method is obtained which takes advantages from both – the high resolution power of the second-order voltammetric techniques as RFP and DFRP and the high sensitivity and instrumental simplicity of the rectangular pulses based techniques as DPP and SWP.

Superimposition of cathodic and anodic rectangular pulses $-dE$ and $+dE$ on the electrode potential E generates corresponding pulse faradaic current components dI_{p-} and dI_{p+} , respectively [7,45,61], described by the following equations:

$$dI_{p-} = \frac{n^2 F^2}{RT} AC(-dE) \sqrt{\frac{D}{\pi t}} \frac{P_-}{(1 + P_-)^2} \quad (2)$$

$$dI_{p+} = \frac{n^2 F^2}{RT} ACdE \sqrt{\frac{D}{\pi t}} \frac{P_+}{(1 + P_+)^2} \quad (3)$$

with: $P_- = \exp[(E - E_{1/2} - \frac{dE}{2}) \frac{nF}{RT}]$ and $P_+ = \exp[(E - E_{1/2} + \frac{dE}{2}) \frac{nF}{RT}]$, where R is the gas constant, T is the absolute temperature, n is the number of transferred electrons, F is the Faraday constant, A is the electrode area, C is the concentration, dE is the pulse amplitude, D is the diffusion coefficient and t is the current measurement delay time.

This equation is valid for reversible electrode reactions, and the reversibility can be quantitatively reliably characterized by the technique proposed by Osteryoung and Kir-

owa-Eisner [62]. According to Eqs. (2) and (3) for $E = \text{const}$, the absolute values of the forward dI_{p+} and the reverse dI_{p-} pulse faradaic current responses are not equals in general. Their difference is due to the nonlinearity of the electrochemical system I/E characteristic, expressed by Eq. (1), illustrated in Fig. 1C. For every value of the main potential E the deviation dI_p of the average of the pulse responses dI_{p-} and dI_{p+} plotted against the potential E yields a first derivative of peak shaped curve, described by the following equation valid for reversible electrochemical reactions:

$$dI_p = \frac{n^2 F^2}{RT} ACdE \sqrt{\frac{D}{\pi t}} \left[\frac{P_+}{(1 + P_+)^2} - \frac{P_-}{(1 + P_-)^2} \right] \quad (4)$$

The dI_p/E curve passes three times through zero, involving anodic and cathodic peaks as shown qualitatively in Fig. 2A. Curves 1 and 2 correspond to the forward and the reversed pulse faradaic current response, according to Eqs. (2) and (3), while curve 3 represents the resulting DAPV faradaic current response – the dI_p/E plot. For irreversible electrochemical reactions, this curve is asymmetrical similar to the RFP plot, which can be very useful in determination of species having near $E_{1/2}$ as discussed above.

According to Eq. (4) the peaks heights (for the same concentration C) depend on the pulse amplitude dE as presented graphically in Figs. 2B and 3A, where a families of normalized theoretical dI_p/E curves for increased pulse amplitude are shown. According to Eq. (4), the current response dI_p , respectively dI_{p+}^{max} and dI_{p-}^{max} rises with the square of the pulse amplitude dE since P_+ and P_- also are functions of dE . A complete 3D presentation of Eq. (4) is shown in Fig. 3A where the current response dI_p is

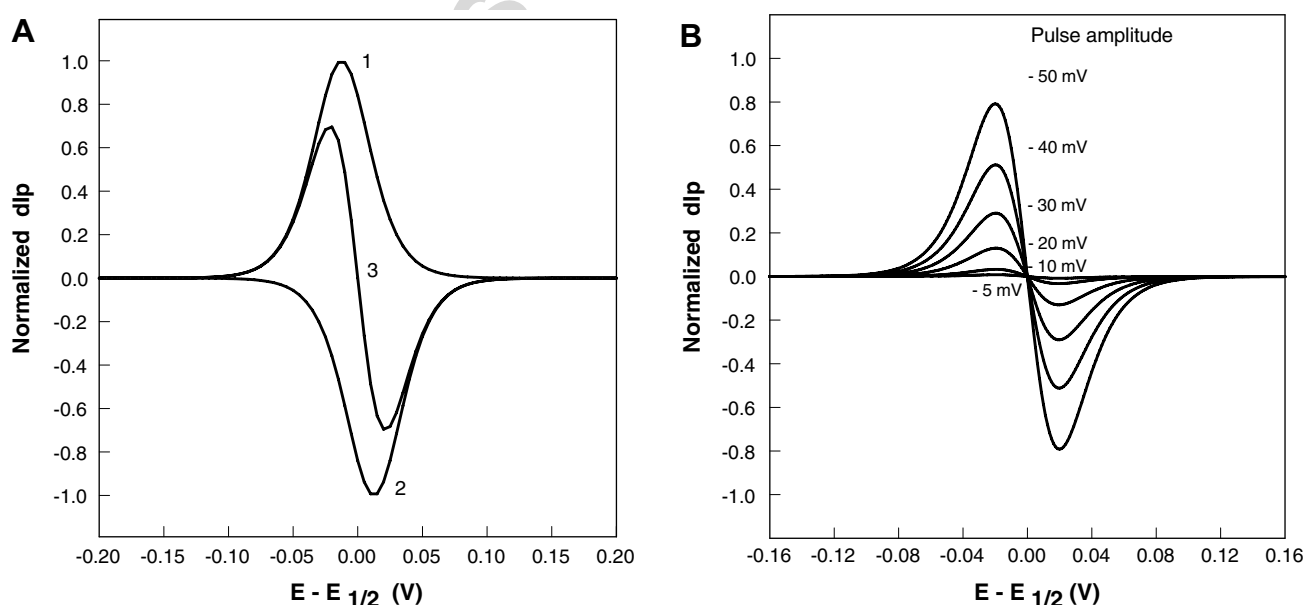


Fig. 2. Theoretical DAPV curves: (A) normalized theoretical curves for forward (curve 1), reverse (curve 2) and DAPV (curve 3) pulse faradaic current responses and (B) family of normalized DAPV curves at different pulse amplitudes.

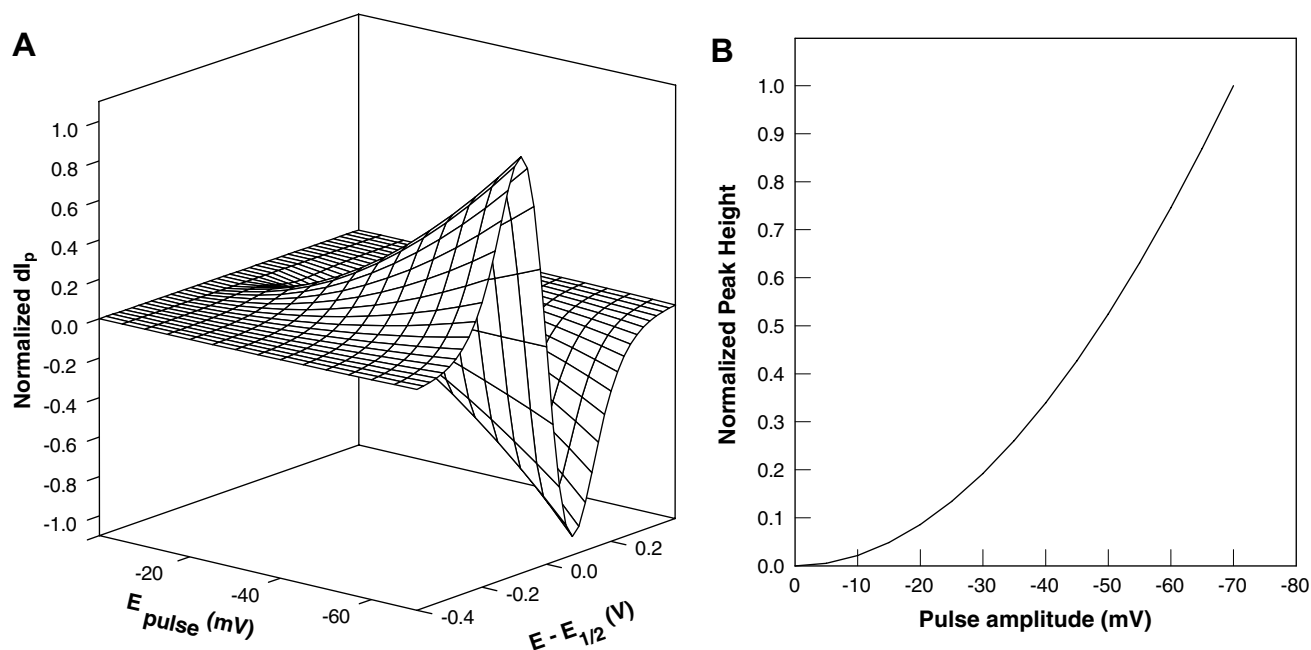


Fig. 3. Theoretical DAPV curves: (A) 3D presentation of DAPV current response equation and (B) DAPV peak height–pulse amplitude profile.

plotted vs. the electrode potential E and the pulse amplitude dE . The parabolic profile of this $dI_p(E, dE)$ surface is shown in Fig. 3B.

The theoretical curve of DAPV fits very well with the plot for 1 mol L^{-1} HCl solution containing $1 \mu\text{mol L}^{-1}$ Pb^{2+} and $1 \mu\text{mol L}^{-1}$ Cd^{2+} , shown in Fig. 4A. In general, the DAPV plot dI_p/E has the shape of first derivative of peak involving cathodic and anodic parts, allowing to distinguish the peaks situated on both side of the zero line in case of overlapping, when species having near $E_{1/2}$ are determined simultaneously.

3.2. Simultaneous species determination applying DAPV

An adequate simultaneous determination of species is possible only if distinguishable peaks can be recorded, thus allowing precise peak height measurement and concentration determination. Complicated cases appear when the $E_{1/2}$ difference of the determined species is small and/or their concentration ratio is high. In these cases, the half-width of the peaks and the shape of the curve are of a great importance for a satisfactory concentration determination. The resolution power of DAPV was tested determining

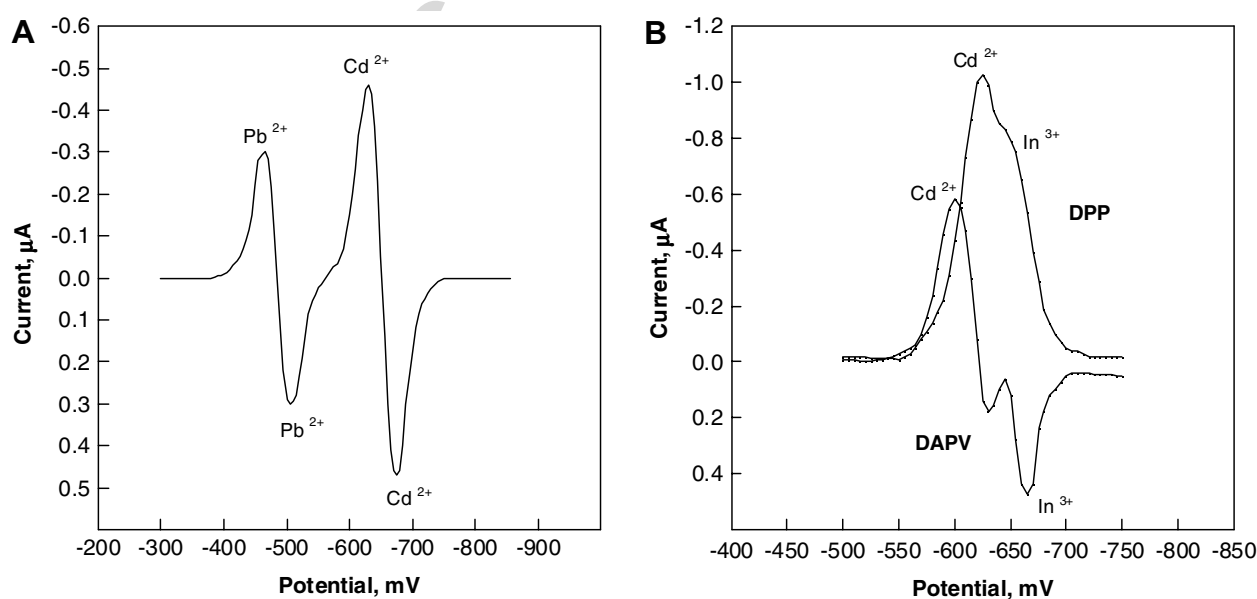


Fig. 4. Experimental DAPV and DPP curves: (A) DAPV curves of $10^{-6} \text{ mol L}^{-1}$ Pb^{2+} and $10^{-6} \text{ mol L}^{-1}$ Cd^{2+} in 1 mol L^{-1} HCl, $dE = -25 \text{ mV}$, pulse width = 60 ms and (B) DAPV and DPP curves of $5 \times 10^{-7} \text{ mol L}^{-1}$ In^{3+} and $10^{-6} \text{ mol L}^{-1}$ Cd^{2+} in 0.5 mol L^{-1} acetate buffer with pH 4.5, $dE = -25 \text{ mV}$, pulse width = 60 ms.

species having $E_{1/2}$ difference in the range from 28 to 50 mV and concentration ratios from 1:1 up to 80:1 in supporting electrolytes with appropriate composition and concentration. A qualitative illustration of the resolution power of the DAPV is shown in Fig. 4B comparatively with that of DPP. Species couple In^{3+} and Cd^{2+} in 0.5 mol L^{-1} acetate buffer with pH 4.5 as supporting electrolyte was employed, having $E_{1/2}$ difference of 28 mV. Being situated on the both sides of the zero line the cathodic and anodic peaks of Cd^{2+} and In^{3+} are completely distinguished on the DAPV curve, while the peaks recorded by DPP are completely overlapped.

The most complicated are the cases when the small $E_{1/2}$ difference is combined with a high concentration ratio. The small peak half-width allows higher concentration ratios to be achieved before the peak overlapping, thus allowing more precise peak height measurement. The experimentally determined half-width of the peak obtained from DAPV curves is 37 mV for reversible electrochemical reactions, equal to that obtained by the application of the second-order polarographic technique DFRP [29]. The $E_{1/2}$ difference of In^{3+} and Cd^{2+} in HCl (6 mol L^{-1}) is only 50 mV and the simultaneous determination of both species applying DPP is impossible at concentration ratios higher than 10:1, because of complete peaks overlapping. DPP and DAPV curves for $2 \times 10^{-4} \text{ mol L}^{-1} \text{ In}^{3+}$ and $5 \times 10^{-6} \text{ mol L}^{-1} \text{ Cd}^{2+}$ in 6 mol L^{-1} HCl, corresponding to concentration ratio of 40:1 are shown in Figs. 5A and B, registered by Z-50 device. On the DPP curve (Fig. 5A) practically exists only one peak – those of In^{3+} , while the Cd^{2+} peak appears as a small change of the curve slope only, because of the overlapping. On the DAPV curve (Fig. 5B) however the two peaks are completely distin-

guishable at these conditions, even up to concentration ratio as high as 80:1 (not shown).

The increased resolution power of DAPV permits its application in multicomponent species analysis without preliminary separation procedures, as demonstrated in Fig. 6B. Voltammograms of Cu^{2+} , Pb^{2+} , Tl^{+} , In^{3+} , Cd^{2+} and Zn^{2+} in acetate buffer solution (0.5 mol L^{-1}) recorded by the application of DPP and DAPV are presented. The peaks of Pb^{2+} and Tl^{+} , as well as of In^{3+} and Cd^{2+} couples, having the smallest $E_{1/2}$ difference among this species group (39 and 28 mV, respectively) are completely overlapped on the DPP curve (Fig. 6A), while their peaks being situated on different sides of the zero line on the DAPV curve are rather distinguishable (Fig. 6B).

The results obtained by DAPV in simultaneous determination of species having small $E_{1/2}$ difference and high concentration ratio was compared also with that obtained by the application of the second-order technique SHACP. The $\text{Pb}^{2+}/\text{Tl}^{+}$ species couple in 0.1 mol L^{-1} HCl having $E_{1/2}$ difference of about 50 mV was employed at concentration ratios $[\text{Pb}^{2+}]:[\text{Tl}^{+}]$ starting from 1:1 up to 20:1. Complete overlapping of the peaks occurs on SHACP curve at ratio 12:1 (Fig. 7A), and 8:1 on the DPP curve, while the two peaks are still distinguishable on the DAPV curve at 12:1 ratio (Fig. 7B), as well as up to 20:1 ratio under the same conditions.

The sensitivity of DAPV determination (i.e. the slope of the calibration plot) was compared with DPP using Cd^{2+} in 1 mol L^{-1} solution of HCl with application of HMDE. It was found that the slope of the calibration plot for DAPV built by the measurement of both the cathodic and the anodic peak heights is the same as those obtained for DPP. The limit of detection (LOD) of DAPV under the mentioned

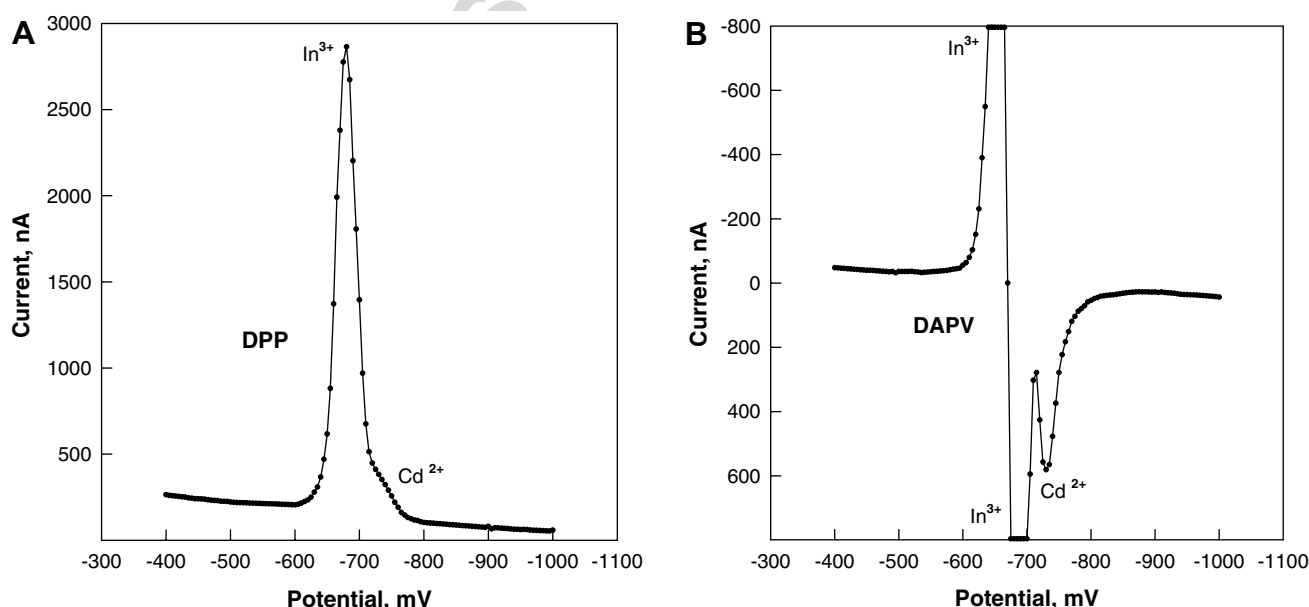


Fig. 5. Voltammograms of $2 \times 10^{-4} \text{ mol L}^{-1} \text{ In}^{3+}$ and $5 \times 10^{-6} \text{ mol L}^{-1} \text{ Cd}^{2+}$ in 6 mol L^{-1} HCl, i.e. in concentration ratio 40:1: (A) DPP curve and (B) DAPV curve.

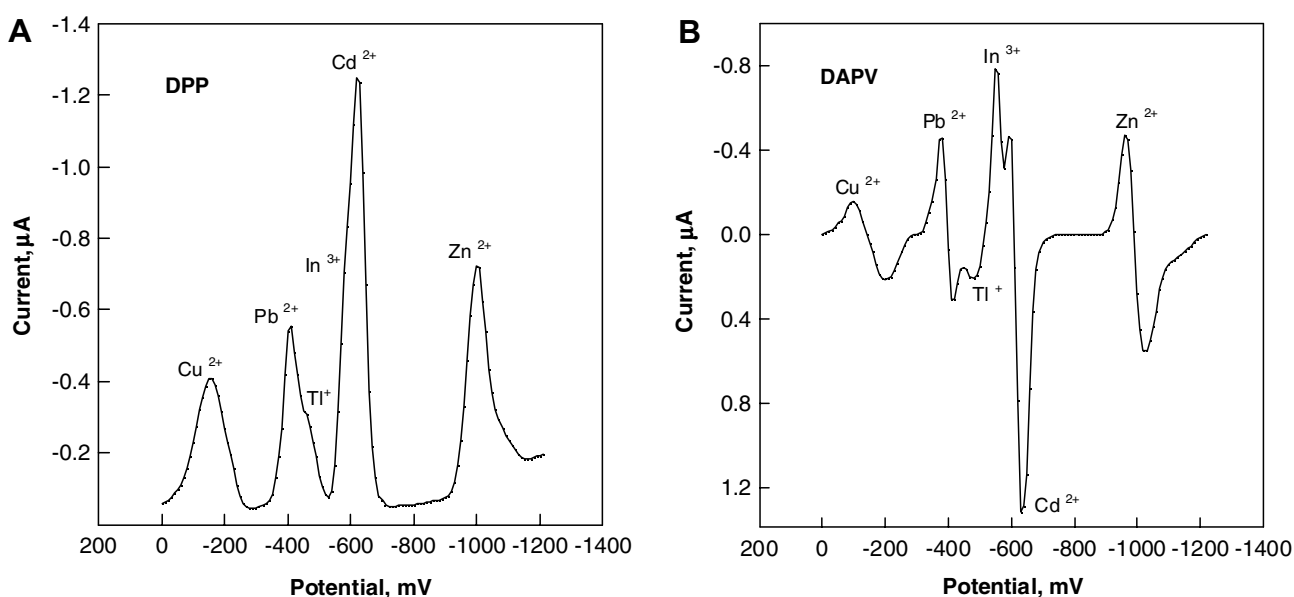


Fig. 6. Voltamograms of Cu²⁺, Pb²⁺, Tl⁺, In³⁺, Cd²⁺ and Zn²⁺ in 0.5 mol L⁻¹ acetate buffer, $dE = -25$ mV, pulse width = 60 ms: (A) DPV curve and (B) DAPV curve.

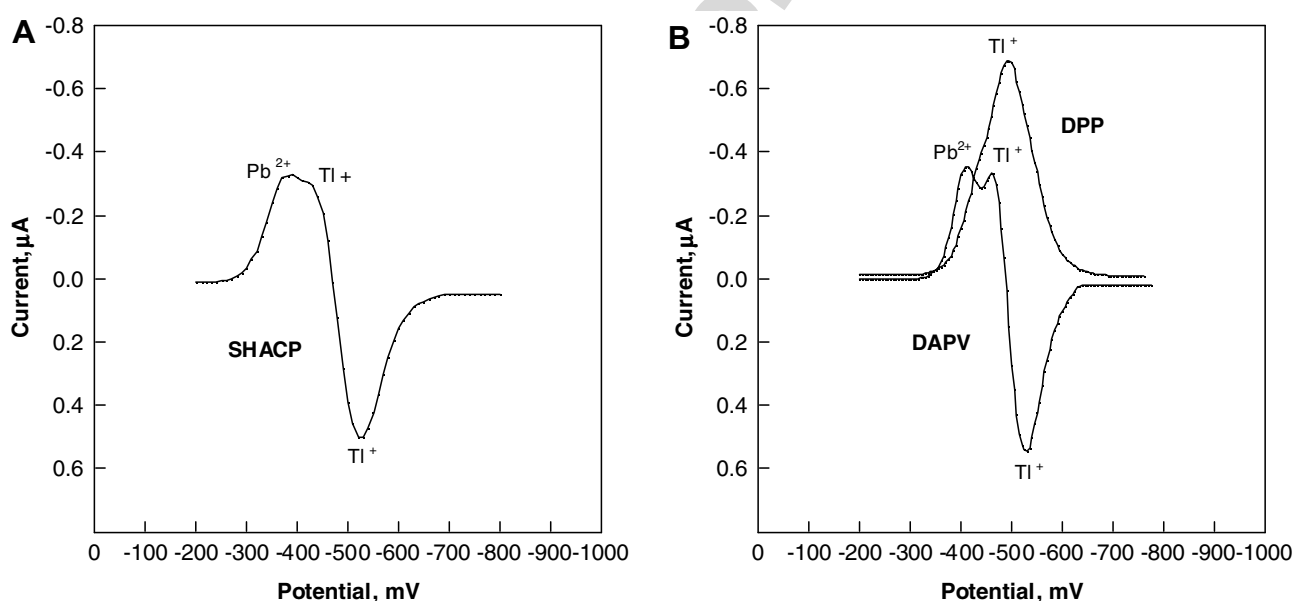


Fig. 7. Voltamograms of Pb²⁺ and Tl⁺ in 0.1 mol L⁻¹ HCl at 12:1 concentration ratio: (A) SHACP curve; $dE = 30$ mV and (B) DAPV and DPV curves; $dE = 30$ mV.

conditions was determined to be 54 nmol L⁻¹, similar to LOD of DPP.

4. Conclusion

Based on the electrochemical systems nonlinear I/E characteristics, a new voltammetric technique – Differential Alternative Pulses Voltammetry (DAPV) was developed. A theoretical equation describing the DAPV current response dI_p/E for reversible electrochemical reactions was derived

and graphically presented. The experimental results obtained by the application of DAPV on real solutions appeared to be in good agreement with this equation.

DAPV was applied for simultaneous determination of species having very near $E_{1/2}$ (between 28 and 50 mV) such as Pb²⁺ and Tl⁺, as well as In³⁺ and Cd²⁺ at concentration ratios ranging from 1:1 to 1:20 and from 1:1 to 1:80, respectively. The comparison with DPP and SHACP shows that DAPV provides higher resolution power than the other two techniques do, thus allowing the simultaneous determi-

nation of species without their preliminary separation, making voltammetric analysis simple, fast and easy for automation.

References

- [1] J. Wang, S. Thongngamdee, D. Lu, *Electroanalysis* 18 (2006) 59.
- [2] E. Kirowa-Eisner, M. Brand, D. Tzur, *Anal. Chim. Acta* 385 (1999) 325.
- [3] S. Laschi, I. Palchetti, M. Mascini, *Sensor. Actuator. B* 114 (2006) 460.
- [4] G.C. Barker, A.W. Gardner, *Z. Anal. Chem.* 173 (1960) 79.
- [5] G.C. Barker, in: P. Zuman, J.M. Kolthoff (Eds.), *Progress in Polarography*, vol. 2, Wiley-Interscience, New York, 1962, pp. 411–427.
- [6] J. Osteryoung, *J. Chem. Educ.* 60 (1983) 296.
- [7] R.A. Osteryoung, J. Osteryoung, *Philos. Trans. Roy. Soc. London A* 302 (1981) 315.
- [8] J. Osteryoung, K. Hasebe, *Rev. Polar.* 22 (1976) 1.
- [9] G.C. Barker, I.L. Jenkins, *Analyst* 77 (1952) 685.
- [10] D.P. Whelan, J.J. O'Dea, J. Osteryoung, K. Aoki, *J. Electroanal. Chem.* 202 (1986) 23.
- [11] G.C. Barker, R.L. Faircloth, A.W. Gardner, A.E.R.E. report, Harwell (1958) C/R 1786.
- [12] K. Aoki, K. Tokuda, H. Matsuda, J. Osteryoung, *J. Electroanal. Chem.* 207 (1986) 25.
- [13] K. Wikiel, J. Osteryoung, *Anal. Chem.* 61 (1989) 2086.
- [14] S.P. Kounaves, J.J. O'Dea, P. Chandrasekhar, J. Osteryoung, *Anal. Chem.* 59 (1987) 386.
- [15] S.P. Kounaves, J.J. O'Dea, P. Chandrasekhar, J. Osteryoung, *Anal. Chem.* 58 (1986) 3199.
- [16] E.J. Zachowski, M. Wojciechowski, J. Osteryoung, *Anal. Chim. Acta* 183 (1986) 47.
- [17] K.B. Oldham, D.J. Gavaghan, A.M. Bond, *J. Phys. Chem. B* 106 (2002) 152.
- [18] R. Bock, *Handbook of Decomposition Methods in Analytical Chemistry*, Verlag Chemie GmbH, Weinheim, 1979.
- [19] R.J. O'Halloran, D.E. Smith, *Anal. Chem.* 50 (1978) 1391.
- [20] D.E. Smith, *Anal. Chem.* 48 (1976) 221A.
- [21] G.C. Barker, *Anal. Chim. Acta* 18 (1958) 118.
- [22] G.C. Barker, A.W. Gardner, M.J. Williams, *J. Electroanal. Chem.* 42 (1973) 21.
- [23] S. Tsuruya, T. Kanno, *Tohoku Daigaku Senko Seiren Kenkyusho Iho* 22 (1966) 17.
- [24] T. Kambara, Sh. Watarai, *Bull. Chem. Soc., Jpn* 39 (1966) 521.
- [25] G. Wolff, W.H. Nurnberg, *Frezenius Z. Anal. Chem.* 224 (1967) 332.
- [26] V.V. Senkevich, L.P. Chernega, V.I. Bodyu, Yu.S. Lyalikov, *Zavod. Lab.* 34 (1968) 1176.
- [27] H.P. Agarwal, M. Saxena, *Ind. J. Chem. A* 16 (1978) 754.
- [28] G.C. Barker, *Proc. Anal. Div. Chem. Soc.* 12 (1975) 179.
- [29] D. Saur, *Frezenius Z. Anal. Chem.* 298 (1979) 128.
- [30] H. Sawamoto, *Kochi Daigaku Gakujutsu Kenkyu Hokoku, Shizen Kagaku* 27 (1978) 181.
- [31] F. Fagioli, F. Dondi, C. Bighi, *Ann. Chim. (Rome, Italy)* 68 (1978) 111.
- [32] F. Fagioli, F. Dondi, T. Garai, J. Devay, *Kem. Kozl.* 48 (1977) 401.
- [33] F. Fagioli, T. Garai, J. Devay, *Ann. Chim. (Rome, Italy)* 64 (1974) 633.
- [34] H. Blutstein, A.M. Bond, *Anal. Chem.* 46 (1974) 1531.
- [35] H.H. Bauer, D.C.S. Foo, *Aust. J. Chem.* 19 (1966) 1103.
- [36] H.H. Bauer, *J. Sci. Industr. Res. India B* 24 (1965) 372.
- [37] R.Z. Neeb, *Anal. Chem.* 188 (1962) 401.
- [38] D.E. Smith, in: A.J. Bard (Ed.), *Electroanalytical Chemistry*, vol. 1, Marcel Dekker, New York, 1966, pp. 1–155.
- [39] G. Wolff, H.W. Nürnberg, *Frezenius Z. Anal. Chem.* 224 (1966) 332.
- [40] C. Peker, M. Herlem, J. Badoz-Lambling, *Frezenius Z. Anal. Chem.* 224 (1966) 284.
- [41] C. Peker, M. Herlem, J. Badoz-Lambling, *Frezenius Z. Anal. Chem.* 224 (1966) 302.
- [42] IUPAC Compendium of Chemical Terminology, second ed. 1997, O.B. 76.
- [43] J. Wang, *Analytical Electrochemistry*, second ed., Wiley-VCH, NY, 2000.
- [44] J.E. Anderson, A.M. Bond, R.D. Jones, *Anal. Chem.* 53 (1981) 1016.
- [45] J. Tacussel, P. Leclerc, J.J. Fombon, *J. Electroanal. Chem.* 214 (1986) 79.
- [46] K.S.G. Doss, H.P. Agarwal, *J. Sci. Industr. Res. India B* 9 (1950) 280.
- [47] K.S.G. Doss, H.P. Agarwal, *Proc. India Acad. Sci. A* 34 (1951) 263.
- [48] K.S.G. Doss, H.P. Agarwal, *Proc. India Acad. Sci. A* 35 (1952) 45.
- [49] K.B. Oldham, *Trans. Faraday Soc.* 53 (1957) 80.
- [50] P. Delahay, M. Senda, C. Weis, *J. Am. Chem. Soc.* 83 (1961) 312.
- [51] P. Delahay, M. Senda, C. Weis, *J. Phys. Chem.* 64 (1960) 960.
- [52] G.C. Barker, in: E. Yeager (Ed.), *Transaction on the Symposium on Electrode Processes*, Wiley-VCH, NY, 1961, pp. 325–364.
- [53] H. Imai, P. Delahay, *J. Phys. Chem.* 66 (1962) 1108.
- [54] M. Senda, H. Imai, P. Delahay, *J. Phys. Chem.* 65 (1961) 1253.
- [55] A.P. Grigin, *Elektrokhimiya* 29 (1993) 1229.
- [56] M.A.V. Devanathan, S. Abeyagunawardene, *J. Electroanal. Chem.* 62 (1975) 195.
- [57] H.P. Agarwal, S. Qureshi, *Electrochim. Acta* 19 (1974) 349.
- [58] H.P. Agarwal, *Electroanal. Chem.* 7 (1974) 161.
- [59] V.I. Chernenko, I.I. Papanova, Yu.E. Udovenko, *Ukr. Khim. Zh.* 50 (1984) 205.
- [60] V.I. Chernenko, I.I. Papanova, Yu.E. Udovenko, *Dopov. Akad. Nauk B* 1 (1984) 52.
- [61] B.B. Damaskin, *Principles of the Modern Methods for Investigation of the Electrochemical Reactions*, MGU, Moscow, 1965, pp. 11–25.
- [62] J. Osteryoung, E. Kirowa-Eisner, *Anal. Chem.* 52 (1980) 62.