THEORETICAL AND EXPERIMENTAL RESOLUTION OF SEMI-DERIVATIVE LINEAR SCAN VOLTAMMETRY

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New procedures, based on the transformation of voltammetric current by semi-differentiation, have been proposed to improve resolution in linear scan voltammetry (LSV). For a reversible charge transfer, the obtained shape of the current semi-derivative is fully symmetrical and even in the case of an irreversible electrode reaction it is considerably more symmetrical compared with the original LSV signal. To evaluate and compare the resolution of semi-derivative linear scan voltammetry (SDLSV) with other techniques, theoretical calculations were performed to determine the qualitative resolution as well as the quantitative resolution defined in our previous work. The following quantities have been calculated: (i) the minimal difference in the peak potentials of two depolarisers, necessary to obtain two distinct peaks on an SDLSV record, (ii) the difference in the peak potentials enabling the determination of the depolarisers with only a 1% systematic error, due to overlapping. Verification of the developed theory was performed experimentally using a set of solutions containing two electroactive components in 1 M HCl: Pb(II)–Tl(I), Pb(II)–In(III), Pb(II)–Cd(II), Tl(I)–In(III), Tl(I)–Cd(II), and In(III)–Cd(II). The proposed mathematical approach and experimental procedures enable a simultaneous SDLSV determination of two or even more depolarisers with a minimal error.

Key words: Semi-differentiation; Semi-derivative linear scan voltammetry; Quantitative resolution; Qualitative resolution; Lead; Thallium; Cadmium; Indium; Electroreductions.

Although resolution of electrochemical techniques is generally not very high, voltammetric methods allow a simultaneous determination of several depolarisers during a single scan. However, the resolution power of a particular voltammetric technique varies depending on a given current–potential relationship. The shape of linear-scan voltammetric (LSV) curves is asymmetrical[1], which diminishes resolution of this technique. In addition to effort to improve resolution of the standard LSV method[2–4], its modifications have been proposed, based on an appropriate signal transformation, namely using differentiation[5–9] or semi-differentiation[10,11] of the LSV data. Semi-derivative linear scan voltammetry, SDLSV, coupled with a curve fitting procedure, has been successfully used by Brown and coworkers[10,11] to resolve overlapping LSV or anodic stripping LSV peaks. The purpose of this work is to derive qualitative resolution as well as quantitative resolution, defined in our preceding papers[1,9,12], for semi-derivative (semi-differentiated) linear scan voltammetry, and to verify the calculated resolution parameters by comparison with the experimental results. Application of the introduced definitions enables a correct comparison of resolution from SDLSV with that obtained by other techniques.

THEORY

As it is evident by comparison of the calculated reversible LSV and SDLSV plots in Fig. 1, the symmetrical semi-differentiated signal $e^{\mathrm{SDLSV}} = f(E)$ is more favourable for a multicomponent voltammetric analysis compared with the common LSV signal $I^{\mathrm{LSV}} = f(E)$. Assuming linear diffusion, theoretical LSV curves were constructed according to Nicholson and Shain[13] in a sufficiently wide range of potentials for an n-electron reduction (n = 1, 2, 3)

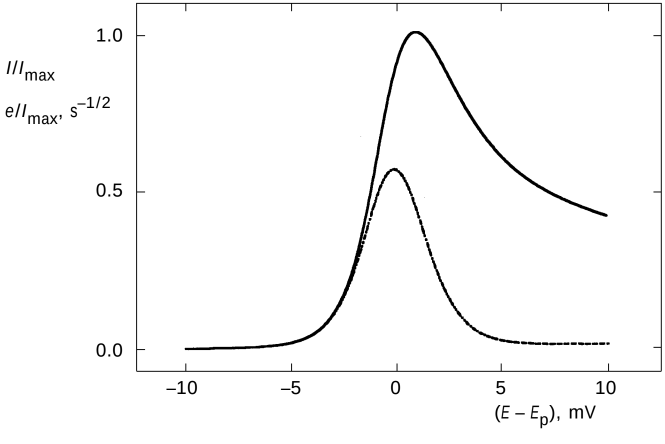

FIG. 1

Normalised plots $I^{\mathrm{LSV}}/I_{\mathrm{p}}^{\mathrm{LSV}} = f(E - E_{\mathrm{p}}^{\mathrm{SDLSV}})$ and $e^{\mathrm{SDLSV}}/I_{\mathrm{p}}^{\mathrm{LSV}} = f(E - E_{\mathrm{p}}^{\mathrm{SDLSV}})$. Calculated for a reversible system and linear diffusion in LSV (—) and SDLSV (– ·· – ··), assuming n = 1, T = 298.15 K, scan rate $\nu = 0.025\ \mathrm{V\ s^{-1}}$. $E_{\mathrm{p}}^{\mathrm{SDLSV}} = E_{1/2}$

with the step equal to 0.025692 mV (*i.e.* 0.001 normalised potential units corresponding to 25 °C). Theoretical SDLSV plots were calculated using the explicit relationship

$$e(E) = [n^2F^2AD^{1/2}\nu/(4RT)]\ \mathrm{sech}^2\{[nF/(2RT)](E - E_{1/2})]\}\ , \qquad (1)$$

where $e(E)$ denotes the semi-derivated current for a reversible charge transfer, all other symbols are used in a way common in electrochemistry.

Resolution in the SDLSV can be theoretically expressed in three main ways:

1. Qualitative resolution R_q – defined as the minimum difference in the reversible peak potential of two depolarisers ΔE_p, which gives rise to the observation of two distinct peaks on the SDLSV e–E curve assuming equality of analytical signals (semi-derivated currents) of both depolarisers if individually measured (*i.e.*, without the other component, see Fig. 2).

As can be seen from Fig. 2 depicting two overlapped signals, not only the maximum heights of the semi-differentiated signals, *i.e.* peaks e_p, but also the corresponding potentials E_p differ from the true values obtained when measurements are made with individual electroactive species under the same conditions.

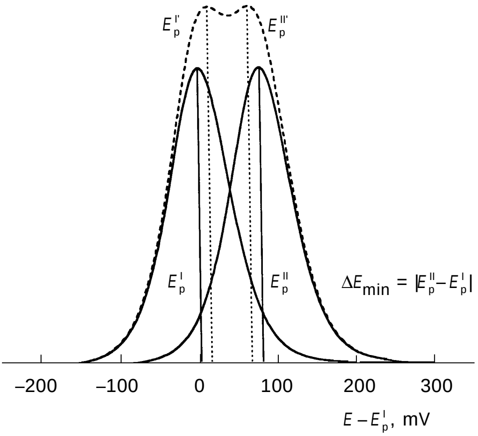

FIG. 2

Qualitative resolution of the SDLSV technique. $\Delta E_{min} = E_p^{I} - E_p^{II}$ indicates the difference in the peak potentials which allows two distinct maxima to appear on the overall e *vs* ($E - E_p^{I}$) curve. Peak potentials changed by the signal overlap are denoted by $E_p^{I'}$ and $E_p^{II'}$. —— First and second peaks, – – – overall signal

2. Quantitative resolution R_E – defined as the difference in the reversible SDLSV peak potentials ΔE_p of two depolarisers required to achieve their determination with only a 1% maximal systematic error due to the peak overlap, assuming equal peak signals of the individual components[12] (measured in the absence of the other component), as it is shown in Fig. 3a. Quantitative resolution defined in this way depends on the number of exchanged electrons n_1, n_2 of both depolarisers, as well as on ΔE_p.

3. Quantitative resolution R_α – defined by the admissible concentration ratio $\alpha = c_{II} / c_I$ of the interfering and the determined electroactive species, respectively, which permits the determination of the latter with 1% maximal error for the given ΔE_p value[14]. The case, when the difference ΔE_p = 100 mV is selected as an arbitrary value, is shown in Fig. 3b. Thus, this approach defines quantitative resolution R_α in terms of the concentration ratio and provides an alternative to the quantitative resolution R_E described above[12,14].

Theoretical calculations of resolution, defined in either of the described ways, have been performed under the assumption that: (i) the electrode processes are controlled by diffusion, (ii) the electrode processes for both

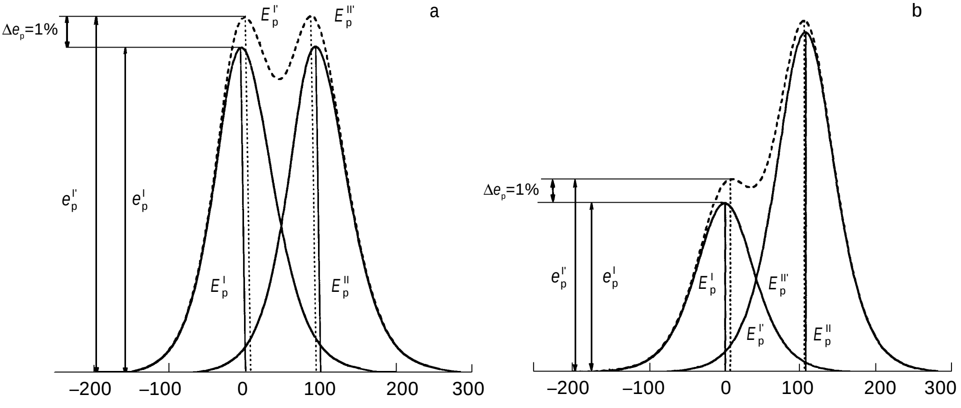

FIG. 3

Quantitative resolution R_E (a) and quantitative resolution R_α (b) in SDLSV technique. —— First and second peaks, – – – overall signal. a: $\Delta E_{min} = E_p^{I} - E_p^{II}$ denotes the minimal difference in the peak potential which enable quantitative analysis with only 1% systematic error due to the signal overlap. It is assumed that the individual component peak ratio $Y = e_p^{I}/e_p^{II} = 1$. The parameters changed by the signal overlap are denoted by $E_p^{I'}$ and $E_p^{II'}$ (peak potentials) and $e_p^{I'}$ (semi-differentiated current); b: parameter $\alpha = c_{II}/c_I$ denotes an admissible concentration ratio corresponding to the peak height ratio $Y = e_p^{I}/e_p^{II}$ which, for the given ΔE_p, permits determination with a 1% systematic error due to the peak overlap. Primed parameters have the same meaning as described above depolarisers are reversible for the sweep rate applied, (iii) no interaction exists between the depolarisers or between any depolariser and any electrolysis product, (iv) no adsorption/desorption process takes place at the electrode, (v) the residual current is negligible so that its influence on the SDLSV signals can be neglected, (vi) the SDLSV signals perfectly additive. Under the described conditions, only a geometrical overlap takes place, so that the overall SDLSV analytical signal e_Σ is equal to the sum of the SDLSV signals of the individual components e_1 and e_2:

$$e_\Sigma = e_1 + e_2 = e_{p,1}\, f[n_1(E - E_{p,1}^{SDLSV})] + e_{p,2}\, f[n_2(E - E_{p,2}^{SDLSV})]\ , \tag{2}$$

where subscript p refers to the peak.

The following operations can be then performed: Eq. (*2*) is divided by $e_{p,1}$, the signal ratio $e_{p,2}/e_{p,1}$ is substituted by the parameter Y, the potential difference $E_{p,2}^{SDLSV} - E_{p,1}^{SDLSV}$ is substituted by ΔE_p, and the equality $E_{p,1}^{SDLSV} = 0$ is conventionally assumed. In this way, the normalised signal $e_\Sigma/e_{p,1}$ is obtained:

$$e_\Sigma/e_{p,1} = f(n_1,E) + Y[n_2(E - \Delta E_p)\ . \tag{3}$$

Based on the calculated dependence of the SDLSV signal on potential and utilising the above given equations, qualitative and quantitative resolutions were enumerated and are shown in Tables I–III.

EXPERIMENTAL

Apparatus and Reagents

A multipurpose electrochemical analyser EA9, produced by Unitra-MTM, Krakow, Poland, was used for all electrochemical measurements. The used voltammetric cell contained a controlled grow mercury drop electrode (CGMDE) used in the hanging mercury electrode mode, a silver–silver chloride (3 M KCl) reference electrode, and a large platinum wire auxiliary electrode. Experiments were made at 25 ± 0.5 °C. All chemicals used were of analytical reagent grade; distilled and deionised water was used in all measurements.

Data Processing

In experimental study, the data were sampled from the LSV curves, recorded in the disk memory, digitally filtered by the moving average 7-point filter, and semi-differentiated. Semi-differentiation was made by using our new numerical differ-integration algorithm GS, enabling integration and differentiation with any order, fractional or integer[15,16], which is described below.

GS Algorithm for Numerical Differintegration

GS algorithm is an adapted G1 algorithm, based on the Grünwald definition of differintegration[17,18] and differing from G1 in the way of signal sampling. The values of independent variable t, at which the signal $y = f(t)$ is sampled in GS algorithm, do not coincide with those used in G1, but are systematically shifted. The shift is expressed by $hq/2$, and depends on the differintegration order q and the sampling step (sampling period) h. The step h is related to the value x of independent variable t (time, potential, *etc.*), at which differintegration is calculated, and to the chosen number of points (subintervals) N, $h = x/N$. Thus, when applying semi-differentiation ($q = 0.5$), the shift is $0.25h$, which, *e.g.* for $h = 1$, means that the signal is sampled at 1.25, 2.25, 3.25, ..., and finally $x + 0.25$, instead of being at 1, 2, 3, ..., x. The recurrent GS formula is then given by equation

$$\left[\frac{\mathrm{d}^q y}{\mathrm{d}t^q}\right]_{t=x} = \frac{N^q}{x^q}[[[\ldots[f\left(h + hq/2\right)\left\{\frac{N-q-2}{N-1}\right\} + f\left(2h + hq/2\right)]\ldots]\left(\frac{1-q}{2}\right) + \\ + f((N-1)h + hq/2)]\left(\frac{-q}{1}\right) + f(Nh + hq/2)]. \qquad (4)$$

TABLE I
Qualitative resolution R_q – theoretical results. Calculated minimum differences in peak potentials ΔE_p necessary to observe two separate peaks on a signal *vs* potential curve in SDLSV and LSV[a] for the signal ratio $Y = 1$ at 25 °C

Number of exchanged electrons		LSV technique ΔE_p, mV	SDLSV technique ΔE_p, mV
n_1	n_2		
1	1	122[b]	68[c]
2	2	61[b]	34[c]
3	3	40.7[b]	22.7[c]
1	2	80	57
2	1	90	57
1	3	60	46
3	1	60	46
2	3	48	33
3	2	54	33

[a] LSV results taken from ref.[1]. [b] $\Delta E_p = 122/n$, mV; $n = n_1 = n_2$. [c] $\Delta E_p = 68/n$; $n = n_1 = n_2$.

TABLE II
Theoretical quantitative resolution R_E. Calculated ΔE_p values required in SDLSV for quantitative determination of two depolarisers with a systematic error to 1% if the maximum signal ratio of pure individual components $Y = e_{p,2}/e_{p,1} = 1$ at 25 °C

Number of exchanged electrons		SDLSV technique	
n_1	n_2	1st species ΔE_p, mV	2nd species ΔE_p, mV
1	1	154[a]	154[a]
2	2	77[a]	77[a]
3	3	51[a]	51[a]
1	2	77	154
1	3	52	154
2	1	154	77
2	3	51	77
3	1	154	52
3	2	72	51

[a] $\Delta E_p = 154/n$, mV.

TABLE III
Theoretical quantitative resolution R_E. Calculated R_E values for SDLSV, LSV, and DLSV assuming $n_1 = n_2$ and equal maximum signals of both depolarisers ($e_{p,2}/e_{p,1} = 1$) at 25 °C

Voltammetric technique	R_E, if the depolarizer is reduced at a more positive potential ΔE_p, mV	R_E, if the depolarizer is reduced at a more negative potential ΔE_p, mV
SDLSV	$154/n$	$154/n$
LSV	$168/n$	$1\,875/n$
DLSV	$148/n$[a]	$850/n$[a]
DLSV	$224/n$[b]	$340/n$[b]

[a] The positive peak signal dI/dE_{p+} was measured. [b] The signal $dI/dE_{p\text{-}p}$ was measured from peak-to-peak.

It should be noted that the order q is negative when performing any kind of integration, therefore the shift in sampling has the opposite direction along the t-axis compared with the case when differentiation is applied.

RESULTS AND DISCUSSION

Experimental and Theoretical SDLSV Signals

Comparison of the experimental SDLSV curve of the two-component system with the theoretical plot calculated for ΔE_p = 208 mV and Y = 0.4, as found from the experiments with the Pb(II)–Cd(II) system, is shown in Fig. 4. A very good agreement between the experimental and calculated plots has been observed. A slight deviation of experiment from theory can be explained by a minor contribution of spherical diffusion to the measured signal. When comparing the theoretical and real LSV signal values with those obtained by SDLSV, the following remarks could be useful. Using the "hastened" infinite series formula[19], we have found[20] accurately the maximum value of the dimensionless current function $\pi^{1/2}\chi(at)$ in LSV (where a is $nF\nu/(RT)$ and t denotes time between the initial and considered potentials) as 0.4462947. An analogous dimensionless function in SDLSV is 1/4, *i.e.*, 0.25 exactly. Denoting these dimensionless values by an asterisk (*), the ra-

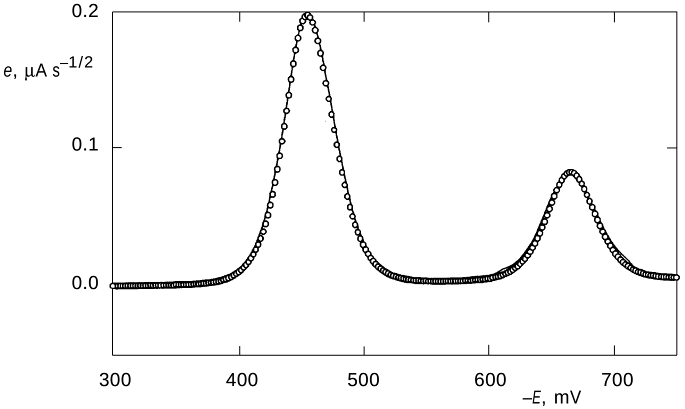

FIG. 4
Comparison of the experimental SDLSV curve (solid line) for the Pb(II)–Cd(II) system with the theoretical dependence (circles), calculated by the GS numerical differintegration algorithm for the individual component signal ratio $Y = e_p^{Cd}/e_p^{Pb}$ = 0.4

tio of the dimensionless peak values for both techniques and a reversible charge transfer is

$$e_p^* \,/\, I_p^* = 0.25/0.4462947 = 0.5601680\ . \tag{5}$$

However, the peak ratio of the real signals is given by dividing Eq. (*1*) (expressed for $E = E_{1/2}$) by the LSV current given in ref.[13]:

$$e_p/I_p = 0.5601680\ [nF\nu/(RT)]^{1/2} \qquad [\text{in s}^{-1/2}]\ . \tag{6}$$

For T = 298.15 K and using common values of R and F in the RT/F term (being equal to 0.0256926 V) the ratio is simplified:

$$e_p/I_p = 3.494735\ n^{1/2}\nu^{1/2} \qquad [\text{in s}^{-1/2}]\ . \tag{7}$$

TABLE IV
Resolution in SDLSV at 25 °C, defined as the concentration ratio $\alpha = c_{II}/c_I$ of the interfering (II) and determined (I) electroactive species, which gives rise to a 1% overlap of the peak current of the determined species if ΔE_p = 100 mV

Number of exchanged electrons		$\alpha_{SDLSV} = c_{II}/c_I$
n_1	n_2	
1	1	0.13
1	2	1.5
1	3	33
2	1	0.50
2	2	6.0
2	3	130
3	1	1.1
3	2	13
3	3	300

If for example $\nu = 0.025$ V s^{-1}, then $e_p/I_p = 0.55256$ s$^{-1/2}$ for $n = 1$, $e_p/I_p = 0.78144$ s$^{-1/2}$ for $n = 2$, and $e_p/I_p = 0.95707$ s$^{-1/2}$ for $n = 3$. For higher scan rates, the nominal value of e_p exceeds that of I_p.

Experimental Evaluation of Quantitative Resolution in SDLSV

The SDLSV method has been used for a simultaneous determination of electroactive species in the following six different two-component systems in 1 M HCl: a) Pb(II)–Cd(II) with ΔE_p^{LSV} = 208 mV, b) Pb(II)–In(III) with ΔE_p^{LSV} = 159 mV, c) Tl(I)–Cd(II) with ΔE_p^{LSV} = 122 mV, d) Tl(I)–In(III) with ΔE_p^{LSV} = 74 mV, e) Pb(II)–Tl(I) with ΔE_p^{LSV} = 70 mV, and f) In(III)–Cd(II) with ΔE_p^{LSV} = 40 mV.

The above systems were selected in a way to receive a different extent of the signal overlap, ranging from the situation when the semiderivative peaks of the overall *e*–*E* dependence are completely resolved, *e.g.* for systems Pb(II)–Cd(II) and Pb(II)–In(III), up to the case with a considerable overlap of the semiderivative peaks, *e.g.*, in the system In(III)–Cd(II). The error ε of the SDLSV determination in solutions containing two depolarisers was investigated by keeping the concentration of one component constant while making standard additions of the other component. To compare the

TABLE V
Error[a] of the analytical signal measurement for thallium(I) in LSV, ε^{LSV}, and in SDLSV, ε^{SDLSV}, when changing the cadmium(II) concentration in the Tl(I)–Cd(II) system containing $1.0 \cdot 10^{-4}$ M Tl(I) in 1 M HCl

$c_{Cd(II)} \cdot 10^5$ mol/l	$c_{Cd(II)}/c_{Tl(I)}$	ε^{LSV} %	ΔE_p^{LSV} mV	ε^{SDLSV} %	ΔE_p^{SDLSV} mV
1.33	0.133	0.21	118	0.96	142
2.66	0.266	0.74	122	0.07	144
5.31	0.531	0.15	126	0.11	142
10.60	1.06	–0.28	124	0.65	142
26.34	2.63	1.17	122	1.14	142
53.16	5.32	2.36	120	1.93	142
102.3	10.23	[b]	[b]	3.94	146

[a] Error $\varepsilon^{LSV} = 100(I_p - I'_p)/I_p$, %; $\varepsilon^{SDLSV} = 100(e_p - e'_p)/e_p$, %. [b] Tl(I) and Cd(II) peaks totally overlapped.

resolution power of the SDLSV and LSV, standard LSV curves were also recorded and the errors of a simultaneous LSV determination of two components were also evaluated. The influence of an excess of the overlapping component on the value of the analytical signal of the determined species is illustrated in Figs 5, 6, and 8 as well as in Tables V and VI.

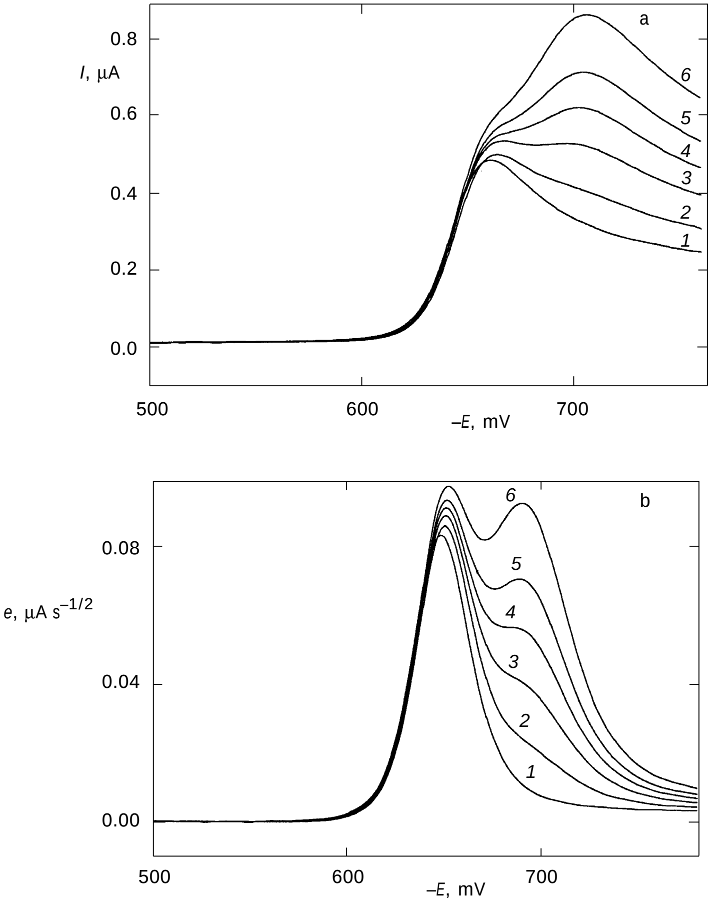

FIG. 5
The LSV I–E (a) and the SDLSV e–E (b) records of the In(III)–Cd(II) system in 1 M HCl. Additions of various molar concentrations of Cd(II) to $1 \cdot 10^{-4}$ M In(III): *1* 0, *2* $2.5 \cdot 10^{-5}$, *3* $5.0 \cdot 10^{-5}$, *4* $7.5 \cdot 10^{-5}$, *5* $1.0 \cdot 10^{-4}$, *6* $1.2 \cdot 10^{-4}$

Qualitative Resolution

Even for the Cd(II)–In(III) system with very close peak potentials of both depolarisers (ΔE_p^{LSV} = 40 mV), qualitative separation of the In(III) and Cd(II) SDLSV peaks was possible (Fig. 5) when the metal ion concentrations were of the same order, the concentration ratio In/Cd ranging from 0.45 to 1.6. For the Tl(I)–Pb(II) system, in spite of a greater difference in the SDLSV peak potentials (ΔE_p^{LSV} = 70 mV), the qualitative SDLSV resolution is limited to a relatively narrow range of the Pb/Tl concentration ratio from 0.25 to 0.8, due to a one-electron reduction process of Tl(I) (corresponding to a broader peak) which considerably overlaps with the Pb(II) peak. The qualitative resolution of other two-component systems investigated in this study has been fully achieved in the investigated concentration range of both elements, from 10 : 1 to 1 : 10. As can be seen from the data presented in Table I, the qualitative resolution of the SDLSV technique significantly exceeds the resolution of the standard LSV procedure.

Quantitative Resolution

Quantitative resolution in SDLSV, as well as the relative error, ε, resulting from the signal overlap (and defined below in Table V), are different for the first depolariser reduced at a more positive potential from those for the

TABLE VI

Error[a] of the analytical signal measurement for indium(III) in LSV, ε^{LSV}, and in SDLSV, ε^{SDLSV}, when changing the lead(II) concentration in the Pb(II)–In(III) system containing $1.0 \cdot 10^{-4}$ M In(III) in 1 M HCl

$c_{Pb(II)} \cdot 10^5$ mol/l	$c_{Pb(II)}/c_{In(III)}$	ε^{LSV}, %			ε^{SDLSV}, %		
		I	II	III	I	II	III
3.28	0.33	7.9	–3.2	–0.34	1.5	1.5	–0.01
6.55	0.66	16.8	–4.2	–0.34	2.0	1.9	–0.02
13.04	1.32	32.4	–7.5	–0.34	4.8	1.4	0.00
25.82	2.63	66.2	–12.0	–0.68	7.9	0.1	0.00
62.71	6.59	151.3	–22.1	0.00	15.8	–1.8	0.00
119.73	13.17	276.2	–33.3	0.10	26.4	–4.0	0.00

[a] Errors ε^{LSV} and ε^{SDLSV} were calculated by the procedures I, II or III of the analytical signal measurement as depicted in Figs 7a, 7b.

other one, reduced at a more negative potential; this is similar to the situation in LSV. As results from the theoretical data presented in Table III as well as from the experimental study shown in Table V, the resolving power of the SDLSV and LSV techniques is similar when determining the first depolariser, reduced at a more positive potential (with an interfering component reduced at a more negative potential). At some concentration ratio of the interfering and determined components, however, it is still possible to

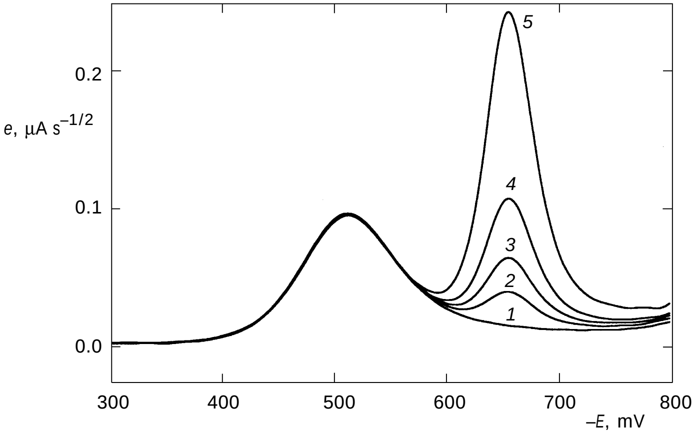

FIG. 6
The SDLSV *e*–*E* record of the Tl(I)–Cd(II) system in 1 M HCl. Additions of various molar concentrations of Cd(II) to 1 · 10^{-4} M Tl(I): *1* 0, *2* 1.33 · 10^{-5}, *3* 2.66 · 10^{-5}, *4* 5.32 · 10^{-5}, *5* 1.06 · 10^{-4}

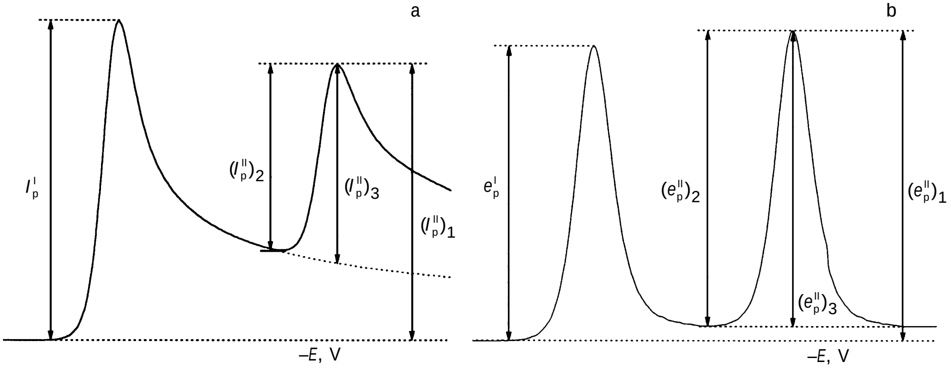

FIG. 7
Signal evaluation in LSV (a) and SDLSV (b). — Peak sum, – – – first peak. Roman numbers denote the first (I) and the second (II) peak

observe a distinguished peak of the determined component on the overall SDLSV curve and to measure its height with a reasonably small error (Table V, Fig. 6). Under the same conditions, the LSV peaks of both components completely overlapped.

In the LSV and the SDLSV techniques, the error of determining the second depolariser, reduced at a more negative potential, depends on the way how the analytical signal is measured. Although the way of measuring the LSV response is well known, for the sake of comparison we will present the ways of the signal evaluation for both LSV and SDLSV. It has been found that the first procedure of the peak evaluation, indicated in Figs 7a and 7b

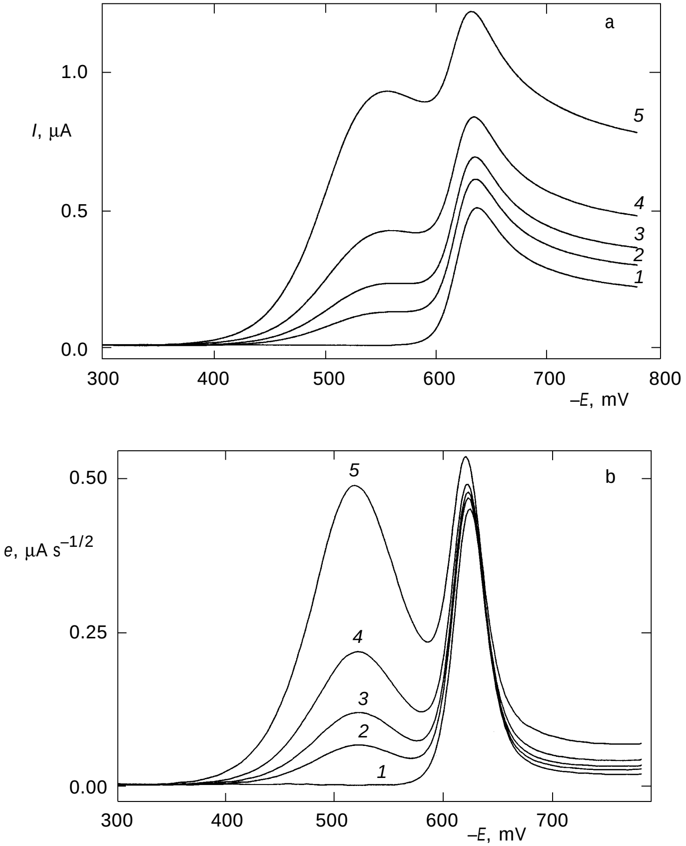

FIG. 8

The LSV I–E (a) and the SDLSV e–E (b) records of the Tl(I)–In(III) system in 1 M HCl. Additions of various molar concentrations of Tl(I) to $1 \cdot 10^{-4}$ M In(III): *1* 0, *2* $5.0 \cdot 10^{-5}$, *3* $9.9 \cdot 10^{-4}$, *4* $2.0 \cdot 10^{-4}$, *5* $4.8 \cdot 10^{-4}$

as $(I_p^{II})_1$ and $(e_p^{II})_1$, respectively, involves a large positive systematic error, the second indicated procedure involving $(I_p^{II})_2$ and $(e_p^{II})_2$, respectively, causes a negative error – depending on the difference in the peak potentials of both depolarisers and their peak ratio. Most close to the real signal value, corresponding to the individual determined component, is the third evaluation procedure, based on the extrapolation of the signal of the first electrochemical step to the peak potential of the second step; the evaluated signals are $(I_p^{II})_3$ and $(e_p^{II})_3$, respectively. When SDLSV is used for determination of the second depolariser, the resolution depends on the difference in peak potentials, concentration ratio, number of electrons involved in both electrode processes (concerning the interfering and the determined components), as well as the way of the peak height measurement. It has been observed with all six investigated two-component systems that the error of the SDLSV determination of the second depolariser (reduced at a more negative potential) is significantly lower than when using the LSV.

For the system Pb(II)–Cd(II), with a relatively great difference in peak potentials (ΔE_p = 208 mV), no influence of the Pb(II) signal on the Cd(II) SDLSV peak was observed when the Cd(II)/Pb(II) concentration ratio did not exceed 10 : 1; this observation was independent of the way of measuring the SDLSV Cd(II) peak. A much better resolution was found in SDLSV than in standard LSV technique, as illustrated in Figs 8a, 8b, where the determination of In(III) in the presence of Tl(I) (ΔE_p = 74 mV) is shown. The experimental error of the In(III) determination, calculated by different procedures of the LSV and SDLSV peak measurement (proposed in Fig. 7), are presented in Table VI. Independently of the way of the peak measurement, the experimental resolution in SDLSV distinctly exceeds that of LSV for all investigated systems. In the case of the systems with very close peak potentials, *e.g.* In(III)–Cd(II) or Pb(II)–Tl(I), the SDLSV technique, in contrast to LSV, still enables determination of the second depolariser in a restricted range of interfering component concentrations (Fig. 5b).

Concluding Remarks

LSV is a popular and useful technique in various analytical, kinetic, and mechanistic studies; moreover, the LSV instrumentation is rather inexpensive. A good resolution of the LSV overlapping signals is therefore of interest for many investigators. As follows from both presented calculations and experimental examples, semi-differentiation of the LSV plots allows for a significant improvement in the signal resolution compared with the standard LSV technique as well as the derivative LSV. A symmetrical (or near-to-symmetrical) SDLSV signal–potential relationship is extremely advantageous for optimisation resolution of the overlapped signals and for accurate quantitative analysis. For linear diffusion and a reversible charge transfer, the shape of individual signals is equal to the waveform of squared hyperbolic secans, hence the theoretical resolution in SDLSV for reversible systems is the same as for differential pulse, square-wave or alternating current voltammetry. A very good agreement between the experimental and calculated SDLSV signal–potential curves has been exemplified for the Cd(II) and Pb(II) reduction.

REFERENCES

1. Bobrowski A., Roterman I.: *Chem. Anal. (Warsaw)* **1986**, *31*, 167.
2. Gutknecht W. F., Perone P. S.: *Anal. Chem.* **1970**, *42*, 906.
3. Sybrandt L. B., Perone P. S.: *Anal. Chem.* **1971**, *43*, 382.
4. DePalma R. A., Perone P. S.: *Anal. Chem.* **1979**, *51*, 825.
5. Davis H. M., Rooney R. C.: *J. Polarogr. Soc.* **1962**, *8*, 25.
6. Shekun L. Ya.: *Zh. Fiz. Khim.* **1962**, *36*, 455; *Chem. Abstr.* **1962**, *57*, 1981.
7. Rooney R. C.: *J. Polarogr. Soc.* **1963**, *9*, 456.
8. Sybrandt L. B., Perone P. S.: *Anal. Chem.* **1972**, *44*, 2331.
9. Bobrowski A.: *Chem. Anal. (Warsaw)* **1987**, *32*, 891.
10. Toman J. J., Brown S. D.: *Anal. Chem.* **1981**, *53*, 1497
11. Toman J. J., Corn R. M., Brown S. D.: *Anal. Chim. Acta* **1981**, *123*, 187.
12. Bobrowski A.: *Chem. Anal. (Warsaw)* **1983**, *28*, 557.
13. Nicholson R. S., Shain I.: *Anal. Chem.* **1964**, *36*, 706.
14. Bobrowski A., Bond A. M.: *Croat. Chem. Acta* **1993**, *66*, 499.
15. Mocák J., Bustin D. I.: Presented at the *Int. Conf. Modern Electroanalytical Methods, Seč, September 22, 1999*; LE/11.
16. Mocák J., Bustin D. I.: *Electroanalysis (N.Y.)*, in press.
17. Oldham K. B., Spanier J.: *The Fractional Calculus*. Academic Press, New York 1974.
18. Bustin D. I, Mocák J., Garaj J.: *Chem. Listy* **1981**, *81*, 1009.
19. Oldham K. B.: *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *105*, 373.
20. Mocák J., Bond A. M.: *Proc. 9th Australasian Electrochem. Conf. Wollongong, NSW, Australia, February 6–10, 1994*. Part 2, p. P74-1.