

Calculation of voltammetric peaks by the transformed Heyrovsky-Ilkovič equation

Simulation of polarograms, smoothing of voltammetric peaks, separation of overlapping peaks

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Summary. Calculating real polarographic or voltammetric peaks is rather difficult. A new possibility to compute such peaks is the use of the transformed Heyrovsky-Ilkovič equation. The calculation allows to simulate polarograms or voltammograms by computer. Furthermore, it is possible to smooth voltammetric peaks without loss of peak height or separation of overlapping peaks.

1 Introduction

The voltammetric methods of DP- and AC-polarography yield signals in the shape of peaks for the depolarisator to be determined. Beside these electrochemical methods, measuring signals in the shape of peaks are obtained in chromatographic methods. In these the calculation and evaluation of peaks is carried out by the well-known Gauß-function of the density of probability [10].

$$P(X) = \frac{1}{\text{sdv} \cdot \sqrt{2 \cdot \pi}} \cdot e^{-[(X - X_0)^2 / (2 \cdot \text{sdv}^2)]} \quad (1)$$

For polarographic application the independent variable X can be replaced by the potential E . Also the position of the maximum of the Gauß-distribution X_0 can be replaced by the peak potential E_p . Because of the manifold applications of equation 1 in chromatographic techniques corresponding computer programs for Gauß-peaks and algorithms describing non-ideal Gauß-peaks were developed. Therefore, it was easy to use the Gauß-distribution to calculate polarographic peaks and to evaluate them by this method, which, for example, is realized in the Metrohm VA-Processor 646 [6].

This method is well suited to evaluate peaks of a two-electron reaction [6]. However, if peaks are very narrow, as for example in the 3-electron reaction of bismuth in 1 mol/l HCl or in some catalytic peaks, the use of the Gauß-function may lead to some errors. The same is true for very broad or unsymmetrical peaks.

Besides these evaluation problems in case of small peaks, further difficulties appear within the scope of evaluation of peaks by the necessary smoothing of the noise of a measuring signal. For example, this is shown in Fig. 1. As reported in [2, 3] a inverse-voltammetric peak of bismuth could be

evaluated very sensitively by computed extrapolation and subtraction of the background current. Figure 1a shows the measuring signal of the inverse-voltammetric bismuth determination and the computed background current. The bismuth peak is so small that it is visually almost not distinguishable from the plotted background current. It needs the subtraction of the computed background current from the measured current-potential curve and the amplification of the resulting signal, to produce a visible bismuth peak (Fig. 1b and c). (The marks at the potential axes drawn in this and the following figures show the value range of the

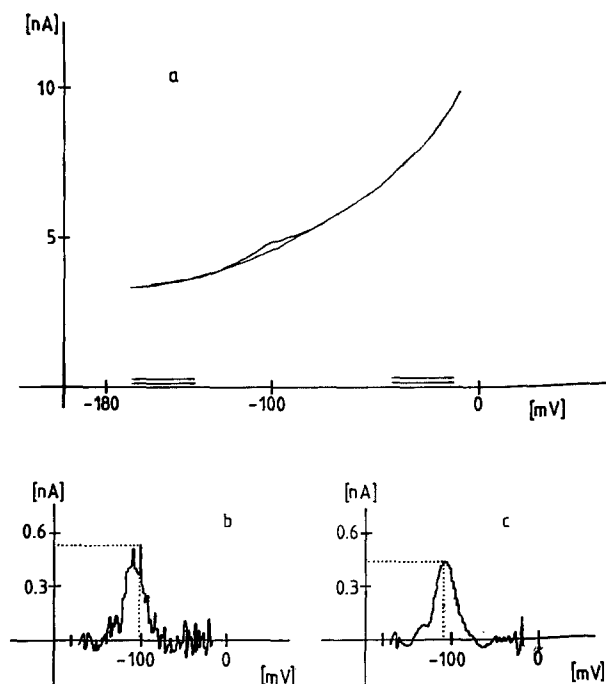


Fig. 1 a–c. Evaluation of a very small bismuth peak after the subtraction of an extrapolated background current, calculated by an 3-order hyperbola, and smoothing of the resulting bismuth peak (see [2]). Supporting electrolyte: 1 mol/l HCl. Concentration: Bi^{3+} 0.03 $\mu\text{g/l}$. Method: HMDE–DPASV–UDP = 10 mV – S = 10 mV/s. Deposition: 1800 s at –200 mV. Distance between two measuring points: 2 mV. **a** Measurement and background extrapolation (sensitivity: 0 to 10 nA, potential axis see **b**); **b** resulting voltammogram unsmoothed; **c** smoothed resulting voltammogram. \equiv Potential range used to calculate the background current

measurement which is used for calculating the background current in the range of the bismuth peak [2, 3]).

As can be seen in this figure, it is necessary to smooth the resulting peak (Fig. 1 b) before the computer determines the peak height. The smoothing of the resulting data eliminates the strong noise and avoids errors in peak evaluation. By using a five-point smoothing according to Savitzky and Golay [8, 9] a peak is obtained that can easily be evaluated (Fig. 1 c). In many cases, however, minor losses of peak height cannot be avoided, especially if more than five points are taken to smooth or when very narrow peaks are smoothed.

If the resulting bismuth peak is not smoothed (Fig. 1 b), the computer will find a peak far too high, because it will only search for the maximum in the peak range. A greater peak height would pretend a higher bismuth content in the sample.

So we are in need of another mathematical method, based on the theory of polarographic curves, to calculate, evaluate and smooth polarographic and voltammetric peaks. A starting point is the so-called Heyrovsky-Ilkovič equation (2), which can be used to calculate the limiting diffusion current of polarographic waves [4]. After mathematical transformation of this equation, which will be shown later, the calculation of the polarographic or voltammetric peak is possible.

2 Experimental

For apparatus, chemicals and instruction for the inverse-voltammetric bismuth determination see [1, 2]. (The measurements were performed with apparatus combination 3 [1]).

3 Results and discussion

The following abbreviations are used in the text and the figures:

a	coefficient
AC1-P	alternating current polarography with the first harmonic wave
AC2-P	alternating current polarography with the second harmonic wave
AC1ASV	alternating current anodic stripping voltammetry
bh	width in half peakheight
c	concentration
df	transfer coefficient
DC-P	direct current polarography
DP-P	differential pulse polarography
DPASV	differential pulse anodic stripping voltammetry
e	the number e
E	potential
Ep	peak potential
E _{1/2}	halfwave potential
F	Faraday constant
HMDE	hanging mercury drop electrode
I, i	current
igr	limiting diffusion current
j	index
k	coefficient
n	order of the equation
P(X)	probability density
R	gas constant
S	scan rate

sdv	standard deviation
T	temperature
UDP	pulse-amplitude
z	number of electrons involved in the charge transfer step

I Transformation of the Heyrovsky-Ilkovič equation

The polarographic limiting current of a depolarizer can be calculated after transformation of the Heyrovsky-Ilkovič equation (2) [4]:

$$E = E_{1/2} + \frac{R \cdot T}{df \cdot z \cdot F} \cdot \ln \frac{igr - i}{i}, \quad (2)$$

$$x = \frac{df \cdot z \cdot F}{R \cdot T} \cdot (E - E_{1/2}). \quad (3)$$

With (3) and transformation of equation (2) we get:

$$i = \frac{igr}{1 + e^x}. \quad (4)$$

The shape of a peak of a voltammetric signal can be described by the first derivation of equation (4):

$$i' = -igr \cdot \frac{e^x}{(1 + e^x)^2}. \quad (5)$$

By separation into partial fractions we get from (5):

$$i' = -igr \cdot \left(\frac{1}{(1 + e^x)} + \frac{1}{(1 + e^x)^2} \right). \quad (6)$$

Under use of:

$$k = -igr, \quad (7)$$

equation (4) will be replaced by equation (8) for further reflections. With equation (4) we could calculate a polarographic wave and so equation (8) is only another mathematical description for a polarographic wave.

$$i = \frac{k}{1 + e^x}. \quad (8)$$

with their derivations:

$$i' = -\frac{k}{1 + e^x} + \frac{k}{(1 + e^x)^2}, \quad (9)$$

$$i'' = +\frac{k}{1 + e^x} - \frac{3k}{(1 + e^x)^2} + \frac{2k}{(1 + e^x)^3}, \quad (10)$$

$$i''' = -\frac{k}{(1 + e^x)} + \frac{7k}{(1 + e^x)^2} - \frac{12k}{(1 + e^x)^3} + \frac{6k}{(1 + e^x)^4}. \quad (11)$$

As shown in [7] a voltammetric signal or peak can be described exactly by the sum of a direct current (polarographic wave), the first, the second and higher order derivations. The addition of equation (8) to (11) as well as higher order derivations could be given by the following sum:

$$I = \sum_{j=1}^n \frac{a_j}{(1 + e^x)^j}, \quad (12)$$

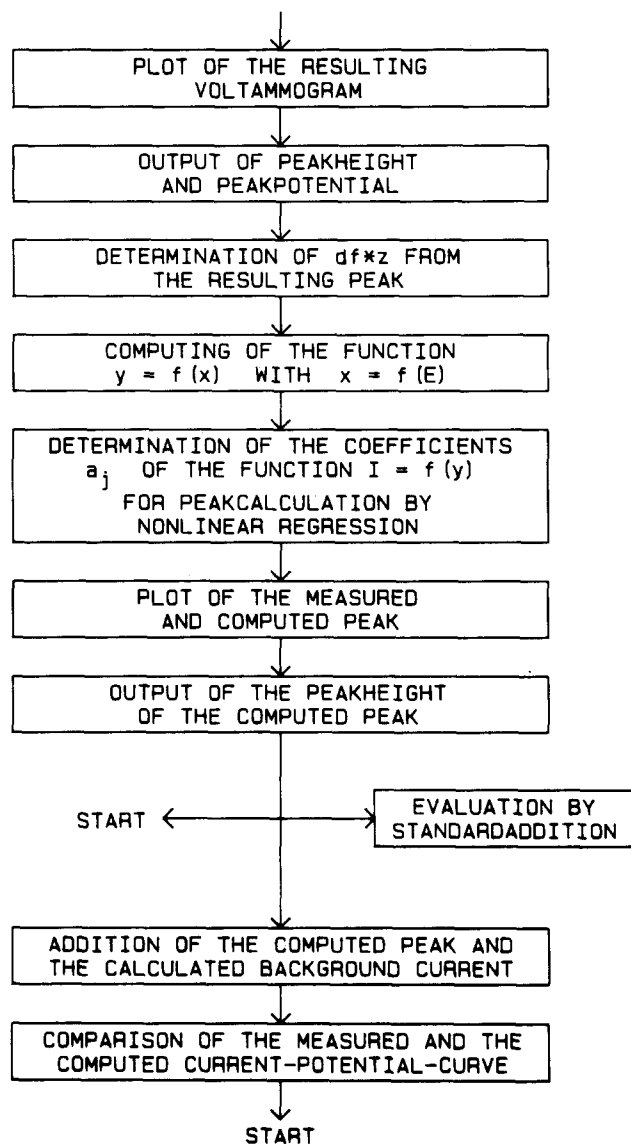


Fig. 2. Flow chart of the part of a computer software, written in BASIC for Commodore 8032 and 64 computers, for computer assisted peak evaluation of voltammetric measurements used for peak calculation applying the transformed Heyrovsky-Ilkovič equation (see [2])

with

$$y = \frac{1}{1 + e^x}, \quad (13)$$

we can transform (12) into

$$I = \sum_{j=1}^n a_j \cdot y_j. \quad (14)$$

Equation (14) has the universal form of an n -order polynomial function. This polynomial function, which we obtain by the transformation of the Heyrovsky-Ilkovič equation, can be used to calculate the different voltammetric signals (wave or peak) by the selection of the corresponding coefficients and the corresponding order of the polynomial function. Furthermore, we can calculate the polynomial function by the method of least squares from peak data of the measured current-potential curve. The resulting polynomial function was used to smooth the peak and also for further

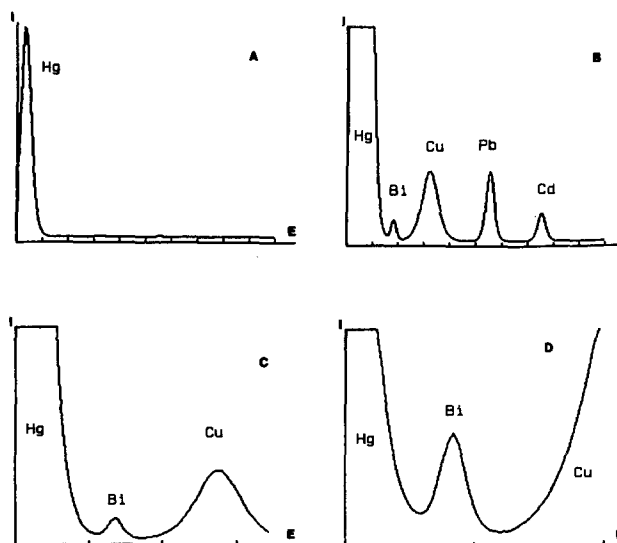


Fig. 3A–D. Simulation of a polarogram of mercury, bismuth, copper, lead and cadmium. Hg: $E_p = 70$ mV, $z = 1.5$, $c = 1$ mmol/l. Bi: $E_p = -80$ mV, $z = 3$, $c = 0.001$ mmol/l. Cu: $E_p = -220$ mV, $z = 1$, $c = 0.01$ mmol/l. Pb: $E_p = -450$ mV, $z = 2$, $c = 0.005$ mmol/l. Cd: $E_p = -680$ mV, $z = 2$, $c = 0.002$ mmol/l. Graduation of the potential axis: 100 mV. A Enlargement: 1, potential range: 100 to -900 mV. B Enlargement: 50, potential range: 100 to -900 mV. C Enlargement: 50, potential range: 50 to -300 mV. D Enlargement: 250, potential range: 0 to -200 mV.

mathematical operations. The necessary parameters $E_{1/2}$, respectively E_p , and z , respectively $z \cdot df$ could be determined by measurement. E_p , the peak potential, could be determined with the maximum of the peak, z , respectively $z \cdot df$ can be determined from the peak width at half peak height [5].

$$bh = 3.52 \cdot \frac{R \cdot T}{df \cdot z \cdot F}, \quad (15)$$

$$df \cdot z = 3.52 \cdot \frac{R \cdot T}{bh \cdot F} = \frac{90.4}{bh} \text{ at } 25^\circ\text{C}. \quad (16)$$

The use of the transformed Heyrovsky-Ilkovič equation for the calculation of voltammetric peaks by polynomial regression is realized in a software package for computer assisted peak evaluation on a Commodore 8032 and Commodore 64 computer. (The first part of this software package was presented in [2].) With peak regression, using the equations above, we could smooth the noise of measured peaks and by use of the calculated polynomial function more mathematical operations of peak evaluation could be performed. The running of the computer program is described as follows (see Fig. 2):

Subsequent to the voltammetric measurement and after subtraction of the background current [2] the computer fixed the position of the peak potential. Then the calculation of $z \cdot df$ is carried out from the width of the resulting peak in half peak height. After E_p and $z \cdot df$ have been determined, the numerical values are inserted in

$$y = \frac{1}{1 + e^{((df \cdot z \cdot F \cdot (E - E_p))/(R \cdot T))}}, \quad (17)$$

and for the $i - E$ pairs of the values of the peak the corresponding $i - y$ values are calculated. These $i - y$ values

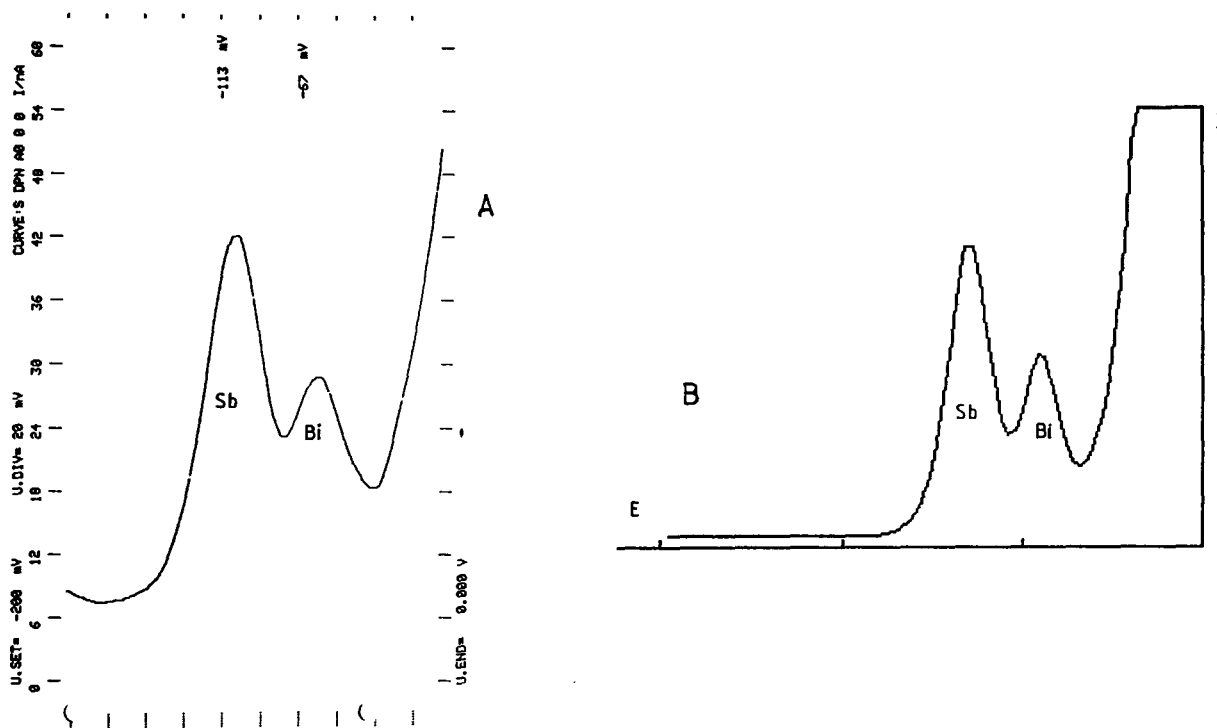


Fig. 4A, B. Comparison of a simulated polarogram of bismuth and antimony with a measured voltammogram of these elements (changed recording direction) **A** (Measurement of $10 \mu\text{g/l Bi}^{3+}$ and $10 \mu\text{g/l Sb}^{3+}$ (molar Bi:Sb ratio: 1:2). Supporting electrolyte: 1 mol/l HCl. Method: HMDE-DPASV-UDP = 10 mV - S = 10 mV/s. Deposition: 120 s at -200 mV. **B** Simulated polarogram of Hg, Bi and Sb (molar Bi:Sb ratio = 1:2, 1000-fold excess of Hg)

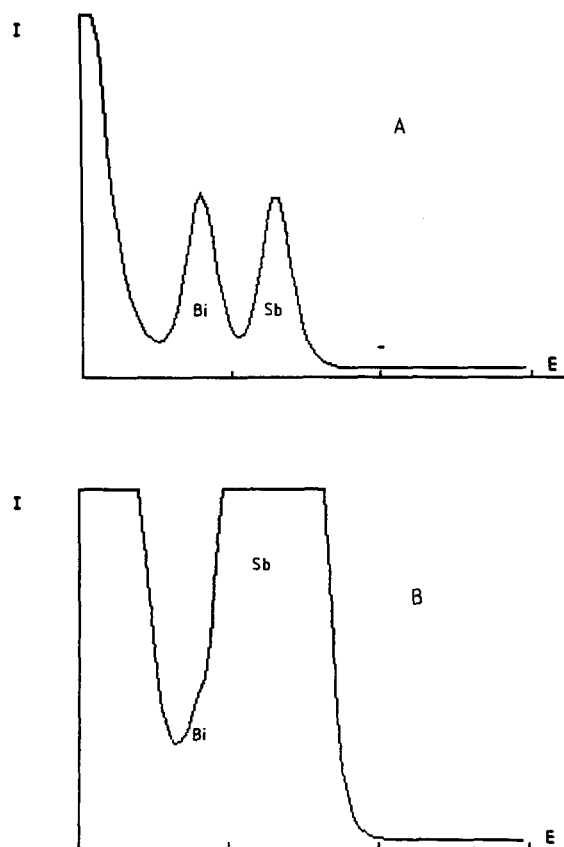


Fig. 5A, B. Polarogram simulations to study excess ratios of bismuth and antimony. **A** Simulation of a Bi:Sb ratio of 1:1. **B** Simulation of a Bi:Sb ratio of 1:200 (calculated Bi:Hg ratio at A and B: 1:1000)

serve to determine the coefficients a_j of an n -order regression polynomial function.

$$I = \sum_{j=0}^n a_j \cdot y^j. \quad (18)$$

With the aid of the resulting polynomial function a measured voltammetric peak can be very well approximated. For application a regression polynomial function of fifth order with correlation coefficients ≥ 0.97 is completely sufficient for a good approximation.

The method of least squares, proceeding from the Heyrovsky-Ilkovič equation, allows a mathematical description of measured voltammetric peaks. The calculated polynomial function represents a sum of different parts of current: A constant part ($j = 0$) (of the current), a DC-part ($j = 1$), which is responsible for the shape of the polarographic wave, a current part ($j = 2$), which is responsible for the form of the DP- or AC1-peak (first derivation of the transformed Heyrovsky-Ilkovič equation), and current parts ($j > 2$), which represent the higher derivations. Dependent on the form of the measured signal, to which the data belonged taken to calculate the regression polynomial function, the different parts of the current are weighted by the calculation relating to their coefficients a_j .

II Applications

a) Simulation of polarograms

For simulation of polarograms equation (18) was used in the following form:

$$I = \sum_{j=1}^n a_j \cdot y^j. \quad (19)$$

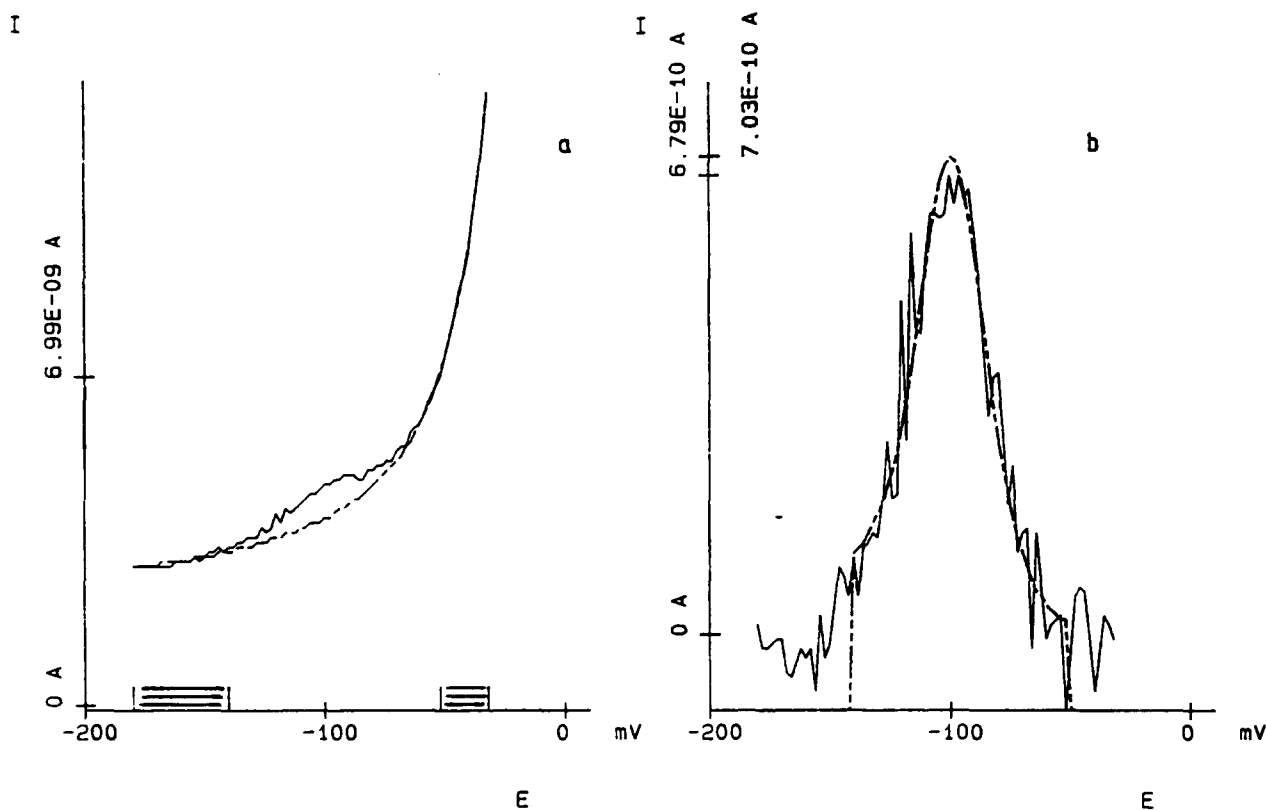


Fig. 6a, b. Peak calculation with the transformed Heyrovsky-Ikovič equation to smooth very narrow bismuth peaks after the subtraction of an extrapolated background current calculated with an 3-order hyperbola. Supporting electrolyte: 1 mol/l HCl. Concentration: Bi^{3+} 0.05 $\mu\text{g/l}$. Method: HMDE-DPASV-UDP = 10 mV - S = 10 mV/s. Deposition: 1800 s at -200 mV. Distance between two measuring points: 2 mV. **a** Recorded voltammogram of the bismuth-measurement (—) and calculated background current (---) in the used value range. **b** Enlarged signal of the resulting bismuth-peak after the subtraction of the calculated background current from the measurement (—). Bismuth-peak smoothed by the transformed Heyrovsky-Ikovič equation (---). \equiv Potential range which was used to calculate the background current (see [2])

In contrast to the mathematical description of a measured peak a third order polynomial function is sufficient to simulate polarograms. The simulations are performed with a written software package called POLAROGRAPH on a Commodore 64 computer. POLAROGRAPH makes possible the calculation of DC-, DP- and AC-polarograms (AC1 and AC2), coulometric curves and cyclic polarograms.

By the input of the half-wave potentials, respectively the peak potential, the number of electrons involved in the charge transfer step and the concentrations of the elements, it is possible to simulate polarograms to study their appearance, excess ratios, separations and other effects.

Figure 3 shows the simulated polarogram of Hg, Bi, Cu, Pb and Cd. To calculate this polarogram, the peak potentials of the elements in a 1 mol/l HCl as supporting electrolyte and the theoretical number of electrons involved in the charge transfer step were given into the computer program. The simulation of the increase of the background current resulted from a calculated Hg-peak. The calculation was performed with a 1000-fold excess of mercury compared to the concentrations of the other elements and 1.5 for the number of electrons involved in the charge transfer step. This number could be determined by measurement or by multiplication of the theoretical number of charge transfer electrons with a transfer coefficient, which is eligible between 0 and 1.

In the simulation shown only a large Hg-peak can at first be seen. After a 100-fold enlargement of the simulated

polarogram the peaks of the other elements become visible, while the mercury peak forms the background current in the area of the bismuth peak. Figure 3D shows an enlargement of this area. This polarogram is rather similar to the measured voltammograms, which are presented in the different figures of parts 1 and 2 of the publication concerning the inverse voltammetric determination of bismuth in biomatrices with computer assisted peak evaluation [1, 2].

Another possibility of polarogram simulation is presented in Fig. 4 by the example of bismuth and antimony. In this figure we can see the simulated polarogram of Hg, Bi and Sb in comparison to a voltammogram of 10 $\mu\text{g/l}$ ($= 48 \text{ nmol/l}$) Bi and 10 $\mu\text{g/l}$ ($= 82 \text{ nmol/l}$) Sb measured at a HMDE by DPASV in a 1 mol/l HCl as supporting electrolyte. There are only little differences between the calculated polarogram and the measured voltammogram. In real measurements the increase of the background current in the area of the bismuth peak was produced by the anodic current of the mercury from the hanging mercury drop electrode. In the simulated polarogram we had to calculate the increase of the background current by a 1000-fold excess of mercury and $z = 1.5$. The molar ratio of bismuth and antimony in the computed polarogram is 1:2. Furthermore, the simulation allows to study the molar excess ratios of Bi and Sb, so that only a few measurements are necessary to confirm the computer calculation. Figures 5 and 4 show the following facts: If the molar ratio is 1:1 we obtain a complete separation of the two peaks (Fig. 5A). If the molar ratio of

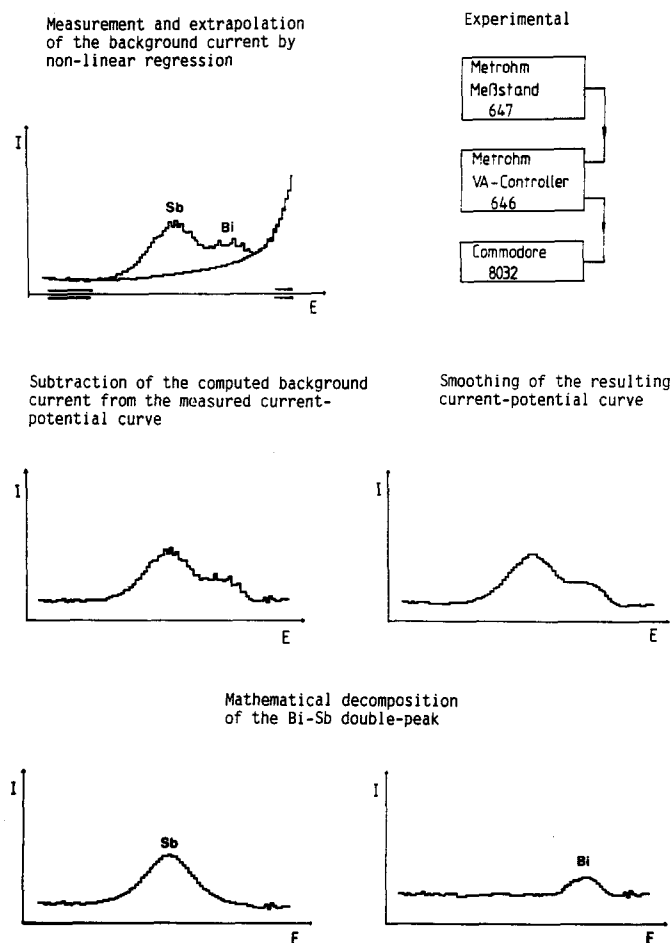


Fig. 7. Evaluation of a bismuth-antimony double-peak with the computer assisted evaluation of measurement signals (changed recording direction). Supporting electrolyte: 1 mol/l HCl. Concentration: Bi^{3+} 10 $\mu\text{g/l}$, Sb^{3+} 10 $\mu\text{g/l}$. Method: HMDE-DPASV-UDP = 10 mV — S = 10 mV/s. Deposition: 20 s at -200 mV. \equiv Potential range which was used to calculate the background current (see [2])

Bi and Sb is 1:2 there is no problem in peak evaluation (Fig. 4). But if the ratio is 1:200 an evaluation of the two peaks is impossible (Fig. 5B).

b) Smoothing of measured peaks

An important application of peak calculation with the transformed Heyrovsky-Ilkovič equation is the possibility to smooth (bismuth) peaks of very low concentrations without loss of peak height. Figure 6b shows the enlarged Bi-peak of a DPASV measurement of 0.05 $\mu\text{g/l}$ in a 1 mol/l HCl as supporting electrolyte after the subtraction of a background current, which is extrapolated by a third order hyperbola [2, 3]. In the resulting Bi-peak the noise of the measurement may be very clearly seen. If the data of this peak are taken and a peak calculation is performed by applying the method of least squares using the transformed Heyrovsky-Ilkovič equation, a mathematically approximated peak without signal noise is obtained. So, by the use of mathematical peak extrapolation an elimination of the noise and a better peak evaluation is possible.

c) Application of the peak calculation to eliminate the Sb(III) interference of the inverse-voltammetric Bi determination

If the inverse-voltammetric bismuth determination in a 1 mol/l HCl as supporting electrolyte is carried out in the presence of antimony(III) and a more than a 2-fold excess of it, the evaluation of the bismuth peak becomes difficult. As shown in [1] this interference can be eliminated by chemical operation or by selection of the deposition potential. As long as we can see a Bi-peak in the flank of a Sb-peak, there are mathematical possibilities to face the interference.

This possibility, which is presented in Fig. 7, shall be briefly explained: After measurement of Bi and Sb the background current would be calculated with data from the background current on the left and right of the bismuth-antimony double-peak [2]. After the subtraction of the calculated background current from the measured current-potential curve we obtain a Bi-Sb double-peak on a near linear background current. From the peakside of the antimony peak, which has no contact to the Bi-peak, data are now taken to calculate an antimony peak. A further approximation of the calculated peak towards the measured Sb-peak is performed by variation of the transfer coefficient df with the given number of electrons involved in the charge transfer step ($z = 3$). After having obtained a sufficient approximation, the calculated Sb-peak can be subtracted from the measured Bi-Sb double-peak. After this operation there remains a Bi-peak, which is easy to evaluate and free of interferences. In Fig. 7, a voltammogram with a very strong noise was deliberately chosen to show the smoothing of the signal clearly.

It takes more mathematical efforts and also more time to calculate both peaks by the transformed Heyrovsky-Ilkovič equation and to approximate the addition of both peaks towards the measured voltammogram by iteration. If the molar Bi-Sb ratio in the sample comes nearer to an 1:1 ratio of both ions or if there is only little difference between the peak potentials, this way of computing becomes more important.

This will be reported later.

4 Conclusions

With the use of the transformed Heyrovsky-Ilkovič equation in the calculation of voltammetric peaks, it is possible to simulate DP- and AC-polarograms. By computer simulation it is possible to make studies about the appearance of current-potential curves without measurements.

Beside this application the peak calculation, respectively the peak regression, makes it possible to smooth voltammetric peaks without loss of peak height. This leads to an increase of the sensitivity of the measurement. Furthermore, the peak calculation enables us to separate overlapping peaks. So the separation and the smoothing of peaks by the presented method allows a better evaluation of narrow peaks especially in ultra trace analysis.

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