Metrohm
Autolab

Autolab Application Note AN-EC-019

How to use the Convolution

Convolution Techniques

Convolution voltammetry consists essentially of a voltammetric, chronoamperometric, or chronocoulometric experiment followed by a mathematical transformation - convolution. The technique delivers quantities directly related to the concentration of electroactive species at the electrode surface (instead of the flux of a compound, as in the case of the original techniques) and it is rather insensitive to iR drop.

In a number of electroanalytical techniques, the current measured displays proportionality to a $t^{-1/2}$ function. The popularity of this type of dependence originates from the solution of Fick's law in the case of semi-infinite linear diffusion, the most common type of the transport of the reagent to the electrode. According to this solution, the gradient of the concentration of a substance, consumed in the electrode process, decreases with the square root of the electrolysis time and so does the current, which is proportional to this gradient. Such a dependence can be easily observed in chronocoulometry, chronoamperometry, and in voltammetry (in this latter case in the descending branch of the peak).

Using a convolution method, the effect of the decrease of the concentration gradient can be eliminated from the total response of the electrode. The surface concentration c^s of the product of an electrode reaction during the experiment can be obtained using the following Equation 1.

$$c^s(t) = \frac{i(t) \otimes g(t)}{nFAD^{1/2}} \tag{1}$$

Where $i(t) \otimes g(t)$ is a convolution operation defined as

$$\begin{aligned} f_1(x) \otimes f_2(x) &= \int_0^x f_1(u) f_2(x-u)\,du \\ &= \int_0^x f_1(x-u) f_2(u)\,du \end{aligned} \tag{2}$$

The function $g(t)$ depends on the transport conditions and the electrode geometry, being in the simplest case $(\pi t)^{1/2}$. The convolution of a voltammogram results in an S-shaped curve, where voltammetric peaks are replaced by waves, very similar to polarographic ones. In the case of a fast and uncomplicated electron transfer, the wave can be described using the equation

$$E = E_{1/2} + \frac{RT}{nF} ln\left(\frac{m_d - m}{m}\right) \tag{3}$$

Where m denotes current convolution (for approximate description of kinetic controlled processes the RT/nF value should be replaced by $RT/\alpha nF$). The height of the plateau is given by the formula

$$m_d = nFAD^{1/2}C \tag{4}$$

It can be shown that such a result is independent of the scan rate used and that the height of the wave is insensitive to *iR*-drop. Convolution of voltammetric data with a $t^{-1/2}$ function results in a curve equivalent to the derivative of the previous one (up to a normalization factor). Valuable features of this new curve can be noted: symmetric, narrow peaks, which are much better resolved compared to asymmetric, "tailing" voltammetric ones. The obtained $t^{-1/2}$ convolution peak follows the function

$$e = \frac{nFAD^{1/2}C}{cosh^2\left[\frac{nF}{2RT(E - E^{0\prime})}\right]} \tag{5}$$

In case of a fast, reversible electron transfer. It is also possible to use other convolution functions, e.g., to separate the spherical diffusion effect, the kinetic effect of the preceding homogeneous reaction etc. [2]. In chronoamperometry, convolution of current with $t^{-1/2}$function results in a horizontal line at the height equal to

$$e = nFAD^{1/2}C \tag{6}$$

If the transport to the electrode follows semi-infinite linear diffusion. For chronocoulometry, convolution with a $t^{-1/2}$ function leads exactly to the same result. It is profitable to distinguish a class of convolutions with a $g(t)$ function in the form $g(t) = t - u$ (u is a real number): such a convolution can be considered as a generalized differentiation/integration (differintegration) operation with respect to the variable t. In this approach, the value of the exponent denotes the order of integration (if positive) or differentiation (if negative) and thanks to the convolution definition, the value of u need not be integer. Differintegration is cumulative, i.e.,

$$\frac{\mathrm{d}^{\frac{1}{2}}}{dt^{\frac{1}{2}}}\left(\frac{d^{\frac{1}{2}}i}{dt^{\frac{1}{2}}}\right)=\frac{di}{dt} \qquad 7$$

or

$$\frac{\mathrm{d}^{-\frac{1}{2}}}{dt^{-\frac{1}{2}}}\left(\frac{di}{dt}\right)=\frac{d^{\frac{1}{2}}i}{dt^{\frac{1}{2}}} \qquad 8$$

From the practical point of view, two forms of convolution, with $t^{1/2}$and $t^{-1/2}$, deserve special attention. They can be considered as, respectively, semi-integration and semi-differentiation. Another reason for mentioning differintegration is that there are special algorithms allowing this operation to be performed rapidly. For more information, please refer to K.B. Oldham, J. Spanier, "The Fractional Calculus", Academic Press, N.Y., 1974. As mentioned before, in case of semi-infinite linear diffusion the results of convolution with the function $t^{\pm 1/2}$ (semi-integration and semi-differentiation) are well defined and quite simple. This suggests that these methods can be used for the investigation of variations of product concentration on the electrode surface as well as detection and studies of phenomena, resulting in deviations from linear diffusion transport. Other practical applications are the resolution of overlapping voltammetric peaks, the determination of the formal potentials and numbers of electrons involved in the reaction step, detection of the adsorption on the electrode as well as of the irreversible homogeneous reaction consuming the product generated by the electron transfer step.

Detection of overlapping peaks

The nature of the voltammetric peak causes overlap in case of complex voltammograms. While the ascending branch of the peak rises rapidly, and the beginning of the rise can easily be found, the descending branch follows a $t^{-1/2}$ function and is characterized with a slow decrease. Even far away from the top of the peak, the value of the current differs significantly from zero. Due to this feature, all following voltammetric peaks rise from the "tail" of the previous one. If the separation of two voltammetric peaks is large enough, they can be detected without any problems. The situation is difficult when the distance between peaks gets smaller: below a certain distance, the first peak is reduced to a shoulder on the rising part of the next peak. The extreme situation is shown in Figure 1 C, where the overlap is very strong, so that only one peak can be observed and there is no indication for the presence of more of them.

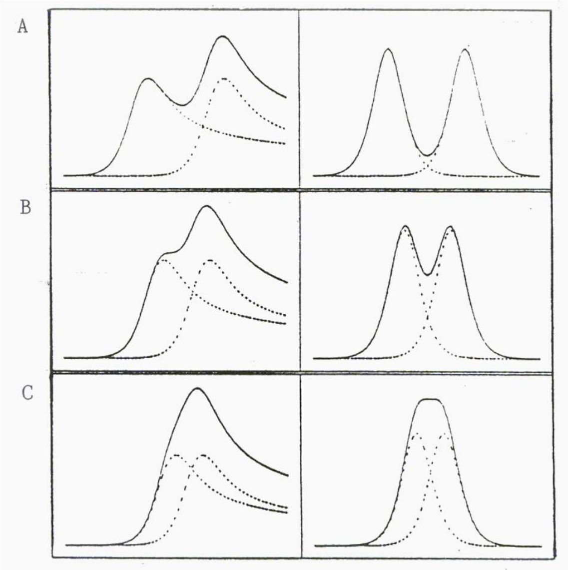

Figure 1 – Overlapping linear voltammetric peaks and their semi-derivatives

In most situations, except in those of extreme overlap, semi-derivative peaks are clearly visible and their number can easily be found. There are, however, three important limitations to this method. First, voltammograms that are to be semidifferentiated should be background-corrected: semi-differentiation changes a constant or a linear background into complicated forms in the semi-derivative domain. Secondly, semi-derivative peak artefacts have to be recognized: consider the case of an uncomplicated slow electron transfer leading to the voltammogram presented in the appropriate figure.

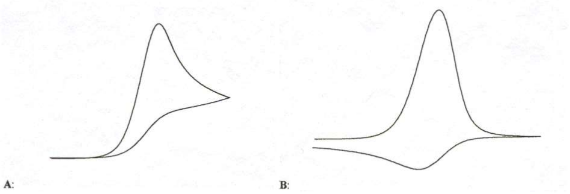

Figure 2 – Peak artefacts in semi-derivative voltammetry

The curve in the above-mentioned figure is the result of semi-differentiation, where two peaks appear, one in the forward and one in the backward branch. The second semi-derivative peak does not represent any hidden voltammetric peak, but is an artefact resulting from semi-differentiation of a wave-like current decay. Such a peak can only appear in the backward branch of semi-derivative voltammograms and has characteristic features: in the potential range, where such a peak appears,

1. there is no backward voltammetric peak,
2. there is a forward peak, and
3. the sign of SCV current values is the same in both branches.

All peaks that satisfy these criteria are probably artefacts.

The third limitation of the method stems from the fact that results presented in the above-mentioned figure concern an uncomplicated electron transfer under semi-infinite linear diffusion conditions. The form of the peak is different when the mechanism of the reaction and the transport type change: usually peaks become less symmetric and broader, resulting in a decrease in separation capability and, in certain situations, leading to deformations of neighboring semi-derivative peaks.

Determination of formal potential and the number of electrons involved

Equation 5 describes the form of a semi-derivative voltammetric peak in a case of uncomplicated fast electron transfer under semi-infinite linear diffusion transport. It is clear that the peak potential is equal to the formal potential of the reacting system and, for cyclic voltammetry that both anodic and cathodic peaks appear at the same potential. This feature can be used as a simple and rapid test for reversibility of the reaction. This test is superior to the well-known test based on the difference of potentials of voltammetric peaks, as it does not require knowledge about the number of electrons involved.

If the rate of electrode reaction is limited by the diffusion or by kinetics of the electron transfer, the number of electrons involved can be determined from the half width of the semi-derivative peak. This half-width should be

$$w = 3.53\frac{RT}{nF} \tag{9}$$

for a diffusion-controlled process and

$$w = 2.94\frac{RT}{\alpha nF} \tag{10}$$

for a rate-controlled process.

Irreversible homogeneous reaction consuming the product of the electrode process

The criterion for the absence of an irreversible homogeneous reaction is restoration of the initial state at the electrode surface after a cyclic change of electrode potential. If such a reaction does not occur, the surface concentration of all species after the experiment should be exactly the same as before.

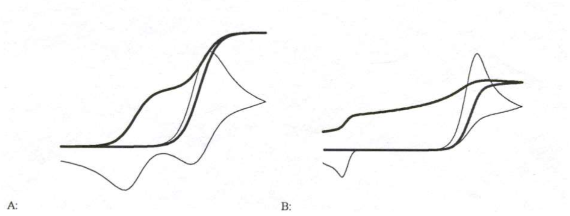

Figure 3 – Semi-integration of voltammograms in case of the absence (A) and the presence (B) of an irreversible homogenous reaction. Thin line - voltammogram, thick line - semi-integral.

As the convolution of the voltammetric current with a $t^{1/2}$ function (semi-integration) produces a value proportional to the surface concentration of the product of the reaction, the convoluted value should return exactly to zero after completion of the cycle, which means that the product of the reaction has been entirely converted back to the substrate [3]. If it does not return to zero, the consumption of the initially present substance is suggested. It should be stressed, however, that this method requires diffusion to be semi-infinite and linear. In situations where this is not the case, corrections have to be made. Such a correction is available for spherical electrodes (mercury drops) under the name of spherical convolution, it requires the values of electrode radius and of diffusion coefficient, delivering the concentration of the reaction product on the surface of a spherical electrode [4].

If the presence of an irreversible homogeneous reaction is detected, its rate can be measured. For this purpose, a so-called kinetic convolution can be used. In this transformation the effect of consumption of the product by the reaction with the rate *k* can be eliminated; by means of inserting different values of *k* one can obtain the result in which a convoluted current at the end of the cycle approaches the same value as on the beginning of the cycle.

Some problems can be expected if the substrate or the product of the reaction is accumulated on (or in) the electrode by adsorption, deposition, or amalgamation. In this case, the initial value of the surface concentration is not restored after the completion of the voltammetric cycle and convoluted voltammograms will not deliver proper results.

Investigations of factors controlling the transport to the electrode

Theoretically, the most simple and quite commonly encountered transport type is semi-infinite linear diffusion: the substance diffuses from the bulk of the solution, where the concentration is constant, to the planar electrode, where it is consumed. The flux of the substance depends on the gradient of the concentration at the electrode surface; this gradient decreases with the rate proportional to the square root of the electrolysis time.

Linear diffusion leads to the simplest description, but unfortunately its conditions are rarely realized in the experimental setups used in electrochemistry. In case of mercury electrodes, the surface of the electrode is not planar, and the diffusion can be approximated using a linear model over a short period of time only. In case of solid electrodes a so-called edge effect occurs: the contribution of spherical diffusion appears. Apart from the geometry of electrodes, chemical processes taking place in the solution can disturb the concentration profiles developed during the electrolysis, for instance, when electroactive species are produced by a homogeneous chemical process; another example of deviations from the linear model may be caused by the adsorption of the compound on the electrode surface.

It can be useful to consider different types of transport as deviations from the semi-infinite linear diffusion case. These deviations can then be classified into two groups: deviations, causing an increase of the transport to the electrode and those causing a decrease. In the first group, spherical diffusion and different kinetic effects are included; the second group covers effects such as limited diffusion and reaction from the adsorbed state.

Spherical diffusion enhances the transport because the spherical expansion of the diffusion zone increases its volume faster than in the semi-infinite linear case. The increased volume results in a larger amount of the substance that diffuses to the electrode.

Kinetic effects occur when the electroactive compound is involved in a chemical equilibrium. The local decrease of its concentration within the diffusion layer disturbs the equilibrium and in consequence leads to the production of the compound in a chemical process. This extra amount increases the flux of the substance to the electrode surface. Such conditions can be called mixed linear diffusion – kinetic effects. For a long electrolysis time, the kinetic increase of the flux can entirely compensate the decrease of the concentration gradient and may lead to steady-state conditions if the amount of compound involved in reagent production is present in large excess.

Another type of effect can be observed when the solution is present in the form of a thin layer. Electrolysis under such circumstances first leads to the depletion of this layer and then to the exhaustion of the entire solution volume. This effect can be observed relatively easily in case of the dissolution of metals from a small amalgam drop or from amalgam film electrodes: the process is initially controlled by linear diffusion, but after some time the drop is depleted and the flux of the substance through the electrode surface drops more rapidly than $t^{-1/2}$. This is called limited diffusion.

An extreme case of this situation is the reaction of a substance adsorbed on the electrode or forming a monolayer on its surface. In such a case, no transport is needed and the whole amount of substance reacts within a very short time. The measured current drops sharply to zero after exhaustion of the compound.

Cyclic chronoamperometry and chronocoulometry

If an electroactive compound reaches the electrode by means of semi-infinite linear diffusion, and the potential of the electrode is such that the surface concentration of the compound is kept zero, the current can be described using Cottrell's equation

$$i = \frac{nFAC\sqrt{D}}{\sqrt{\pi t}} \qquad 11$$

Where

- n is the number of electrons involved,
- $F = 96450\ C\ mol^{-1}$ is the Faraday's constant,
- $A\ (cm^2)$ is the electrode area,
- $D\ (cm^2\ s^{-1})$ is the diffusion coefficient of the compound
- $C\ (mol\ cm^{-3})$ is the bulk concentration of the compound,
- $t\ (s)$ is the time from the beginning of electrolysis.

Integration of this equation leads to the expression for the charge

$$i = \frac{nFAC\sqrt{D}}{\sqrt{\pi}}\sqrt{t} \qquad 12$$

Semi-integration of Equation 11 or semi-differentiation of Equation 12 leads to the formula

$$m = FAD^{1/2}C \qquad 13$$

In case of additional contributions enhancing the transport due to, for instance, spherical diffusion or a kinetic effect, the semi-charge is greater than predicted from the purely linear model and the line displays positive bias. The inverse effect appears when the transport is slower than for limited diffusion or if the reagent is strongly adsorbed on the electrode.

There are a number of experimental problems that should be mentioned here. First, the data used for studies of transport phenomena should be corrected for the background otherwise deviations from linearity of the graphs can have other reasons.

In case of kinetic control of the process, the time scale of the experiment also determines the range of reaction rates and equilibrium constants that can be detected.

The quantitative discussion of influences of different experimental factors on the convolution curve can be found in [5].

Linear and staircase voltammetry

The convolution techniques facilitate the interpretation of voltammograms, particularly the information included in the peak shape. As already said, this shape can be considered as produced by the convolution of two functions: function I, describing the surface concentration of the reaction product, and function II, representing the flux of the reaction substrate, depending on the geometry of the measuring system.

In the simplest case of semi-infinite linear diffusion and fast electron transfer, function I has the form of an S-shaped wave and function II is a $t^{-1/2}$ decay. The character of function I is well reflected in the ascending branch of the voltammetric peak; function II is responsible for the $t^{-1/2}$ - proportional decay of the descending branch of the peak. Semi-integration (convolution of the SCV peak with a $t^{1/2}$ function) should therefore give a wave with a horizontal plateau.

When the transport to the electrode is enhanced or diminished compared to semi-infinite linear diffusion, the descending branch of the SCV peak can be approximated using a t^{u} function, where $u > -0.5$ for faster transport (slower decay) and $u < -0.5$ for slower transport (faster decay). Changes in transport result in semi-integrated waves with a biased plateau (negative for slower transport, positive for a faster one).

Algorithms for convolution

As mentioned before, there are special algorithms for differintegration as well as for other convolution. Below, four algorithms used for differintegration and convolution are described in short.

G0 algorithm (Grünwald-0)

This algorithm can be used to carry out differintegration to any order. The data must be acquired in constant intervals. For the order = 1 the operation is equivalent to differentiation, for -1 - to integration using rectangle method. For +½ the G0 algorithm is the same as semi-differentiation. For −½ the G0 algorithm is the same as semi-integration. Error in results increases with the length of the interval and accumulates, i.e., error in latter points is larger than in earlier ones. Important advantage is that this algorithm does not require the value of the function for $t = 0$, which makes it very well suited for transformation of chronoamperometric data (where $i_{t=0} \rightarrow \infty$. The disadvantage of the algorithm is that the total number of operations is proportional to the square of the number of data points, so calculation time grows fast with the length of the data set. The fundamentals of this algorithm are described in [6].

FRLT algorithm (Fast Riemann-Liouville Transform)

This is a fast, approximate algorithm based on a recursive digital filter. It is best suited for differintegration in the range of $0.0 \ldots -0.5$ (up to semi-integration). It is less precise than G0 algorithm, but the number of operations is linearly related to the number of data points. For details, please refer to [7].

Spherical convolution

The algorithm is used to carry out convolution of the data measured using a spherical electrode and staircase potential waveform. Values of the diffusion coefficient, the electrode radius as well as the delay between begin of the potential step and the current sampling moment are necessary. The number of operations is proportional to the square of data points. Details of the algorithm can be found in [8].

Kinetic convolution

This algorithm carries out kinetic convolution according to [9]. The number of operations is approximately proportional to the square of the number of points. This convolution requires the value of the rate constant of irreversible homogeneous follow-up reaction (ECi mechanism).

Convolution in Practice

The convolution option can be selected for data measured with cyclic and linear sweep voltammetry. This convolution menu offers a number of transformations of the data set, like differentiation, integration, and convolutions.

There are three principal types of convolution available: differintegration (convolution with $t-u$ function, equivalent to fractional differentiation or integration, depending on u), using G0 or FRLT algorithm, spherical convolution, and kinetic convolution. The difference between G0 and FRLT algorithm is that G0 is more exact, while FRLT is faster with large data sets. Two items: semi-integration and semi-differentiation denote differintegrations using FRLT with the u value equal to -0.5 and 0.5, respectively.

It is possible to carry out more transformations in succession. Because differintegration is an operation that can be cumulated, double semi-differentiation is equivalent to differentiation and the integration followed by semi-differentiation is equal to semi-integration. Please note that some combinations, especially those involving differentiation are not equivalent: differentiation + integration is not the same as integration + differentiation.

In all convolutions the scale on the Y axis represents $c^s(t)nFAD^{1/2}$, where $c^s(t)$ is the concentration of the product of the electron transfer step on the surface of the electrode.

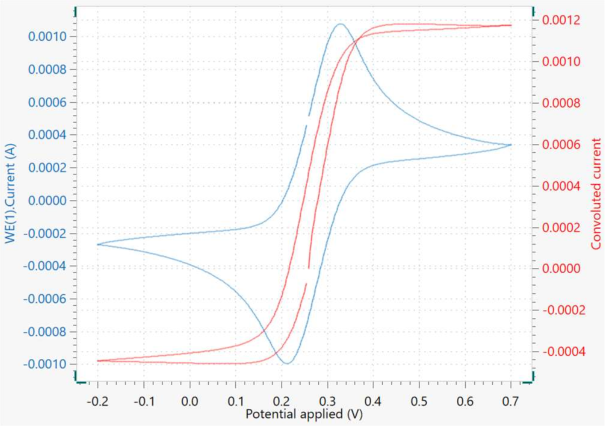

Figure 4 – Example of a convoluted voltammogram

It is also possible to perform the convolution on part of the voltammogram (See Set window option of the Plot menu). It is recommended that the cyclic voltammogram starts at zero current. This can be achieved by performing a baseline correction.

iR Drop Correction

iR drop correction allows for software correction of the potential data for the Ohmic drop in the solution. This option can be used for data from cyclic and linear sweep voltammetry.

After supplying a value for the solution resistance, the measured and corrected curve are shown. The question appears whether the data are corrected.

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Date

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