

# The Use of Fractional Differentiation or Integration for Signal Improvement

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**Abstract.** *Differentiation or integration with fractional order (differintegration) is favourable mainly in the form of the semiintegral or semiderivative of the original measured signal. It is used for substantial improvement of the signal shape and, consequently, the way how the measurement is evaluated. In the case of semidifferentiation also a better signal resolution is observed. A new, effective GS numerical algorithm of differintegration is here presented.*

**Keywords:** *signal shape, fractional differentiation, fractional integration.*

## 1. Introduction

In chemistry, the differentiation and integration of instrumental signals is frequently used to improve data analysis and perform data manipulation. After a proper signal transformation more useful information can be extracted, which has been approved by many examples in analytical chemistry and related sciences [1]. For instance, chromatographic or spectroscopic signals are differentiated and then the individual signals can be detected and finally resolved.

The first derivative of a symmetrical signal is frequently used as an aid in finding the exact peak location. Development of signal differentiation in spectroscopy several decades ago led to the technique of *derivative spectroscopy*. There are several applications of the signal differentiation also in electrochemistry where it improves e.g. indicating the end-point detection of titration curves.

Integration is also an essential part of several techniques of instrumental analysis. It is used for quantitative analysis, e.g. in chromatography, flow injection analysis, and stripping analysis, where the peak areas are calculated. Alternatively, it is used for a convenient signal transformation, as takes place in controlled-potential coulometry or chronocoulometry, where the primarily measured currents are integrated to obtain the corresponding charge.

Entirely new perspectives have been outlined in instrumental analysis after the first application of the signal *semidifferentiation* and *semiintegration*, which are the most important orders used in *fractional differintegration* [2]. Since fractional differentiation and integration may be more widely employed in science and technology, this paper will demonstrate their background, way of calculation and applications.

## 2. Subject and Methods

*Fractional differintegration*, invented by Leibnitz [3], is a common designation both for differentiation and integration. Its positive sign is valid for any differentiation and the negative sign is appropriate for integration. The order  $q$  of differintegration can be both,

integer and fractional. Then, e.g. for  $q = -1$ , the expression  $d^{-1}f(x)/dx^{-1}$  is just another form of writing the symbol of the definite integral having *zero* as the lower and  $x$  as the upper limits. It is important to note that the integration limits must be considered in all kinds of differintegration except the cases of differentiation with integer orders where the limits are senseless. The literature on this topic [2,4] provides many examples of *analytical* as well as *numerical* ways of differintegration, mainly the calculation of semiintegral  $d^{-1/2}f(x)/dx^{-1/2}$ , denoted usually  $m(f(x))$  and semiderivative  $d^{1/2}f(x)/dx^{1/2}$ , denoted usually  $e(f(x))$ .

The experimental signals which are to be differintegrated often cannot be described by some analytic mathematical function so that the ways of analytical differintegration, based mainly on Grünwald or Riemann-Liouville definitions [2,4], cannot be implemented. Therefore two other ways, more or less general, have to be used, which will be designated here as the hardware and the software approaches.

The *hardware approach* is based on the utilization of a special analog instrumentation, i.e. the RC circuits for differentiation and the RC ladder circuit network for semidifferentiation and semiintegration [5]. Such circuits have already been successfully applied in different cases [4]. However, a necessary condition for their correct utilization depends on adjusting their construction to a proper time window, which renders this approach less flexible. Another drawback of the hardware approach is about 5 % relative error and its limitation to the integer or half-integer differintegration orders.

### 3. Results

We have used the *numerical* way of fractional differintegration, which can be considered as the most useful and versatile. There are known several numerical algorithms, described mostly in the book [2] and reviewed in the paper [4]. With respect to the independent variable, they use equidistant points in the interval between the lower limit (zero) and the upper limit of differintegration and the dependent variable values (i.e. the signals), corresponding to these points, are summed in the way pertinent to the given algorithm. Some algorithms, like  $G1$  and  $G2$ , where  $G$  denotes that they are based on the Grünwald definition, are universally applicable for any differintegration order  $q$ . Others, like those based on the Riemann-Liouville definition, are applicable only for the selected  $q$  values interval. We have compared the computational accuracy of the differintegration algorithms and ranked their effectiveness [4]. However, the achieved results as well as the optimal choice of the order  $q$  depend significantly on the type of the differintegrated function (i.e. the measured dependence).

The  $G1$  algorithm does not require the value of the function at the lower limit (usually zero), which is an important advantage in cases where the signal at  $x=0$  goes to infinity. The disadvantage of the  $G1$  and several other algorithms is that the total number of operations grows more than linearly with the number of data points so that the calculation time increases remarkably with the length of the data set.

Our recent studies have led to the discovery of a new, more efficient  $GS$  algorithm (Grünwald definition with Sampling), optimised with respect to the computational error both in fractional differentiation and integration. The details are described in the following subchapter.

#### *New GS Algorithm of Numerical Differintegration*

Our new  $GS$  algorithm is adapted from the  $G1$  algorithm. Unlike in  $G1$ , the points where the signal  $y$  is sampled do not coincide in the  $GS$  algorithm with the points, at which the

differintegrated  $d^q y/dt^q$  values are calculated but are shifted. The shift equals to  $hq/2$  and depends on the differintegration order  $q$  and the sampling step (sampling period)  $h$ . The sampling step is related to the value  $x$  of the independent variable  $t$  (time, potential, etc.), at which differintegration is calculated, as well as the chosen number of points (subintervals)  $N$ ,  $h=x/N$ . Thus, when applying semidifferentiation ( $q = +0.5$ ), the shift is  $0.25h$ , so that e.g. for  $h=1$  the sampling points are 1.25, 2.25, 3.25, ...,  $x+0.25$  instead being 1, 2, 3, ...,  $x$ . The recurrent GS formula is given by equation

$$\left[ \frac{d^q y}{dt^q} \right]_{t=x} = \frac{N^q}{x^q} \left[ \left[ \dots \left[ f(h+hq/2) \left\{ \frac{N-q-2}{N-1} \right\} + f(2h+hq/2) \right] \dots \right] \left( \frac{1-q}{2} \right) + f((N-1)h+hq/2) \right] \left( \frac{-q}{1} \right) + f(Nh+hq/2) \quad (1)$$

where

- $y$  dependent variable
- $t$  independent variable (e.g.  $t$  - time)
- $x$  the value of the independent variable where  $d^q y/dt^q$  is calculated
- $q$  order of differintegration
- $h$  sampling period
- $N$  number of subintervals

When performing any kind of integration, the order  $q$  is negative so that the sampling shift has the opposite direction along the  $t$ - axis compared to that for differentiation.

#### 4. Discussion and conclusions

*Signal resolution* in electrochemical analytical techniques is generally not very high. Voltammetric methods allow a simultaneous determination of only few electroactive species during a single scan and the resolution power of a particular voltammetric experiment depends on the given current-potential curves pertinent to the electrolyzed species. A disadvantage is the asymmetrical shape of linear scan voltammetric (LSV) curves, which diminishes resolution of this technique [6]. To improve resolution the semidifferentiation of the LSV data was recommended [7]. Such a modification of the LSV method is semiderivative linear scan voltammetry (SDLSV). Coupled with an appropriate data processing procedure (e.g. digital filtering of the LSV data by the Moving Average 7-point filter [6]), it has been successfully applied to resolve overlapping LSV signals [6,7]. The application of our new, more precise

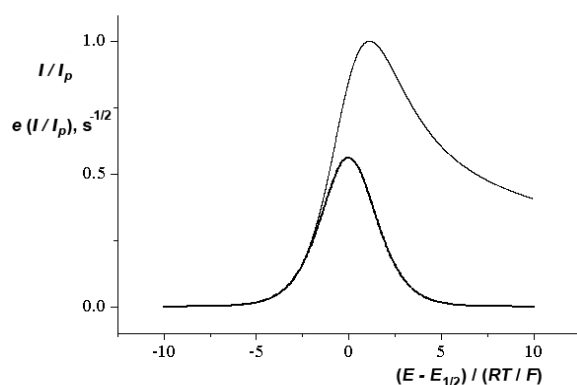


Fig. 1. Comparison of the asymmetric dependence  $I/I_p$  vs.  $[(E-E_{1/2})/(RT/F)]$  obtained by linear scan voltammetry (upper curve) with its semidifferentiated symmetric form (lower curve). Symbols  $I$  and  $I_p$  refer to instantaneous and maximum currents, resp.,  $E$  and  $E_{1/2}$  refer to the working electrode and half-wave potentials, resp.; normalized dimensionless potential is represented by  $[(E-E_{1/2})/(RT/F)]$ ,  $R$  – gas constant,  $T$  – absolute temperature,  $F$  – Faraday constant,  $e$  – semiderivative operator,  $e(f(x)) = d^{1/2}(f(x))/dt^{1/2}$ .

GS algorithm allows to achieve a rapid and quantitative signal resolution - practically at the time when the experiment ends. Fig. 1 demonstrates the shape change after performing the numerical semidifferentiation of the LSV signal. The semidifferentiated signal is narrower so that the resolution of two or more signals is better compared to the original LSV record.

Further signal transformations are shown in Fig. 2, where the original chronocoulometric signal  $Q = k_{CC}t^{1/2}$  is semiintegrated and semidifferentiated;  $k_{CC}$  is given by equation

$$k_{CC} = 2zFAD^{1/2}c/\pi^{1/2} \quad (2)$$

where

- $z$  number of exchanged electrons
- $A$  electrode surface area
- $D$  diffusion coefficient
- $c$  concentration of electroactive species

Both transformed (differintegrated) signals provide much better possibility for determining the concentration  $c$  than the original signal, which depends on time non-linearly.

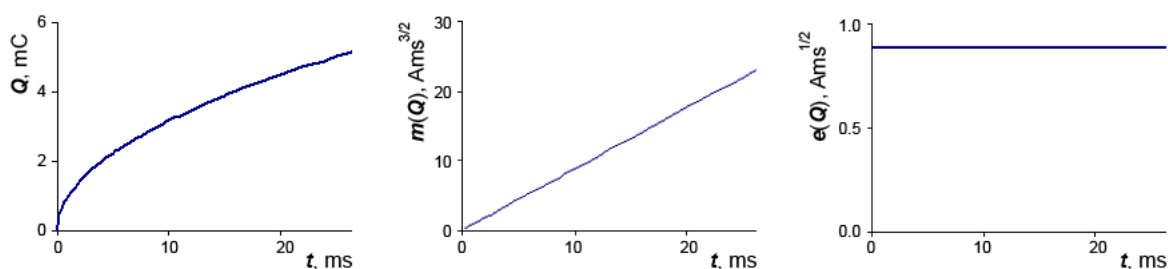


Fig. 2. Comparison of the chronocoulometric  $Q - t$  dependence (left) with the corresponding semiintegrated (middle) and semidifferentiated (right) dependences. Symbols  $m$  and  $e$  denote the semiintegral and the semiderivative operators, respectively. The analytically calculated semiintegral  $m(Q) = k_{CC} \pi^{1/2} t/2$  and the analytically calculated semiderivative  $e(Q) = k_{CC} \pi^{1/2}/2$  [4];  $k_{CC} = 1$  are considered.

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