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End-point detection in potentiometric titration by continuous wavelet transform

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ABSTRACT

The aim of this work was construction of the new wavelet function and verification that a continuous wavelet transform with a specially defined dedicated mother wavelet is a useful tool for precise detection of end-point in a potentiometric titration. The proposed algorithm does not require any initial information about the nature or the type of analyte and/or the shape of the titration curve. The signal imperfection, as well as random noise or spikes has no influence on the operation of the procedure.

The optimization of the new algorithm was done using simulated curves and next experimental data were considered. In the case of well-shaped and noise-free titration data, the proposed method gives the same accuracy and precision as commonly used algorithms. But, in the case of noisy or badly shaped curves, the presented approach works good (relative error mainly below 2% and coefficients of variability below 5%) while traditional procedures fail. Therefore, the proposed algorithm may be useful in interpretation of the experimental data and also in automation of the typical titration analysis, specially in the case when random noise interfere with analytical signal.

1. Introduction

Titration is a very useful and reliable technique, which is widely used in different fields such as the food industry, scientific research, and also chemical, clinical and pharmaceutical laboratories. Titrimetric procedures based on a detection of the end-point, i.e., the point at which volumetric titration is completed, are successfully employed over a wide range of concentrations and are popular because of their simplicity, speed, accuracy and good reproducibility. The importance of titrimetric analysis has increased with the advance of instrumental methods (potentiometric, amperometric, conductimetric, photometric) of end-point detection. The accuracy and precision of the results of a titrimetric determination depend on the nature of the titration reaction, but they are also influenced by the technique of the end-point location.

The methods for the determination of the end-points of titration can be graphical or numerical [1,2]. Graphical methods are simpler and are based on the graphical determination of the end-point by searching for the inflection point. The mathematical methods were developed in two ways: as numerical approximate and numerical modeling methods. The approximate methods are based on the presumption that the end-point of a titration is the inflection point of the titration curve. In these methods, the chemical reaction is not important. Only a small number of points in the vicinity of the inflection point are used for the calculation. Common methods of automated end-point detection rely on using the first and second derivatives of the classic sigmoid titration curve. The end-point usually occurs at the point of maximum deflection, where the absolute value of the first derivative reaches a maximum and the second derivative changes sign. Unfortunately, they lack of accuracy in the end-point calculation. In Ref. [3] a new method that belongs to the differential category is presented. It uses a preprocess to find first derivative values, by fitting four data points in and around the region of inflection to a non-linear function Then the end-point is usually calculated as maximum or minimum. In Ref. [4], the end-point is found by means of the Fibonacci method, adapted to act as a one-dimensional optimization algorithm for fast titration. The category of differential methods depends on the presence of an inflection point of function, but does not require any prior information about the nature of the analyte. The imperfection of approximation methods for the determination of the inflection point relies in the fact, that it considers only measurements in the vicinity of the equivalence point, what may result in increasing of errors.

In contrast to approximate methods, the numerical model methods are used for the determination of the end-point on the basis of the mathematical model of the titration curve, which presents the interdependence of the volume of the titrant added and the potential of the indicator electrode. The precision of the method depends on the accuracy of model parameters. In most cases, they involve a derived equation for each analyte and titration type considered without the necessity of the presence of an inflection point in the titration curve. Gran's linearization method is one of the examples known since 1950 [5–11]. Each type of analyte and titration requires

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a specific derived function based on prior knowledge about the stoichiometry of the reactions, in such a way that the method cannot be easily generalized. This method is usually specific to the type of analyte and/or shape of titration curve. In the same category, Fortuin's method [12] is generally applied to symmetrical potentiometric titration curves with equidistant titrant volumes in the region of inflection, and is based on a derived equation. The method uses four points in the region of inflection to calculate two parameters related to the transition in the region. Ingman et al. [13,14] and Johansson [15,16] developed methods based on chemical equilibrium equations, from which it was possible to determine the acid constituents in their mixture by submitting the measured data to regression analysis. Michalowski et al. [17] provided an overview on the Gran and other mathematical methods involving potentiometric titrations.

Potentiometric titration methods for complex systems were significantly improved after introduction of the multivariate calibration approaches [18]. The multivariate calibration techniques adequate for the described problem would be, for example, partial least square (PLS) regression or multiple linear regression (MLR) with preliminary reduction of variables by principal component analysis (PCA). An alternative method is based on the artificial neural networks (ANN) [19].

The experimental measurements of the titration procedure are subject of various influences, which are sources of systematic and random errors. Under real conditions, i.e., when perturbations in the signal are present, the response function has a random component. Unfortunately, all of the methods of the end-point location suffer from sensitivity to noise. Derivatives amplify noise, since they plot the rate of change of the signal. This method also requires the introductory designation of the end-point location.

In this work, a new method of end-point location in the potentiometric titration curve, based on wavelets, is proposed. The wavelet theory [20,21], which has been for 30 years a popular and useful tool in signal and image processing, found its place in many practical applications, from physics, medicine, image processing, acoustics, climatology, and seismology to the compression of data. The main feature of the wavelet transform is that it decomposes a signal into contributions which represents the information of different frequencies. There are many examples of application of wavelet transformation in processing of electrochemical and analytical signals [22–26]. The most commonly used applications of wavelet transform (WT) in processing data collected in chemical instrumental analysis are elimination of noises [27–31], baseline removal [31], zero crossing point location, data or image compression, detection and extraction of overlapping peaks [32–38], derivative computation [39–42] or calculations of other characteristic features of measured curves. Quantitative analysis, so important in analytical chemistry, is also possible but may be realized in wavelet coefficients space. Some recent applications of WT in chemical signals processing are described in works [43–50]. The wavelets are a widely used tool for these purposes, because the unique properties of the wavelet function allow separation of data components and observation of the features of experimental data in the proper scale. In this work, the continuous wavelet transform (CWT) is applied. As a wavelet function, specially defined dedicated mother wavelet for potentiometric titration is used.

At the beginning of this work, the theoretic fundamentals of continuous wavelet transforms are presented and their operation is demonstrated in signal-processing procedure. The definition of the dedicated mother wavelet in the case of the considered problem is given. Than, the operation of the algorithm is shown for simulated curves. The results are discussed when the noise level and the titrant volume increment, which has influence for resolution of curve, were changed in wide range.

Some instrumental tasks were chosen to demonstrate the advantages of the new approach. It was a simple NaOH/HCl experiment, determination of phenol and determination of aluminium in industrial solution. In each case optimization of CWT parameters was performed.

Reliability, i.e., an accuracy and precision, of the estimated end-point are examined when the new algorithmic strategy is applied to different simulated and experimental titration curves.

2. Theory

In the work, the CWT was applied, to construct a time–frequency representation of a signal. The CWT of the input signal $x(t)$ is expressed as

$$\mathrm{CWT}_x(a,b)=\int_{-\infty}^{\infty}x(t)\Psi_{ab}^{*}(t)dt \tag{1}$$

where the asterisk in Eq. (1) stands for complex conjugation, while $\Psi_{ab}(t)$ can be derived from the mother wavelet $\Psi(t)$ by scaling and shifting according to the following formula:

$$\Psi_{ab}(t)=\frac{1}{\sqrt{a}}\Psi\left(\frac{t-b}{a}\right) \tag{2}$$

The results of the CWT are wavelet coefficients $\mathrm{CWT}_x(a,b)$, which are the functions of a and b. The a and b parameters are called scale and translation parameters, respectively. There are no restrictions to the values of the indices a, b except that a must be higher than zero.

The parameter scale in the wavelet analysis is similar to the scale used in maps. High scales correspond to a non-detailed global view (of the signal), and low scales correspond to a detailed view. The term translation is related to the location of the window, as the window is shifted through the signal. This variable, obviously, corresponds to time information in the transform domain. For all practical purposes, the signals are band-limited, and therefore, computation of the transform for a limited interval of scales is usually adequate. In this study, some values for a were used.

The CWT cannot be practically computed by using analytical equations, integrals, etc. It is therefore necessary to discretize the transforms. Both parameters, a and b, are increased by a sufficiently small step size. This corresponds to sampling the time-scale plane.

In wavelet analysis the choice of the mother wavelet is arbitrary. The mother wavelet depends on the non-dimensional “time” parameter and must have a zero mean and squared norm equal to one. When choosing the wavelet function, there are several factors which should be considered. The one from most important is the shape of the function, which should reflect the type of features present in the analyzed signal. It should be very similar to the shape which will be searched in the analyzed signal. For a smoothly varying signal, one would choose a smooth function. Many types of wavelets are both defined in literature and implemented in computational software. But none of the accessible function shapes is similar enough to the ideal potentiometric titration curve. Therefore the basic aim of this work, was construction of the new mother wavelet which should be comparable to the sigmoid potentiometric signal. This wavelet function (Fig. 1) was constructed by the authors on the base of the ideal potentiometric titration curve, obtained from the Nernst equation. Calculations were performed using the Misiti et al. [51] algorithm which utilizes the least-squares method. The defined mother wavelet is an asymmetrical, equidistant function, which is 2000 points long. Outside the interval presented in Fig. 1 it reaches 0 value. The new wavelet dedicated for potentiometric titration is correctly defined—its square norm equals one and fulfils the condition of zero mean. In computations described in this work, this especially defined new potentiometric titration wavelet function is applied.

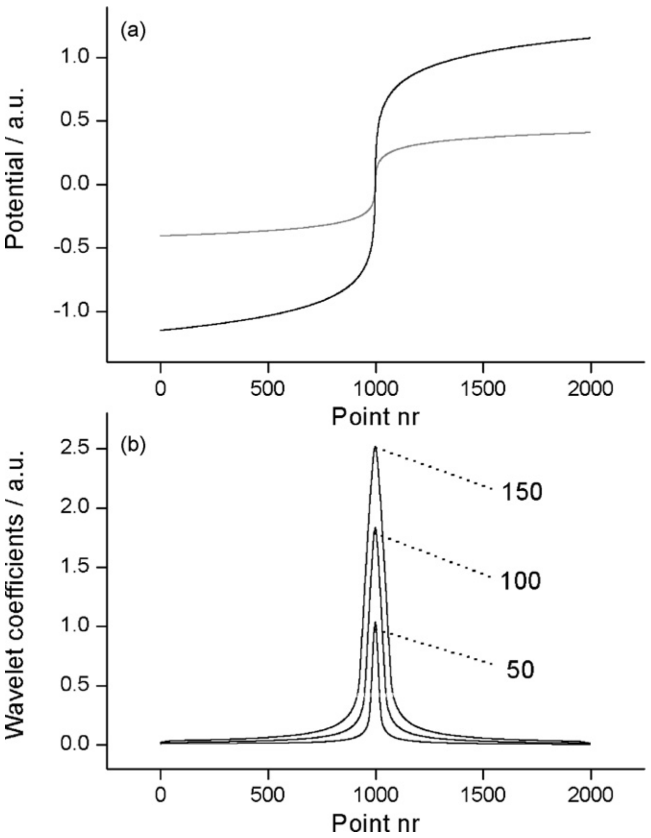

Fig. 1. (a) Simulated ideal sigmoid curve (gray) and the mother wavelet (black) defined on the base of it and (b) result of CWT transformation of ideal sigmoid curve, in the scales 50, 100 and 150.

In this paper, the choice of the wavelet function is not very critical. The mother wavelet may be also defined on the base of theoretic curve, simulated or of a very smooth experimental one. Little differences in the shape of the function, which is a typical titration sigmoid curve, have no influence for end-point detection and give very similar qualitative results. Only in the case of very complicated experimental curves a consideration of different shapes of the mother wavelet is important. Such a problem and its solution are presented later in this work.

The generation of the dedicated wavelet and the wavelet transform were performed using Matlab for MS Windows, version 7.3, with Wavelet Toolbox 3.1. For the remaining calculations, the OriginPro software (OriginLab Corporation, USA), version 7.5, was used.

3. Experimental

3.1. Instrumentation

All potentiometric measurements were performed using a homemade potentiometer. The input impedance was greater than $10^{13}\,\Omega$ and the input current was lower than 0.1 pA. The potentiometer was coupled to a personal computer equipped with data acquisition card PCI-DAS 1716 (Advantech) with A/D converter of the resolution of 16-bits. Since the titration process required a very small volume of the titrant to be added in steps, a microburette (2.5 ± 0.01 ml) was used for precise control and accuracy. The programs for data acquisition and system control were developed by authors in NI LabView 8.0. A combined glass electrode Ω Metrohm (6.0233.100 Metrohm AG) was used as the indicator electrode. All the experiments were performed at temperature 21 ± 2 °C.

3.2. Chemicals

All chemicals used were analytical grade and were obtained from POCh, Merck, or Fluka and used as received. Doubly distilled and deionized water (Millipore, France) was used. All the solutions with a concentration lower than 0.01 mol dm^{-3} were prepared immediately prior to use. The preparation of solutions used in aluminate determination was done as described in [52].

4. Results and discussion

4.1. Simulated curves

At the beginning, some ideal and specially distorted simulated titration curves were exploited for demonstration of the proposed algorithm behavior. The optimization of the wavelet transformation parameter, which is the scale, was demonstrated also for these artificial signals. The influence of two factors: noise level and titrant volume increment for the precision and accuracy were tested and their optimal limits were described. The calculated end-point position was compared with the true one and expressed as the percentage relative to error. Precision was expressed as a coefficient of variability (CV).

The simulated curves were obtained according to the Nernst equation and the antisymmetrical concatenation of the curve. The assumed titrant volume increments were 0.001 ml, 0.002 ml, 0.004 ml, 0.01 ml and 0.02 ml for one point. Because the volume which relates to the whole curve was equal to 2 ml, therefore the number of points in the simulated signal, which depends on the titrant volume increment, was 2000, 1000, 500, 200 and 100. Such prepared ideal curves were especially distorted by the random noise. The considered amplitude of the disturbances was 10%, 20%, 50%, and 100% in relation to the difference of maximum and minimum of the signal. It is very important to note that the shape of random noise in the region of inflection of the curve has a great influence on end-point detection. Therefore, in the case of noised curves, tests were repeated 10 times and, as the final estimation of accuracy, the maximal error is given.

All input curves were extended before transformation on both sides by duplication of the first and last point. The number of added points was equal to 100 at the beginning and 100 at the end. Therefore in this way border effects may be eliminated. For convenience, the CWT procedure was started from scale 10 and was continued for the increasing (by the step 10) values of scale, i.e., the analysis was started from high frequencies and proceeded towards low frequencies. This first value of scale corresponded to the most compressed wavelet. As the value of scale was increased, the wavelet dilated.

The major effect of operation of the proposed algorithm is the transformation of the sigmoid-shaped curves to the peak-shaped ones. In the ideal case, the position of the maximum is the same as the inflection point of the input curve. In the single step of calculation, denoising is done and improvement of the resolution of the very complicated experimental signals is realized. It means that when two inflection points are difficult to identify and lie near each other, they are transformed to two separated peaks. The advantage of the proposed procedure relies also upon the fact that it does not require the prior determination in which segment of experimental data lies the inflection point of the curve. For example, Gran's method involves performing a different transformation on the experimental data according to the segment prior to the equivalence point or after it.

Selection of the optimal scale for CWT plays an important role in getting maximum resolution, accuracy and precision. By the application of the optimal scale, the peaks should be narrow and smooth,

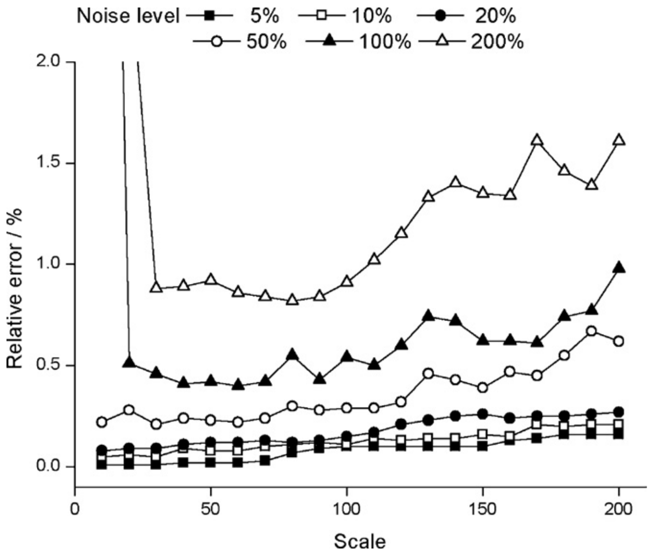

Fig. 2. Optimization of the CWT scale for different noise levels. Titrant volume increment 0.001 ml.

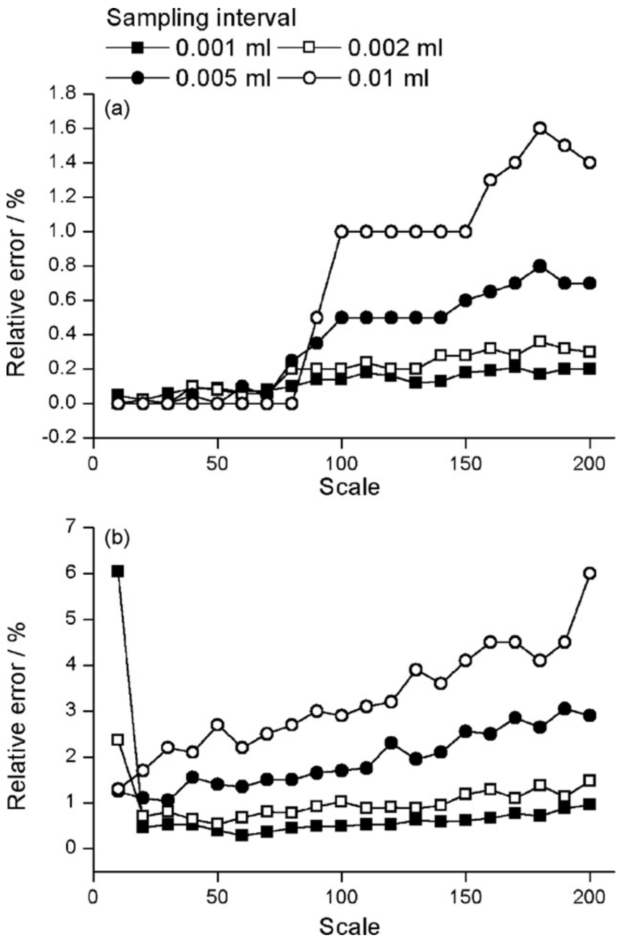

Fig. 3. Optimization of the CWT scale for different titrant volume increments and noise levels: (a) noise level 10% and (b) noise level 100%.

and the position of the maximum should be the same as the inflection point. The interval of optimal scales relies on the noise level. Therefore, different noise amplitudes in relation to useful components of the signal were tested. Fig. 2 presents the effects obtained for scales 10–200, changed by 10 in each step. Lower scales were omitted because they give information about random noise only, while those higher than 200 do not give better effects than these from intervals 10–200. It may be concluded that, generally, the interval of the optimal scales is relatively wide. For the typical potentiometric titration, by the low level of noise (e.g. not greater than 20%) in the whole tested range of scales, the relative error is lower than 0.2%. For the distinctly larger noise level, even up to 200%, in the optimal scales band (i.e., 30–90) the relative error is not greater than 1%. It is very important to notice that, by the high noise, the components of the signal obtained by the low scales are characterized by the great error, even to a few percent. These scales should not be selected in CWT.

Also, the titrant volume increment has an influence on the accuracy of the end-point detection. If this parameter increases then the number of points in the region of inflection is lower. In the effect, the error of end-point detection may be higher. However, by the low noise level and greater titrant volume increment, an appropriate scale may be selected, which gives an accepted error of end-point detection. The influence of the greater titrant volume increment may be eliminated. If noise was at the level of 10–20%, then the optimal scales band would be from 10 to 80 (Fig. 3a). At that time, the relative error of end-point detection is not higher than 0.2%. For higher noise level, the influence of the large titrant volume increment is substantial. In the case of titrations in steps equal, e.g. to 0.01 ml it is difficult to obtain an error lower than 2%. The optimal scales interval contains scales from 30 to 60 (Fig. 3b).

The performance of the new method was tested in comparison to the results which were obtained by application of the first derivative method preceded by Savitzky–Golay smoothing [53]. The parameters of the lately mentioned procedure were chosen after some steps of optimization. In the effect, polynomial of 2/3 degree in the 9–13 points frame was applied. Comparison was done for simulated curves distorted by random noise of the level from 1% to 20%. Also different titrant volume increments were used in simulation. Calculations were done by the CWT scale equal 50. The evaluation of the effects of the mentioned two algorithms relied on calculation of variability (after 100 repetitions in which noise was separately generated) and relative error of end-point detection. The new procedure, which utilizes CWT with a dedicated mother wavelet and the algorithm which applies Savitzky–Golay smoothing and differentiation gave the possibility of accurate end-point designation in all considered cases. Additionally, the values of the coefficient of the variability and relative error in the case of wavelets were always no higher than by application of the first derivative algorithm after filtration. In the proposed new approach the level of the variability and relative error is almost constant and only slightly increases while the noise level increase. Figs. 4 and 5 show the results of calculations for curves simulated with titrant volume increment equal 0.02 ml and 0.002 ml for point. Figs. 4c and 5c present the effect of the transformation of the noised sigmoid curve in comparison to the results which were obtained by application of the algorithm in which before differentiation Savitzky–Golay smoothing was applied. The noise level was 20%. In the case of titrant volume increment equal 0.02 ml two tested algorithms give the possibility of end-point detection but in the case of CWT the quality of determination is always better.

Proposed algorithm is also useful in separation of the overlapping curves. In Fig. 6 the simulated signals in the shape of overlapping curves are presented. The input one sigmoid curve used in generation of these data had 200 points. After numerical overlapping process, the distance between inflection points position was 20 and 8 points. These signals were translated into the wavelet coefficients space be means of dedicated wavelet. The optimal scale—different for each curve—was chosen. The obtained peak-shaped signals are presented in Fig. 6a and b in connection

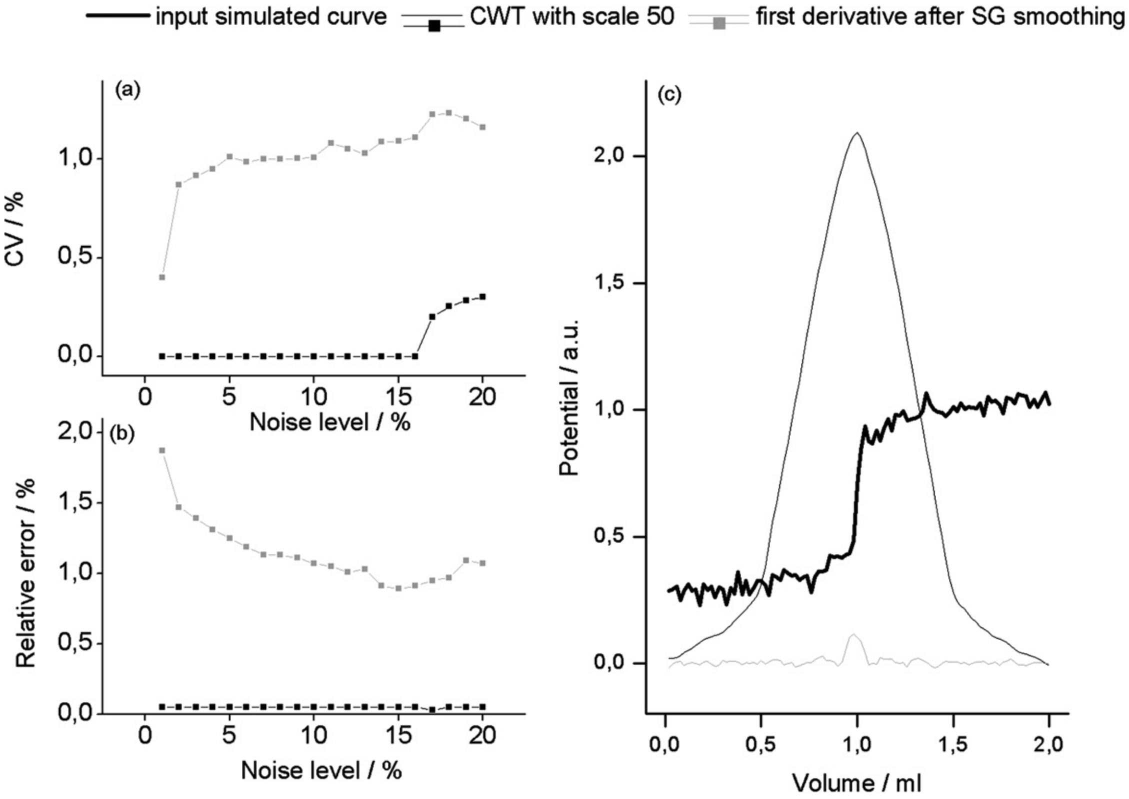

Fig. 4. Comparison of end-point detection algorithms—results for simulated curve with titrant volume increment 0.02 ml: (a and b) CV and relative error for different noise levels and (c) results for curve with 20% noise.

with input curves. The effect of separation of the overlapping signals was achieved—even when the distance between inflection points position was 8 points. Additionally the positions of inflection points on the sigmoid curve and the positions of the extreme points on the peak-shaped signal were identical.

4.2. Determination of hydrochloric acid

The proposed end-point detection algorithm was, at the beginning, tested in the typical for potentiometric titration experiment—determination of HCl by 0.1 M NaOH. The same stan-

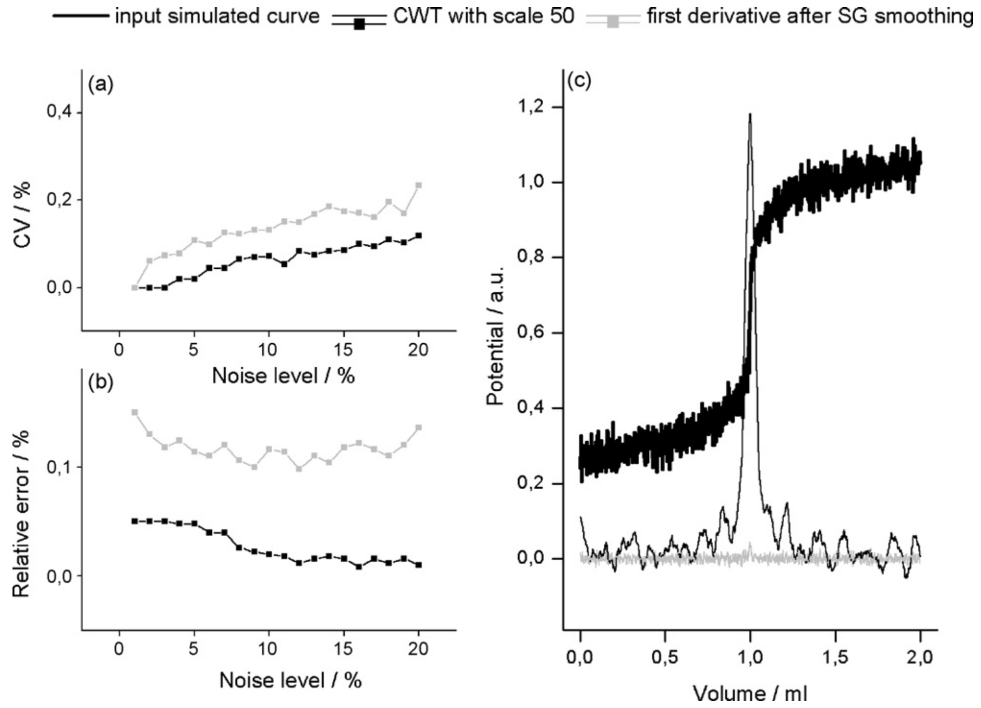

Fig. 5. Comparison of end-point detection algorithms—results for simulated curve with titrant volume increment 0.002 ml: (a and b) CV and relative error for different noise levels and (c) results for curve with 20% noise.

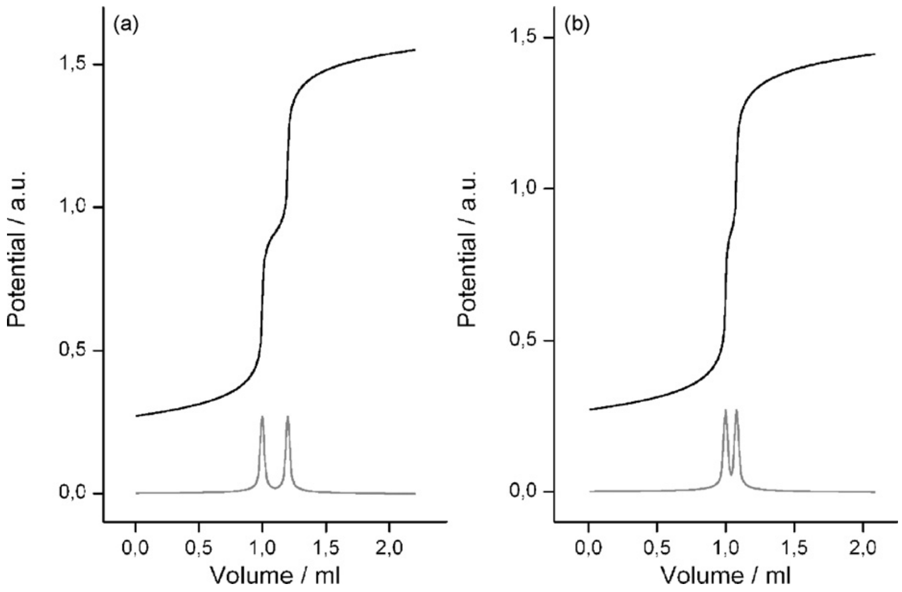

Fig. 6. Separation of overlapping signals, titrant volume increment 0.01 ml: (a) distance between inflection points positions—20 points, CWT scale 10, (b) distance between inflection points positions—8 points, CWT scale 5.

dard solution, i.e., 12.5 ml of 0.01 M HCl was analyzed in each experiment in the series.

Before further computations the noise characteristics was considered. It was concluded that in all conducted experiments the noise component had random character—normal distribution and zero mean. Accuracy and precision of the determination method were controlled for different outflow speed (from ca. 5–40 μl/s) and sampling interval (from 125 to 8000 ms). These evaluation parameters were compared with results obtained by application of the first derivative method of end-point detection preceded by Savitzky–Golay smoothing (polynomial of 2/3 degree in the 9–13 points frame). Algorithm which computes first derivative might be applied because of the typical sigmoid shape of the curves and very low noise level (below 2%). The coefficients of variability (CV) obtained for three repetitions by application of CWT (scale 20) are from 0.08% to 1.78% while by calculation of first derivative with filtration are from 0.19% to 1.90%. They agree with what one would expect from this analytical technique and/or type of analyte to be titrated. The accuracy expressed by the relative error was in the case of wavelets between −0.63% and 0.88% and between 0.50% and 2.59% in case of application of the first derivative preceded by smoothing (Table 1).

It was also observed that the more slowly the titrant is delivered, the better is the precision and accuracy. The sampling frequency also has a typical influence on precision and accuracy. Longer sampling intervals give less satisfactory results. After a comparison of two mentioned end-point detection procedures, it may be concluded that the results do not differ so much. Only in the case of a lower sampling frequency, the algorithm based on CWT and specially defined mother wavelet allows one to obtain better accuracy and precision of analyte determination.

4.3. Determination of phenol

Phenol is the most detrimental pollutant of the environment. It enters the soil and water through different pathways such as cooking, plastic manufacturing, oil purification, timber and pharmaceutical products. Natural sources of phenol include the degradation of natural plant products such as the carbonization of coal, carvacrol, thymol and vanillin. Biologically important compounds such as amino acids (tyrosine and estrone) also contain phenol rings [54].

The potentiometric titration method for the estimation of phenol in aqueous solutions is a sensitive and accurate method, if phenol concentrations are high, on the order of few g L^{-1}. However, in cases where the phenol is present at milligram levels, the method fails miserably, since both identification of the equivalence point of the titration and the subsequent quantification are adversely affected by the dilution effect. In addition, there is no warranty of sharp inflection points on the titration curve. An attempt was made during the present study to improve the procedure of numerical detection of the end-point of titration.

The problem was resolved in a more advanced way than in other considered titrations. The CWT was applied two times. In the first step the sigmoid mother wavelet was used (as in Fig. 1) and scale 150. Unfortunately no explicit peak-shaped curve was obtained. In

Table 1
Accuracy and precision of determination of HCl (by 0.1 M NaOH). First derivative computation preceded by Savitzky–Golay smoothing.

Outflow speed (μl/s)	Sampling interval (ms)	Wavelets		First derivative	
		Relative error (%)	CV (%)	Relative error (%)	CV (%)
38.075	125	0.88	0.44	1.02	0.77
19.292	250	−0.63	0.54	0.37	0.79
9.731	500	0.37	0.22	0.76	0.22
4.759	1000	0.37	0.24	0.63	0.38
4.759	2000	0.51	1.58	0.77	1.17
4.759	4000	1.03	1.54	1.56	1.77
4.759	8000	0.52	1.78	2.59	1.90
4.759	200	0.17	0.08	0.50	0.19

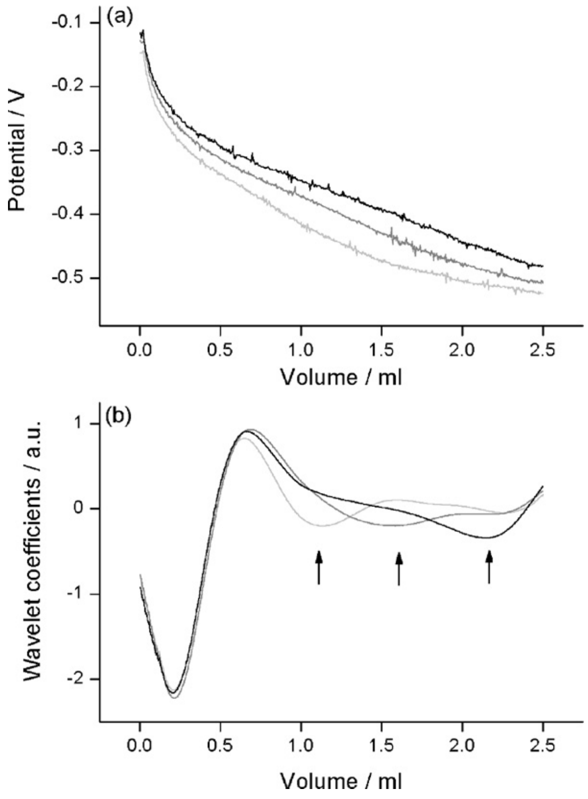

Fig. 7. Determination of phenol in standard samples: (a) experimental curves in the case of 10 ml (light gray), 15 ml (gray) and 20 ml (black) of 0.01 M solution and (b) the same curves after double CWT transformation, arrows indicate the end-points of titration. The titrant was 0.1 M NaOH.

Table 2
Accuracy and precision of phenol determination (by 0.1 M NaOH).

Volume of 0.01 M phenol (ml)	Relative error (%)	CV (%)
10	7.8	4.1
20	1.2	4.2
30	1.7	0.4

the aim to intensify the effect, in the second step of calculations, the CWT was once more applied with a peak-shaped mother wavelet by the scale 250. This mother wavelet was defined on the basis of the function which was obtained as the result of a continuous wavelet transform of the sigmoid mother wavelet.

The results obtained for three different amounts of phenol (10 ml, 15 ml and 20 ml of 0.01 M solution) are presented in Fig. 7. The titrant was 0.1 M NaOH solution. The sampling interval was 500 ms. The evaluation of the proposed signal-processing method was done by estimation of accuracy and precision (Table 2). The accuracy was expressed as a relative error of determination of phenol concentration, while precision as a coefficient of variability (CV), was calculated for 3 repetitions. Satisfactory results which fulfill validation criteria were obtained.

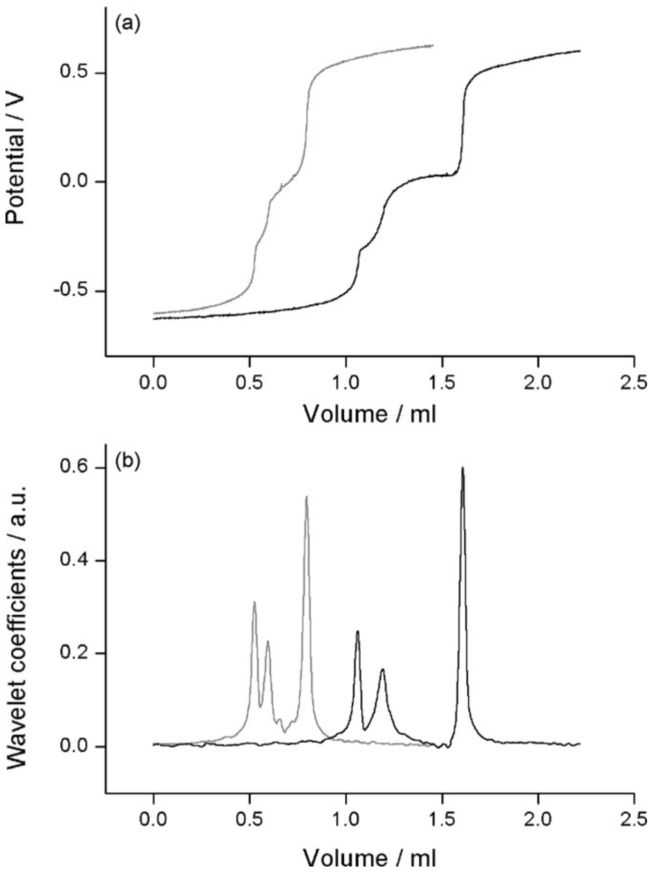

Fig. 8. Determination of hydroxide, aluminate and carbonate in sodium aluminate solutions: (a) experimental curves 12 ml of 3.5 g L^{-1} NaOH, 5 g L^{-1} Al_2O_3 and 7 g L^{-1} Na_2CO_3 (gray), 12 ml of 7 g L^{-1} NaOH, 10 g L^{-1} Al_2O_3 and 14 g L^{-1} Na_2CO_3 (black) and (b) the same curves after double CWT transformation by the scale 20. The titrant was 2 M HCl.

4.4. Determination of hydroxide, aluminate and carbonate in sodium aluminate solutions

The determination of hydroxide, aluminate and carbonate in sodium aluminate solutions is important for the industrial production of aluminium oxide. But there is a complicated equilibrium between these three species in alkali aluminate solution. Direct titration of an alkali aluminate solution with hydrochloric acid is impossible because carbonate and aluminate reacts with acid in the same pH range. In the work [29] a potentiometric titration method was proposed in which the addition of barium chloride before titration with hydrochloric acid enables the three components determination in one run. Barium carbonate precipitated under suitable conditions dissolves quickly on titration with hydrochloric acid, giving well-shaped one-step potentiometric curve. Finally, the result titration curve has three steps: neutralization of hydroxide, protonation of aluminate and dissolution of barium carbonate. Unfortunately there are problems

Table 3
Accuracy and precision of aluminate solution analysis (by 2 M HCl).

Volume of $BaCl_2$ (ml)	Concentration (g L^{-1}), volume 12 ml		Relative error (%)	CV (%)
0.5	NaOH	3.5	0.6	5.3
	Al_2O_3	5	0.8	3.3
	Na_2CO_3	7	0.7	2.9
1.0	NaOH	7	1.3	4.9
	Al_2O_3	10	0.8	2.8
	Na_2CO_3	14	1.5	2.3

of the accurate end-point detection, mainly in the case of some noise.

The accuracy and precision of the analytical method with end-point detection described in this work were done for two standard solutions of aluminate obtained by mixing three components—sodium aluminate, carbonate-free sodium hydroxide and sodium carbonate solutions. In the second solution, the concentration was two times greater than in the first. The titration was done by 2 M HCl after addition of required quantity of barium chloride. The sampling interval was 500 ms. The recorded curve has a shape of three waves (Fig. 8a) and was transformed to the shape of three peaks by CWT with dedicated mother wavelet. The peaks are separated and have well defined maxima which are interpreted as end-points of titration (Fig. 8b). Precision and accuracy were tested and expressed as earlier (CV and relative error, respectively). Results are presented in Table 3.

5. Conclusions

The algorithm which utilizes continuous wavelet transform and dedicated wavelet function provides an objective criterion for the determination of the end-point in potentiometric titration. The proposed procedure allows end-point determination and can be used both in the titration of pure substances as well as in that of mixtures. In the single step of calculations, denoising and improvement of the resolution of the very complicated experimental signals is realized.

The only decision that needs to be made, is the selection of the optimal scale. Although the optimization of this parameter should be done, it may be chosen from a wide interval. The effect of operation of the proposed algorithm is the transformation of the sigmoid-shaped curves to the peak-shaped ones. It gives the possibility of non-complicated end-point detection because the inflection point is transformed to the extreme of the curve (one or more explicit extremes, each connected with one determined substance). There are many algorithms for automated detection of the maximum or minimum of the signal. What is more, wavelet transformation limits the influence of random noise and outliers, produced by experimental errors or in the acquisition of data, for the final result of the titration.

The described method has been tested on various simulated and titration signals. Even for the complicated experimental data recorded during the determination of phenol, accurate and precise results were obtained. Generally, the success of the end-point calculation depends heavily on the selection of the proper scale of CWT.

The proposed algorithm which applies CWT with a specially defined new wavelet function may be useful in interpretation of the experimental data and also in automation of the typical titration analysis, specially in the case when random noise interfere with analytical signal.

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