



Hybrid signal processing in voltammetric determination of chromium(VI)

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ABSTRACT

This study presents different hybrid signal processing algorithms which are useful in the interpretation of voltammetric signals recorded on mercury film electrodes for the determination of Cr(VI). Because of the complex character of the distortions (random, fast increasing, nonlinear, background noise and other perturbations) the application of a complex numerical procedure is necessary. In this work different variants of hybrid algorithms are utilized: adaptive degree polynomial filter, baseline generation and subtraction, signals ratio method, orthogonal signal correction and continuous wavelet transformation with dedicated mother wavelet. The operation and effectiveness of proposed procedures were tested by the determination of very low concentrations of Cr(VI) in synthetic and river water samples.

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1. Introduction

The interest in the determination of chromium (Cr) speciation originates from the fact that the two common oxidation states of Cr present in the environment, i.e. Cr(III) and Cr(VI), are discernibly different in their physicochemical properties as well as chemical and biochemical reactivity and their role in the human body. Chromium(III) is an essential trace element for the proper functioning of living organisms that improves the efficiency of insulin in individuals with impaired glucose tolerance. Chromium(VI), however, exerts a toxic, and/or carcinogenic influence on biological systems. The toxicity, as well as the mobility and bioavailability of Cr depend fundamentally on its chemical form. Cr(VI) compounds are usually highly soluble, mobile and bioavailable compared to less soluble trivalent Cr species [1].

Chromium can be found in air, soil, and water after release from the manufacture, use, and disposal of chromium-based products, as well as during the manufacturing process. Its use in iron, non-ferrous alloys, and steel is for the purpose of enhancing hardening ability or resistance to corrosion and oxidation. The production of stainless steel and nonferrous alloys are two of its more important applications. Other applications are in alloy steel, catalysts, leather processing, pigments, wood preserving, metal plating, refractories, and surface treatments.

Chromium chemical speciation is an important factor in chromium toxicity. Many different analytical techniques have been set up in an effort to quantify the various Cr forms present in

the natural environment and in industrial samples [2–18]. The instrumental techniques for the Cr(VI) trace determination may be divided into two main kinds [19].

- (1) Speciation techniques, which enable the direct measurement of Cr(VI) in the presence of Cr(III), such as molecular absorption spectrophotometry or voltammetry [20,21]. These methods are based on a different ability of Cr(III) and Cr(VI) to form complexes.
- (2) Non-speciation methods, based on the preliminary separation of both chromium forms or on selective removing of one chromium species from the sample and subsequent, non-specific measurement of the separated form by means of AAS, ICP-AES or ICP-MS. They enable only the determination of total chromium [2].

Voltammetric methods, including adsorptive and catalytic adsorptive stripping voltammetry at liquid mercury, metallic films, and modified carbon paste electrodes are applied in chromium determination. A review of such methods is presented in Ref. [19] while the most recent investigations are described in Refs. [22–44]. In many works, the HMDE was used as a voltammetric sensor but also some mercury-free solid electrodes, such as bismuth film electrodes [24,27,29], stannum film electrode [36], the disposable screen-printed electrodes modified with poly-L-histidine film [37], gold and silver nanoparticles [38,42], nano-sized gold particles deposited on glassy carbon [43] or on the conductive substrate modified with sol-gel derived thiol [44] have been applied. Also modern designs, such as the silver–amalgam electrode with a refreshable surface [28] have been used. The important prob-

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lem of elimination of the influence of the surface-active substances and organic matter which substantially reduce or completely suppress the signal by the blockage of the electrode surface was also recently investigated [34,36,40]. The voltammetric method coupling adsorptive accumulation and the catalytic reaction, called the catalytic adsorptive stripping voltammetry (CAAdSV) method of chromium(VI) determination in the presence of the various complexing and oxidizing or catalytic agents, belongs to the most sensitive analytical methods and has been widely applied in trace analysis. The last progresses in catalytic systems of chromium applied in adsorptive stripping voltammetry were presented in Refs. [22,25,26,28,30–35,39–41]. In this work determination of Cr(VI) will be done in the presence of DTPA and nitrate on the silver–amalgam electrode with a refreshable surface [28].

An observation of scans obtained in Cr(VI) determination suggests that the high quality of calibration model parameters and the results of the concentrations of chromium are closely connected to effective and correct numerical algorithm realizing baseline correction. Therefore the goal of the work is the proposition of the strategy of background removal which may be used in voltammetric determination of Cr(VI). Two cases will be considered separately—baseline correction done for synthetic samples where determination is done using standards (interpolative calibration) method and for real samples when calibration is realized by standards addition (extrapolative calibration) method. In the first case an experimental curve recorded for supporting electrolyte may be used in calculations. In the second case a more advanced strategy should be considered because it is impossible or very difficult to determine baseline in an arbitrary experiment which is lead by extrapolative methodology. It is very difficult to obtain background for the sample with a complex matrix but which does not contain analyte. Such an experimental baseline keeps all the above unknown. In the case of the Cr(VI) investigation of baseline correction for real samples, it will be preceded by some optimization tests for simulated curves. Some numerical formalisms, such as baseline approximation by functions of different shapes, signals ratio method, continuous wavelet transform with dedicated mother wavelet and orthogonal signal correction are applied in calculations.

2. Theory

Obtaining high quality results by catalytic adsorptive stripping voltammetry (CAAdSV) determination of chromium(VI) requires the application of an advanced signal processing algorithm. In this work a hybrid procedure is proposed which consists of three main steps: smoothing by adaptive degree polynomial filter (ADPF), baseline correction realized by signals ratio method (SRM) or baseline subtraction method (BSM) and orthogonal signal correction (OSC). Additionally, another procedure is considered which utilizes continuous wavelet transform and dedicated mother wavelet.

2.1. Signals ratio method

The algorithm belongs to the group of method based on signal division. The mathematical principles of this algorithm and its application for quantification of individual analytes from their global signals obtained from binary, ternary and higher multianalyte mixture are in details presented in Refs. [45–48]. The basic idea of SRM, in the version applied in this work, is the point by point division of the signal recorded for the successive concentration of analyte by the baseline signal obtained for a supporting electrolyte. The operation of the algorithm is expressed by the formula:

$$I_{ps} = \frac{I_{anal} + c}{I_{bkg} + c} - 1 \quad (1)$$

where I_{ps} is called pseudo-current because it has no unit value but expressed as the experimental current in relation to the baseline; I_{anal} and I_{bkg} mean the current signal of analyte and baseline, respectively. The constant c was introduced in order to avoid division by zero or very small numbers which may result in very high values of the pseudo-signal. Subtracting 1 gives signals with a zero baseline because in parts with no analyte influence I_{anal} is similar to I_{bkg} and therefore the fraction in the formula (1) is near one.

2.2. Orthogonal signal correction

A novel filtering technique called orthogonal signal correction (OSC) was developed in 1998 by Wold et al. [49]. Operation of this algorithm relies on the removal of systematic variations in the signal matrix X that are orthogonal to the vector or matrix Y which contains values of modeled property or properties of the samples of interest prior to calibration. Namely, that which is removed from X should be mathematically independent of Y . The example of properties given in matrix Y in voltammetry is, in almost all cases, concentrations of ions. By filtering orthogonal variance the intent is that most of the variation in experimental data attributed to various undesirable extraneous effects is removed, while variance attributed to the target analyte is retained. Filtered data are obtained after iterative removal of the first (usually) 2–3 orthogonal components. In most cases, filtering with the OSC reduces the complexity of the model by the number of OSC components removed without noticeable enhancement in prediction performance [50,51].

There are several algorithmic approaches to the OSC concept [52–59], a well documented comparison is presented in Refs. [51,58]. The version applied in this study is based on the algorithm described in Refs. [52,60]. The signal matrix X should usually be centered by subtracting the mean signal from all curves. It may also be scaled [54].

In the application of OSC in connection with extrapolative calibration, additional aspects should be considered. Removal of orthogonal components is possible when the values of the determining attribute for each signal in the processed set are known. In standard addition method only increments of concentration are given. The effect of using, in OSC, the values of concentration from zero, etc. is a decrease of the signal for the sample also to zero and in consequence an obtained set of curves is useless for calibration by standard addition method. Therefore in this work a more useful strategy is proposed. Firstly background correction should be done. Calculated preliminary values of the concentration of analyte and in solution after standard additions may be used as an input to OSC procedure. In such a case the orthogonal signal correction algorithm will not have an influence on the accuracy of determination (the known imperfection of this procedure) but other parameters of the calibration model will be improved. The system of considered curves will be arranged and also undesired additive and multiplicative distortions of the signals will be removed. The number of removed OSC components should be matched in connection with the considered problem—in principle the removal of 2–3 components should be tested.

2.3. Adaptive degree polynomial filter

The adaptive degree polynomial filter (ADPF) for data smoothing is further improvement of the least-squares regression formalism introduced to the experimental data processing by Savitzky and Golay. The adaptive approach is based on the statistical testing of the fitting quality of polynomial function to the experimental data in the smoothing window sliding along the curve. It allows the automatic choice of the proper degree of polynomial function in the various parts of the experimental curve [61].

2.4. Continuous wavelet transform with dedicated mother wavelet

The operation of continuous wavelet transform with dedicated mother wavelet and the methodology of the definition of the mother wavelet for the considered problem was described in previous works [62,63]. Here this algorithm will be applied for baseline correction in the case of the voltammetric determination of Cr(VI). As a mother wavelet, a function will be used which was defined on the basis of an ideal simulated voltammetric peak. The operation of CWT bases on the assumption that baseline is an undesired component of the signal of low frequency. Therefore an optimal frequency component (connected with appropriate scale) of the signal should be chosen, which allows the possibility to observe only useful components. By the application of CWT, smoothing is not necessary—usage of proper scale, which is an important parameter of transformation, guarantees the removal of high frequency components. Because it is a linear transformation, further calculation (i.e. construction of the calibration model) may be realized in the space of wavelet coefficients.

2.5. Methodology of calculations and evaluation of results

The investigation of baseline correction strategy in the voltammetric determination of Cr(VI) and its optimization requires the application of coefficients to correct the evaluation of the effects. In this work a typical approach was applied—the influence of different numerical procedures for accuracy (expressed by recovery), precision (expressed by coefficient of variability, CV), linearity (expressed by correlation coefficient, r) and the possibility of achieving the determination in restricted conditions (expressed by the detection limit, DL) was tested. The sensitivity ($a \pm sa$) and intercept ($b \pm sb$) of the calibration line were also controlled. The prediction ability in the calibration model constructed for synthetic samples was determined by computing the prediction error sum of squares (PRESS (2)) [64] for cross-validated models, which is defined as follows:

$$PRESS = \sum_{i=1}^n (y_i - \hat{y}_i)^2 \quad (2)$$

where y_i is the reference concentration for the i th sample and \hat{y}_i represents the estimated concentration. A cross-validation method was employed to eliminate only one sample at a time and then algorithm models for the remaining Y matrix and corresponding X matrix. By using the established calibration model the concentration of the sample left out was predicted. This process was repeated until each standard had been out once.

During the calculations for simulated data that was deliberately randomly corrupted (noise, additive and multiplicative distortions), the evaluations were done after 30 separate repetitions. The minimal and maximal value of recovery was given. Such an approach allows for the possibility of formulating more general and adequate conclusions.

3. Experimental

3.1. Catalytic adsorptive stripping voltammetric determination of Cr(VI)

The voltammetric method coupling adsorptive accumulation and the catalytic reaction, called catalytic adsorptive stripping voltammetry (CAAdSV) belongs to the most sensitive analytical methods. It has been widely applied in trace analysis [19] and the catalytic system Cr(III)-DTPA + NO₃⁻ ions has been the most popular one in CAAdSV analysis. The speciation of Cr(III) and Cr(VI) by

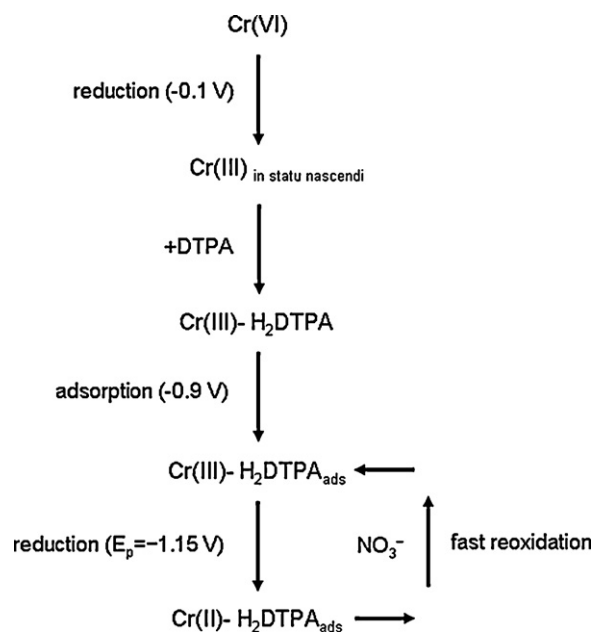


Fig. 1. General scheme of the quantitative determination of Cr(VI) by means of CAAdSV in the presence of DTPA and nitrate ions.

means of the CAAdSV is based on the difference in the voltammetric response in the solutions containing DTPA and NO₃⁻ ions [22]. The suggested mechanism of the reactions in determination of Cr(VI), taking place on the electrode surface is presented in Fig. 1. It was reported that 20–40 min after addition of DTPA to the sample in which Cr(III) and Cr(VI) are present, inactive complex Cr(III)-DTPA is created while Cr(VI) remains in the solution. In determination of Cr(VI) the Cr(III)_{in statu nascendi} is formed as a product of electrochemical reduction of Cr(VI). This Cr(III) creates an active complex Cr(III)-H₂DTPA which by the potential -0.9 V is adsorbed on the electrode surface. During the electrode polarization in more negative potential Cr(III)-H₂DTPA_{ads} is reduced to Cr(II)-H₂DTPA_{ads}. This reaction is the source of the recorded analytical signal. In the presence of nitrate ions the reoxidation process occurs and the Cr(III)-H₂DTPA_{ads} complex is regenerated.

3.2. Instruments

An M161 Electrochemical Analyzer (MTM-ANKO, Poland) was used in this study. All experiments were performed employing a classical three-electrode quartz voltammetric cell of volume 5 mL consisting of a homemade refreshable mercury film silver based electrode (Hg(Ag)FE) as a working electrode, a Pt as an auxiliary electrode, and an Ag/AgCl/3 M KCl as a reference electrode. The mercury film area was 7 mm². All experiments were performed at room temperature.

3.3. Reagents

All solutions and sample preparations were made using quadruple distilled water. Chromium(VI) standard stock solutions (1000 mg L⁻¹) were obtained from Merck and diluted as required. Diethylenetriaminepentaacetic acid (DTPA) solution (0.2 M) was prepared by dissolving an appropriate amount of the reagent (Merck) and pH adjusted to 6.2 by the addition of 25% ammonia (Suprapur[®], Merck). Acetic buffer (2 M, pH 6.2) was prepared by mixing the corresponding amounts of 96% acetic acid and 25% ammonia solution (Merck). 2.5 M KNO₃ was prepared by dissolving a corresponding amount of salt (Suprapur[®], Merck) in distilled water.

3.4. Recommended measuring procedures

The preparation and construction of the refreshable Hg(Ag)FE were precisely described in detail in Ref. [28]. The procedure of refreshing the mercury film is based on pulling up the silver wire electrode base into the mercury chamber placed in an electrode corpus (during this time, the silver wire base is covered with the new mercury film) and then pushing it back outside the electrode corpus to an analyzed solution just before voltammetric measurement. Quantitative measurements were performed using differential pulse catalytic adsorptive stripping voltammetry (DP CAdSV). The water sample was transferred to a supporting electrolyte (0.25 M KNO₃, 0.1 M acetic buffer and 0.01 M DTPA) in the electrochemical cell and then the solution was purged with pure argon for 5 min. Next, the silver wire covered with mercury film was pushed outside the working electrode corpus and the preconcentration was carried out at -0.95 V for 20 s. After 5 s equilibration time the negative going potential scan was initiated to -1.35 V and the response was recorded. A scan rate of 25 mV s⁻¹ and the amplitude 40 mV were used. After recording the signal, the silver wire with mercury film was pushed back inside the electrode corpus to the mercury chamber.

3.5. Simulation

The generation of curves was performed by digital simulation based on the Feldberg model [65,66]. A simple electron transfer reaction at a stationary planar electrode was simulated. Curves of 200 points in the potential range -300 to $+100$ mV were generated assuming reversible process. To obtain a set of curves for calibration, the concentration parameter was increased by a constant value. Data for standard addition calibration was generated by the assumption that the concentration of analyte in the sample amounts 0.2, 0.4, 0.6, ... or 2.0 a.u., but as an addition 1 a.u. was presumed. As a result of the simulation, a set consisting of a signal representing the sample and 4 curves, after standard additions, were obtained. For each concentration 4 repetitions were considered. Signals were specially distorted by a random noise and additional additive and multiplicative distortions were included, which pretended to imitate the situation and distortions that would be found in a real system during the determination of Cr(VI).

3.6. Software

Calculations were performed using Matlab for MS Windows, version 7.3 and the OriginPro software (OriginLab Corporation, USA), version 7.5. The computation was supported by homemade programs which were used for sets of simulated or experimental curves for calibration.

4. Results and discussion

The operation, final results and the evaluation of some signal processing algorithms useful in the voltammetric determination of Cr(VI) are presented separately for synthetic samples and real samples. In the case of the latter, presentation of the procedure for experimental data is preceded by optimization, done for simulated curves, because in this case some additional numerical problems occur.

Before the presentation of numerical algorithms and their results it should be underlined what characterizes the experimental curves recorded in the determination of Cr(VI) and why they required the application of signal processing procedures. The large baseline is present in all recorded curves. The background is constant from the start of the registration interval, i.e. circa -900 mV to -1150 mV and then visibly increases. That increase may be even greater than the increase of the useful component of the signal. In principle it contradicts the popular understanding of the baseline as a slowly changing component, i.e. changing slower than signal. The next component of the recorded signal is a random noise. In considered experimental data its amplitude is not greater than 5% of the peak height. Further, the problem of a lack of repeatability of the signal is present. This distortion has additive or multiplicative character. All afore mentioned distorting components have influence for the result of determination—therefore they should be removed before its calculation. The main problem is with baseline correction because without its removal the calculation of the real peak height is impossible.

4.1. Synthetic samples

The calibration set of curves obtained for concentrations 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, and

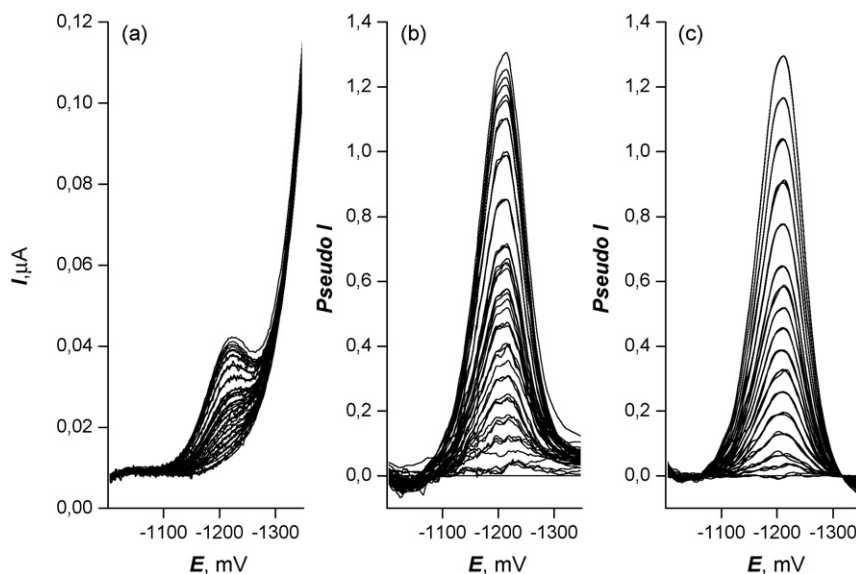


Fig. 2. Voltammograms of 0, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 nM of Cr(VI) (4 repetitions): (a) experimental data, (b) the same data after application of signal ratio method and (c) curves after removal of 3 OSC components.

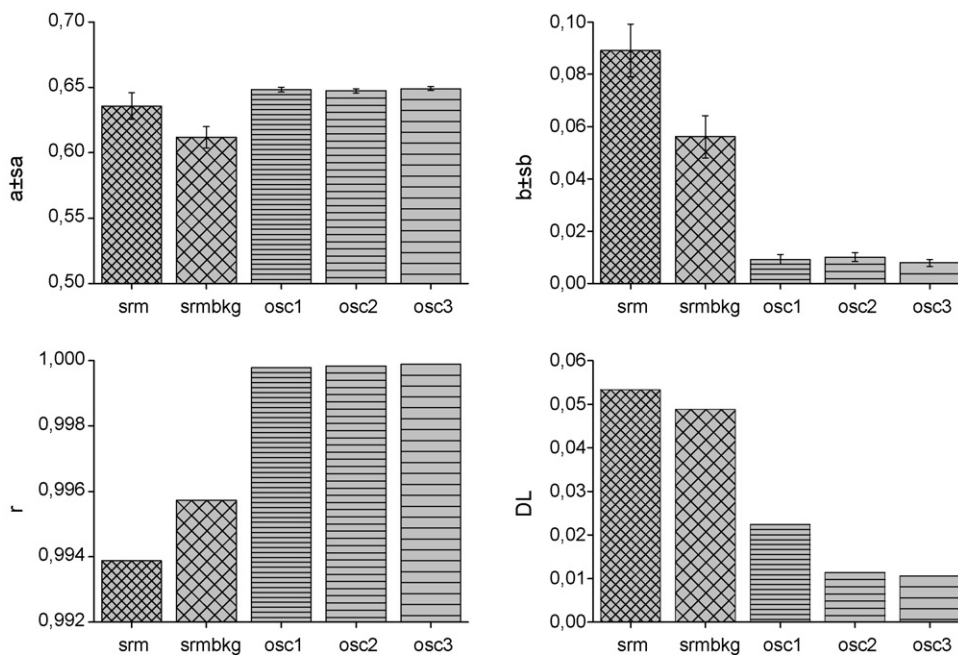


Fig. 3. Evaluation of processing of signals presented in Fig. 2a: srm—after processing by means of signals ratio method, srmbkg—after processing by means of signals ratio method and baseline correction, OSC_{*i*}—after removal *i* OSC components preceded by signals ratio method and baseline correction.

2.0 nM of Cr(VI) which includes 4 repetitions for each concentration, is presented in Fig. 2a. These curves were transformed using the following algorithm which includes some steps connected with removal of various distorting components.

Algorithm 1

1. Smoothing done by application of ADPF.
2. Baseline correction by application of signals ratio method, as a real baseline a signal for supporting electrolyte was chosen (mean of 4 recordings).
3. Because of the great deviation of curves—correction by approximation using linear function which was fitted separately to each experimental curve, the same approximation interval was used for each curve in the set for calibration.
4. Orthogonal signal correction—removal of 1, 2 or 3 OSC components.

Further calibration using a series of standards method was performed. Curves obtained after the calculation of signals ratio method are presented in Fig. 2b. Fig. 2c illustrates data after linear correction of the baseline and orthogonal signal correction—removal of 3 OSC components. In the last step some additive and multiplicative components were removed, with the effect of ordering the set of curves. The improvement of analytical parameters confirms that signal processing applied in this case gives the effect expected by the experimenter. The values of $a \pm s_a$, $b \pm s_b$, r and DL obtained after each step of signals transformation are presented in diagrams in Fig. 3. It is important that immediately after the calculation of signals ratio these analytical parameters have acceptable values. By the application of OSC and the removal of the first OSC component they fulfill validation criteria. In a considered case, in the last step of calculations, the following values were obtained: sensitivity $0.6491 \pm 0.0012 \mu\text{A/nM}$, intercept $0.0071 \pm 0.0012 \mu\text{A}$, $r > 0.9999$, $DL = 0.01 \text{ nM}$. The ability of the system to give accurate determination results describes parameter $PRESS$, presented in Fig. 4. The visible, satisfactory influence of the applied signal processing procedure is observed. It should be underlined that the proposed algorithm which consists of some separated numerical steps, gives demanded effects and is useful in

the voltammetric determination of Cr(VI) by a series of standards calibration method. This last remark is very important because typically OSC may be applied to the set of curves for calibration, when the concentrations of each sample are known.

4.2. Real samples

The operation of the signal processing algorithm in the case of the determination of Cr(VI) in real samples was tested on the basis of determinations done in the water from the Bialka river. It is characterized by great cleanness, only sometimes polluted by wastes from tanneries. Here, application of the numerical algorithm prepared for synthetic samples is impossible. The first reason is a lack of knowledge of the real baseline, the second is a lack of knowledge of the concentration of Cr(VI) in the successive steps of calibration by standard addition method—only concentrations of standard additions are known. Because in this case the signal processing is much more complicated, some calculations were done for simulated data. A prepared set of curves, described in Section 3.5, ideally imitates

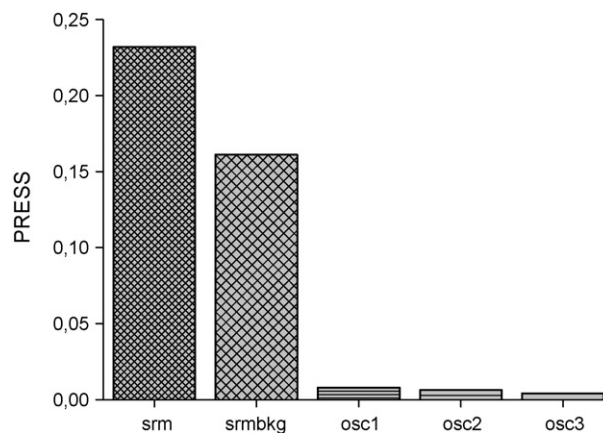


Fig. 4. Evaluation of the processing of signals presented in Fig. 2a—ability to accurate determination expressed by $PRESS$. Identification as in Fig. 3.

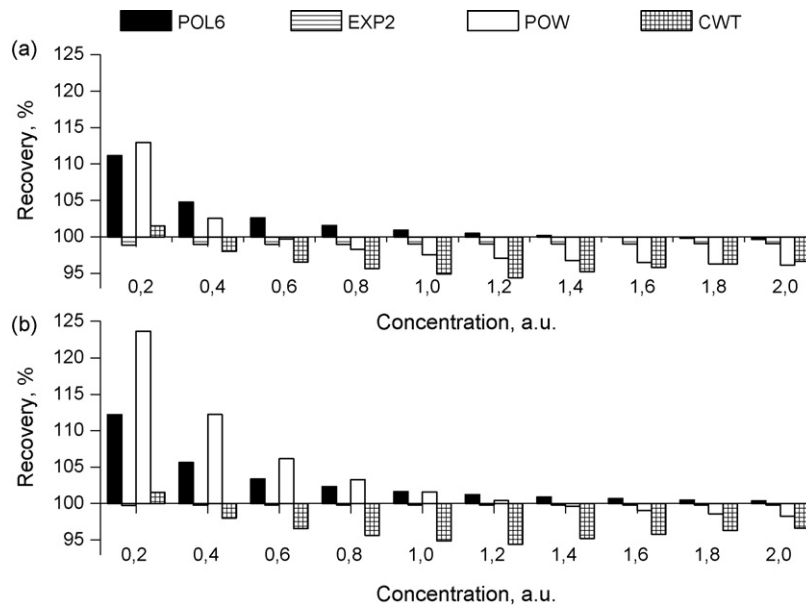


Fig. 5. Recovery for ideal simulated voltammograms in the case of standard addition calibration (4 additions by 1 a.u.), on x-axis—concentration of the sample: (a) baseline subtraction; (b) signals ratio method (CWT—the same values as in (a)).

the shape, noise level and character of other distortions of recordings done for samples from the Bialka river. Signal processing was done using two strategies.

Algorithm II

1. Application of the continuous wavelet transform (CWT) with dedicated mother wavelet with the same scale for all curves. Earlier smoothing is not necessary because it is realized by CWT, only the proper scale should be chosen.

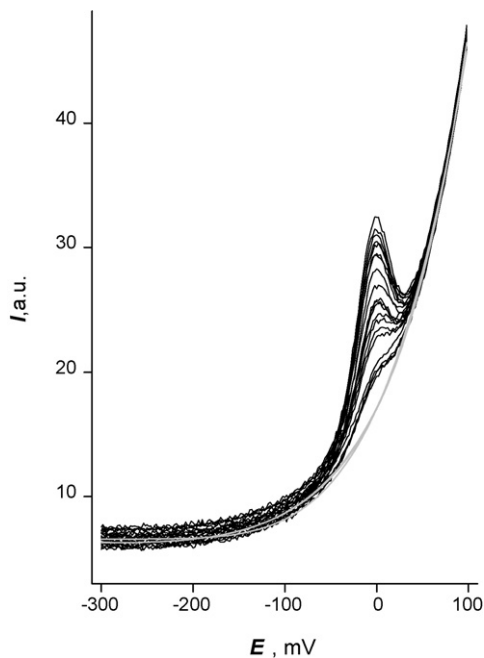


Fig. 6. Simulated voltammograms (black) in the case of standard addition calibration: potential step -0.2 mV, experimental baseline recorded in Cr(VI) determination, experimental baseline, random noise: 5% of the mean peak height, random additive and multiplicative distortions: 10% of the mean peak height, concentration of the sample 1 a.u., 4 additions by 1 a.u., 4 repetitions for each concentration. Additionally 3 different lines of approximated background (grey).

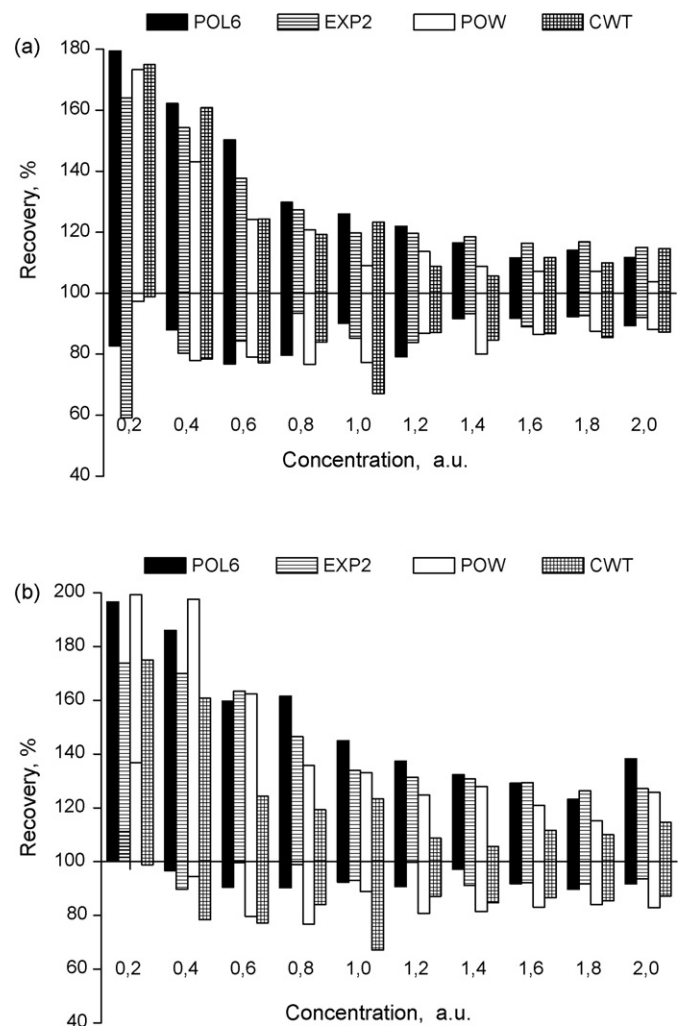


Fig. 7. Recovery for noised simulated voltammograms (random noise, additive and multiplicative distortions) in the case of standard addition calibration (4 additions by 1 a.u.), on x-axis—concentration of the sample: (a) baseline subtraction; (b) signals ratio method (CWT—the same values as in (a)).

Algorithm III

1. Smoothing done by application of ADPF.
2. Baseline approximation achieved using a mean signal for the sample. Three different functions were selected as giving the best fit of the real background (typical fitting coefficients were calculated and shape was observed). The same function and approximation intervals were used for each curve in the set of curves for calibration.
3. Baseline subtraction or baseline correction by application of the signals ratio method.
4. Because of the great deviation of curves—correction by approximation using a linear function which was fitted separately to each experimental curve, the same approximation interval was used for each curve in the set for calibration.
5. Orthogonal signal correction—removal of 1, 2 or 3 OSC components using the methodology described in Section 2.

Further calibration by standard additions method was performed.

Application of the signal processing algorithm was evaluated and recoveries are presented in Fig. 5. These data are for curves which were intentionally distorted by a nonlinear baseline increasing identically as in experimental recordings. Random noise and other distortions were here not included. X-axis presents different sample concentrations. Fig. 5a gives results for baseline subtraction whereas Fig. 5b after the calculation of signals ratio. Also, recoveries after the application of CWT and dedicated mother wavelet are given for comparison. It may be observed that except for very small concentrations, i.e. 0.2 nM or 0.4 nM, recovery is always in an interval of 90–110%.

Investigations were continued for the same simulated data additionally distorted by random noise of amplitude 5% in relation to 1 a.u. concentration peak height and other additive and multiplicative perturbations (Fig. 6). Obtained recoveries for proposed signal processing strategies are presented in Fig. 7. Diagrams give mini-

mal and maximal recoveries obtained after 30 random generations of distortions. The first observation is that results in principle do not rely on the shape of the approximation function and also the application of CWT gives similar results. It may be observed that recovery approximates to 100% when concentration of the analyte increases. Only in cases of concentration 1 a.u. and greater were recoveries in the range 80–120% obtained. It was also calculated that CV which expresses precision decreases alongside concentration increase—from 20% for 0.2 a.u. to circa 5% for 1.0 a.u. and higher. The correlation and detection limit *DL* do not rely on concentration and *r* amounts 0.991–0.993, whereas *DL* 0.18–0.23 a.u. Application of OSC does not improve recovery or CV but has an influence on correlation, *r* increases to values greater than 0.9999, and *DL* decreases to value 0.05–0.06 a.u. while in the case of CWT to value 0.15 a.u.

Fig. 8a presents experimental curves obtained for the water from the Bialka river. The gray color illustrates mathematically generated baselines (3 variants: $POL6(x) = \sum_{i=0}^6 a_i x^i$, $EXP2(x) = ae^{bx} + ce^{dx}$, $POW(x) = ax^b + c$). In signal processing these 3 different functions were applied, when baseline subtraction or signals ratio were calculated. Also CWT was applied in scale 88 which was earlier chosen as optimal. Also, in each case, correction was done using OSC. Analytical parameters which were calculated for the evaluation of different strategies are presented in Table 1. The final result, which was the concentration of Cr(VI) in the Bialka river, was obtained by the application of different signal processing strategies in the range 0.65–0.773 nM. After the OSC precision of determination increases, *r* is greater than 0.9999 whereas *DL* oscillates in the range 0.03–0.09 nM. Only after the application of CWT the final result is below the detection limit and *r* is low (0.9929), but after the application of OSC obtained values of analytical parameters they are acceptable. Exemplary results of signals transformation present Fig. 8b–e. Finally, it may be concluded that different signal processing strategies give approximate final results of Cr(VI) determination and acceptable values of analytical parameters. Problems which may occur were signalized in the description of the processing of simulated data. Only CWT should be applied with close attention. It

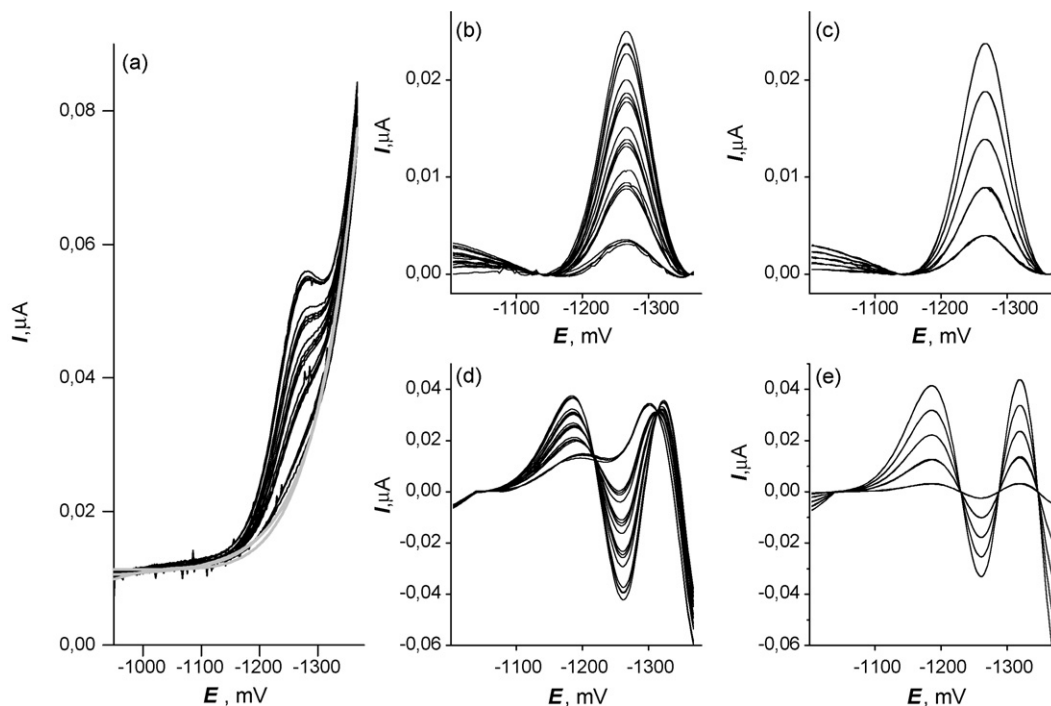


Fig. 8. Voltammograms for the water from Bialka river and after standard addition of 1, 2, 3, 4, 5 nM of Cr(VI) (4 repetitions): (a) experimental curves (black) and 3 different lines of approximated background (grey); (b) curves after $EXP2$ baseline subtraction; (c) the same curves after removal of 3 OSC components; (d) curves transformed by means of CWT and dedicated mother wavelet (scale 88); (e) the same curves after removal of 3 OSC components.

Table 1
Parameters of calibration model and results of Cr(VI) determination in Bialka river.

Baseline correction algorithm	$a \pm sa$ ($\mu\text{A/nM}$)	$b \pm sb$ (μA)	r	DL (nM)	Result \pm STD (nM)
Approximation by function $POL6(x) = \sum_{i=0}^6 a_i x^i$					
Baseline subtraction	0.0058 \pm 0.00015	0.0038 \pm 0.00036	0.9940	0.2	0.66 \pm 0.08
Baseline subtraction and removal of 3 OSC comp.	0.0057 \pm 0.00001	0.0039 \pm 0.000027	1	0.03	0.673 \pm 0.006
Signals ratio method	0.0046 \pm 0.0012	0.0305 \pm 0.0029	0.9939	0.2	0.67 \pm 0.08
Signals ratio method and removal of 3 OSC comp.	0.00455 \pm 0.0001	0.0310 \pm 0.0002	1	0.03	0.682 \pm 0.005
Approximation by function $EXP2(x) = ae^{bx} + ce^{dx}$					
Baseline subtraction	0.0057 \pm 0.00014	0.0042 \pm 0.00036	0.9940	0.2	0.74 \pm 0.08
Baseline subtraction and removal of 3 OSC comp.	0.0057 \pm 0.00001	0.0043 \pm 0.000024	1	0.05	0.759 \pm 0.006
Signals ratio method	0.0045 \pm 0.0012	0.0340 \pm 0.0029	0.9940	0.2	0.76 \pm 0.08
Signals ratio method and removal of 3 OSC comp.	0.00447 \pm 0.0001	0.0346 \pm 0.0002	1	0.06	0.773 \pm 0.005
Approximation by function $POW(x) = ax^b + c$					
Baseline subtraction	0.0058 \pm 0.00014	0.0042 \pm 0.00036	0.9941	0.2	0.72 \pm 0.08
Baseline subtraction and removal of 3 OSC comp.	0.0058 \pm 0.00002	0.0042 \pm 0.00004	1	0.08	0.732 \pm 0.01
Signals ratio method	0.0046 \pm 0.0012	0.0341 \pm 0.0029	0.9940	0.2	0.74 \pm 0.08
Signals ratio method and removal of 3 OSC comp.	0.0046 \pm 0.0001	0.0344 \pm 0.0003	0.9999	0.09	0.748 \pm 0.008
CWT with dedicated mother wavelet					
Scale 88	0.0012 \pm 0.00035	0.00081 \pm 0.00009	0.9929	0.9	0.65 \pm 0.10
Scale 88 and removal of 3 OSC comp.	0.0012 \pm 0.00013	0.00088 \pm 0.00003	0.9990	0.7	0.73 \pm 0.04

may not be rejected because of the great advantage—the generation of baseline is not required. Removal of random noise and baseline correction is done in one step of calculations.

5. Conclusions

In the study some different hybrid signal processing algorithms are presented which may be applied in the interpretation of voltammetric signals recorded on mercury film electrode in the determination of Cr(VI). In the case of synthetic samples a proposed strategy: ADPF, signals ratio and OSC gives satisfactory values of fundamental analytical parameters (sensitivity $0.6491 \pm 0.0012 \mu\text{A/nM}$, intercept $0.0071 \pm 0.0012 \mu\text{A}$, $r > 0.9999$, $DL = 0.01 \text{ nM}$), which fulfill typical validation criteria. Algorithm removes distorting components and enables unique signal interpretation. The relevant influence for the final precision, sensitivity, correlation, detection limit and ability to giving accurate results has the removal of orthogonal components done by the application of OSC.

In the case of river water samples, different strategies were tested which apply as a main step-generated baseline subtraction, signals ratio calculation or continuous wavelet transform with dedicated mother wavelet. In each variant of calculations similar values of Cr(VI) concentration were obtained, though very low level of Cr(VI) were determined (below 1 nM). Many variants of hybrid procedure with baseline subtraction, signals ratio calculation followed by OSC give satisfactory values of analytical parameters. The application of CWT linearity or DL is not so good, but this algorithm, in opposition to others, does not require baseline generation. Consequently, manual pointing of the approximation interval and the choice of the approximation function is not realized. Only optimization of scale is required. It gives fundamentals to the automation of the determination process.

Finally it should be underlined that the proposed hybrid algorithms are the complex numerical tool which definitively resolves the problem of the processing of voltammetric signals recorded in the determination of Cr(VI) in synthetic and real samples.

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