

## SQUARE WAVE VOLTAMMETRY AT CARBON PASTE ELECTRODE MODIFIED WITH SURFACTANT FOR ALPHA TOCOPHERYL ACETATE DETERMINATION IN COSMETICS

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### ABSTRACT

The aim of this study was describe electrochemical properties of a carbon paste electrode (CPE) bulk modified with 30% (w/w) surfactant sodium dodecyl sulphate (CPE/SDS) and demonstrates its application in the determination of  $\alpha$ -tocopheryl acetate ( $\alpha$ -TAc), known as vitamin E acetate, in selected cosmetic products, especially body creams. In addition to anionic SDS, cationic hexadecylpyridinium chloride monohydrate (CPC) was also tested as possible modifier. It was found that selection of surfactant type and its content significantly affect an electrical conductivity and mechanical stability of these heterogeneous electroanalytical sensors in pure organic solvents. Under this study, it was found that CPC is a totally inappropriate mediator due to very high backgroundcurrent. Together with other lipophilic vitamins characterized by antioxidant activity (dominantly retinoids), this completely synthetic substance is widely used as significant cosmetic additive due its preservative properties. Monitoring of its content in cosmetic products is usually performed by high-performance liquid chromatography (HPLC) with UV detection. This standard analytical protocol is always burdened with the complex and time-consuming preparation of the sample before analysis. For that reason, robust and simple electroanalytical method based on anodic oxidation of the  $\alpha$ -TAc at CPE/SDS by square wave voltammetry (SWV) performed in pure organic electrolyte (99.8% acetonitrile containing  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ LiClO}_4$ ) was developed. Moreover, simple dissolution of sample in supporting electrolyte using ultrasonic bath and subsequent filtering through a stacked filter included all the necessary procedures for sample preparation. The linear range from 0.1 to  $1.2 \text{ mmol}\cdot\text{L}^{-1}$  and limit of detection  $37 \text{ }\mu\text{mol}\cdot\text{L}^{-1}$  were found at pulse amplitude 10 mV and frequency 10 Hz as optimum. In analysis of selected cosmetics, the developed electroanalytical method was not validated using comparison with standard HPLC. At least, the recovery was verified by analysis of model sample and value 95.8% was calculated.

**Keywords:** carbon paste electrode; surfactant; tocopheryl acetate; square wave voltammetry; cosmetics

### INTRODUCTION

The first description of the carbon paste electrode (CPE) was recorded in short communication (Adams, 1958). At first, it was thought as a voltammetric alternative to, in those times a very popular, dropping mercury electrode (DME) used in polarography. The attempt to construct a dropping electrode which can be polarized in an area of positive potentials has not been successful. However, the CPE has found a wider application in electroanalysis together with the progression of modern voltammetric techniques, especially with the development of stripping analysis (Švancara et al., 2012). From a physical point of view, CPE is a dispersion of carbon particles (spectrographic carbon, glassy carbon, pyrolytic carbon, etc.) in a viscous lipophilic binder (paraffin or silicone oil,

Vaseline, paraffin wax, etc.). After the precise homogenization, the resulting dispersion is pressed into Teflon cavity of electrode holder. A simple modification of the carbon paste (by mixing another components, e.g. mediators in the form of platinum and metal oxide powders (Labuda et al., 1998), enzymes (Gorton, 1995), carbon nanoparticles (Punbusayakul, 2012), surfactants (Digua et al., 1994), etc., can achieve different desired properties. Carbon paste electrodes modified with the anionic surfactant sodium dodecyl sulphate (CPE/SDS) or the cationic surfactant hexadecylpyridinium chloride monohydrate (CPE/CPC) represent specific sensors which can be used for voltammetric measurements in pure organic solvents.

These electrodes can be utilized for sensitive determination of lipophilic vitamins with antioxidant

properties and their analogues (most often esters of acetic, propionic or palmitic acid) in many cosmetic products (Thiele and Hsieh, 2005; Ramos-e-Silva et al., 2001). These substances are able to prevent the rancidity. Thus they function as preservatives and prolong the expiration date (Sýs et al., 2017).

Retinol acetate (vitamin A) and  $\alpha$ -tocopherol (vitamin E) have been already electrochemically studied and several voltammetric methods focusing on their voltammetric determination were described (Atuma et al., 1974; Wilson et al., 2006). Generally, both of these substances have strong antioxidant properties. In previous studies, it was found that  $\alpha$ -tocopherol provides only one oxidation peak in a non-aqueous solution (Sýs et al., 2016). On the other hand, retinol acetate provides three oxidation steps under the same conditions (da Silva et al., 2015). Fortunately, potential values of these three oxidation peaks of the retinol acetate are sufficiently distant from the potential value of  $\alpha$ -tocopherol peak. For that reason, the peaks of retinol acetate and  $\alpha$ -tocopherol can be distinguished well. Nevertheless, it is necessary to mention that synthetic  $\alpha$ -tocopheryl acetate ( $\alpha$ -TAc) is more common additive in the cosmetic products than pure  $\alpha$ -tocopherol due to its higher chemical stability.

This substance is usually determined by standard high-performance liquid chromatography (HPLC) with UV or electrochemical detection (Wang and Wang, 2001; Almeida et al., 2009; Nada et al., 2010). The HPLC with fluorescence detection has been used for determination of tocopherol acetate in nutritional supplements (Iwase, 2000), vegetable oils (Yang et al., 2018), dairy products (Sunarič et al., 2017) infant formulas, breakfast cereals, multivitamin juices, and isotonic beverages (Balz et al., 1993). The  $\alpha$ -TAc is also used as an internal standard in liquid chromatography for the determination of its analogues (Hewavitharana et al., 2004). Rodas Mendoza et al. (2003) applied HPLC on reverse phases to determine retinyl acetate and tocoferyl acetate in infant formulas.

The aim of this work is presented simple electrochemical method based on anodic oxidation of  $\alpha$ -TAc utilizing the square wave voltammetry at CPE modified by ionic surfactant sodium dodecyl sulfate (SDS) performed in a non-aqueous medium. Except for individual optimization steps, an electrochemical behaviour of the  $\alpha$ -TAc is also included.

### Scientific hypothesis

Sodium dodecyl sulphate represents common surfactant which is widely used as CPE modifier. Within scientific hypothesis, it was necessary to verify the fact that anionic surfactants are better choice than cationic surfactants. In this case, CPC was used as suitable example. Generally, organic compounds carry a certain charge depending on the pH of the medium used. It is known that value of acetonitrile (ACN) pH decreases with higher content of water (Barbosa and Sanz-Nebot, 1992). Therefore, it can be assumed that 99.8% ACN represents weak acidic medium.

A determination of the electrical charge of  $\alpha$ -TAc (ester) in such a medium can be very difficult because it does not contain any well dissociating functional groups in its molecular structure. It should be evident that only one of

this surfactant can be useful due to electrostatic interactions.

## MATERIAL AND METHODOLOGY

### Chemicals and reagents

All the reagents such as  $\alpha$ -tocopheryl acetate, acetonitrile (ACN) suitable for HPLC of purity 99.8 %, and anhydrous  $\text{LiClO}_4$  were purchased from Sigma-Aldrich, spol.sr.o. (Prague, Czech Republic). Spectrographic carbon powder with a particle size  $>5 \mu\text{m}$  from Graphite Týn, s. r. o. (Týnec nad Vltavou, Czech Republic), paraffin oil (PO) from Merck (Darmstadt, Germany), and surfactants sodium dodecyl sulphate (SDS) with cetylpyridinium chloride (CPC) from mentioned Sigma-Aldrich were used for preparation appropriate modified CPEs. Other chemicals were of the required analytical purity.

### Electrochemical setup

A three electrode system consisting of modified CPE (working),  $\text{Ag}/\text{AgCl}/3.0 \text{ mol}\cdot\text{L}^{-1} \text{ KCl}$  (reference) from Methrom, Prague, Czech Republic, and platinum wire (counter electrode) connected to Autolab PGSTAT 101 compatible with software Nova 1.11 from the above company was used for all electrochemical measurements.

### Preparation of modified carbon paste electrode

To prevent a damage of the electrode material by presence of an organic solvent, the CPE has to contain a sufficient quantity of surfactant (Digua et al., 1994). In our case, 0.5 g of the carbon powder, 0.2 g of the paraffin oil and 0.3 g of the SDS were used for the preparation of working electrode (CPE/SDS). All the components were homogenized in a ceramic mortar for 20 min. The resulting homogeneous paste was packed into the Teflon piston holder (2 mm inner diameter). Generally, fresh electrodes, especially modified ones, should not be used for any measurement due to their unstable characteristics. This negative phenomenon is attributed to the incomplete homogenization of all components. Therefore, it is recommended to allow the CPE to rest at laboratory conditions for one day. After this time, the auto-homogenization process is completed and the electrode can be used for analysis. It is known that surface of CPE can be regenerated by renewing and polishing using wet filter paper before each measurement. Surprisingly, it was found that this procedure is not necessary in our case.

### Procedure

All experiments were carried out in  $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ LiClO}_4$  in 99.8% ACN as supporting electrolyte. The cyclic voltammetry (CV) was used for study of  $\alpha$ -TAc electrochemical behaviour at CPE/SDS. Conditions of CV were as follows: potential range from  $-0.4$  to  $+1.6 \text{ V}$ , scan rate  $50 \text{ mV}\cdot\text{s}^{-1}$ , minimally 5 repetitive cycles. Analysis of cosmetic products was done by square wave voltammetry (SWV) with potential window from 0 to  $+1.6 \text{ V}$ , at potential step 5 mV, potential amplitude 10 mV and frequency 10 Hz. A volume of 10 mL  $0.01 \text{ mol}\cdot\text{L}^{-1} \alpha$ -TAc in pure ACN without content of salt was prepared as stock solution. Measurement of calibration curve was done by addition of appropriate volume of this stock solution into 10 mL of supporting electrolyte. All changes in parameters

of CV or SWV are mentioned in legends under corresponding figures.

#### Analysis of cosmetics

Several cosmetic products, especially body creams (hand cream Diamonds and Pearls from Oriflame; Sweden, refreshing cleansing milk from Nivea; Germany, and suntan cream with protective factor UVA + UVB 30 from Astrid Cosmetics; Czech Republic), commonly available in the Czech stores were selected for analysis. Usually, 5 g of sample were dissolved in 50 mL volumetric flask using supporting electrolyte and ultrasonicated for 30 min at 25°C. The resulting sample solution had to be filtered through a stacked filter. After that 1 mL of resulting filtrate was added into 9 mL of supporting electrolyte and analysed by standard addition method (at least three additions of 200 µL  $\alpha$ -TAc stock solution in pure ACN only). Each sample analysis was minimally three times repeated ( $n = 3$ ). To verify the accuracy of the results obtained, the RSD values were compared with calculated value of significance level  $\alpha = 0.05$ .

Generally, body/hand creams can be classified as complex mixture developed by producers. In a narrower sense, they represent emulsions of water in several oils which are completely soluble in used electrolyte. For that reason, all complicated steps needed in the HPLC as standard reference method are not necessary.

For the desired rheological properties, they usually contain many accompanying substances such as glycerin, caprylic/capric triglyceride, cetyl alcohol, dimethicone, stearyl alcohol, glyceryl stearate, several emulsifiers etc. Most of these substances are not electroactive so they cannot interfere the determination.

#### Statistic analysis

Aritmetic mean ( $\bar{x}$ ) and standard deviation ( $\sigma$ ) of minimally five repetitives ( $N = 5$ ), and slop of linear calibration curve ( $k$ ) represent data which are necessary for the calculation of important parameters (limit of detection; LOD, limit of quantification; LOQ, accuracy, and correctness) of each developed analytical method. Values of LOQ and LOD were calculated according to follow equations  $LOQ = 10\sigma/k$  and  $LOD = 3\sigma/k$ , respectively, where  $\sigma$  is the standard deviation of five repetitive measurements of the concentration for lowest concentration of calibration curve (MacDougall and Crummett, 1980).

There is necessary to mentioned that only three examples of body/hand cream were analysed. Due to the low number of samples ( $N$ ), standard reference method was not applied. For that reason, any statistical methods for comparison of obtained results such as ANOVA or t-test were not needed. A precision of developed voltammetric method was validated using recovery (%) of model sample.

## RESULTS AND DISCUSSION

#### Characterisation of surfactant modified electrodes

Surfactants as SDS and CPC contain a long non-branched aliphatic chains with 12 or 16 carbons in their structure, respectively. Therefore, they are well soluble in lipophilic pasting liquid like PO which behaves like electric insulators. It was experimentally confirmed that an increasing content of surfactant caused significant

reduction of carbon paste viscosity ( $\eta$ ). Evidently, distance between each carbon particle increased due to increasing of pasting liquid volume. The dependency of ohmic resistance ( $R$ ) on the content of surfactant in CPE is very similar to curves contributed to  $R$  on the volume of pasting liquid (Mikysek et al., 2009). Generally, increasing content of any electric isolant in each electrode material usually worse electrochemical properties, especially capacitance current current which is needed to charging of working electrode.

However, it was found that presence of organic solvents has much more influence because carbon particles are more exposed to ACN with decreasing content of surfactant. It can be stated that modified CPEs with content of surfactant low than 30 % provided satisfactory electrochemical properties.

Under repetitive CV of pure 0.1 mol·L<sup>-1</sup> LiClO<sub>4</sub> in 99.8% ACN, it was observed that an increasing content of SDS significantly decreases the current response of base line. Peak current ( $I_p$ ) of clearly visible reduction peak at voltage ( $E_p$ ) +1.1 V obtained at CPE with 20% SDS (w/w) increased with each repetition (not shown). This parasitic peak is probably attributed to the presence of water (2%; v/v) in the basic electrolyte. Lower contents of water did not have any significant effect on shapes of voltammograms.

#### Selection of a suitable surfactant

Two different kinds of surfactants were tested, namely anionic SDS and cationic CPC. Although CPEs modified by monohydrate of CPC provided better electrical conductivity ( $G$ ), extremely high background current response has been observed at SWV (not shown). An explanation can be the isolation of the electrode surface that is essentially represents a capacitor. For that reason, the CPC cannot be used as suitable modifier of CPE for the determination of lipophilic compounds in cosmetic products. Unlike this, satisfactory base line current responses ( $>0.5 \mu A$ ) at CPEs with 30 and 40% content of SDS ( $R$  from 90 to 100  $\Omega$ ) were observed.

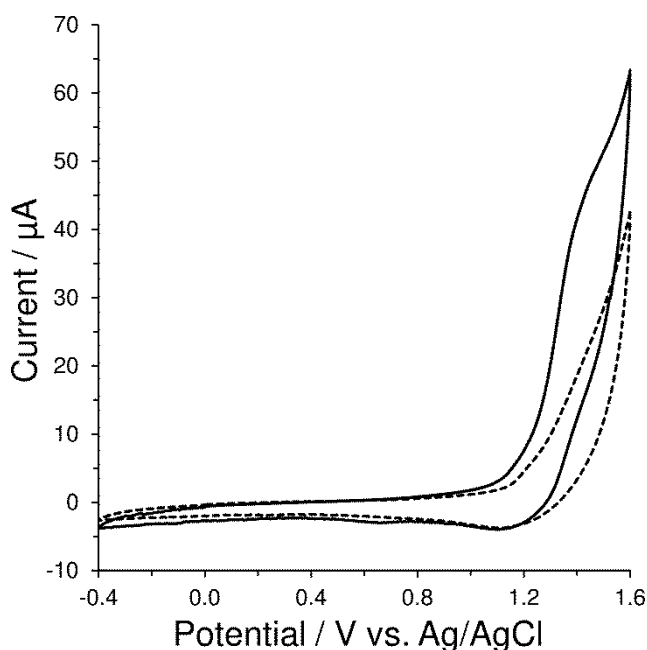
In addition, evidently better plotting of peak shape (more narrow) was obtained at CPE with 40% SDS than those with a lower content. Nevertheless, higher content than 30% SDS caused dramatically decreasing of peak current (sensitivity). For that reason value 30% SDS was chosen as optimum.

The scientific hypothesis in the previously mentioned paragraph was confirmed. A surface of CPE/SDS is evidently negatively charged due to presence of HSO<sub>3</sub> functional group in the chosen weak acidic medium (99.8% ACN). Unlike this, the  $\alpha$ -TAc is a neutral form of vitamin E (pH 6-8) which has the role of base in the acidic media and its repulsion from the electrode surface can not become like in the case of CPE/CPC.

#### Electrochemical behaviour of $\alpha$ -tocopheryl acetate

Electrochemical behaviour of  $\alpha$ -TAc in an organic medium at CPE/SDS was studied by cyclic voltametry with potential window from -0.4 to +1.6 V. Only one oxidation peak at +1.35 V (none in reverse scan) was observed (see Figure 1). Herein, it is necessary to state that this voltage is only approximate value because exact determination is quite difficult in the base line escape.

From chemical point of view, the  $\alpha$ -TAc is a synthetic analogue of  $\alpha$ -tocopherol ( $\alpha$ -TOH) which is known as the most biologically active form vitamin E (Sýs et al., 2017). As ester of acetic acid and  $\alpha$ -TOH, it lacks a free hydroxy group in its structure which can be involved in an electrochemical reaction (Sýs et al., 2016). Moreover, the ester functional group is not electron-rich for anodic oxidation as the delocalized electron system of benzene ring. It should be remembered that all tocopherols are oxidized by radical mechanisms in non-aqueous media (Wilson et al., 2006). The oxidation of the  $\alpha$ -TAc at CPE/SDS occurs in one electron step and is probably irreversible. Mikheeva and Anisimova (2007) supposed that possible formation of the intermediate and its subsequent chemical conversion to the final products is proceeded.

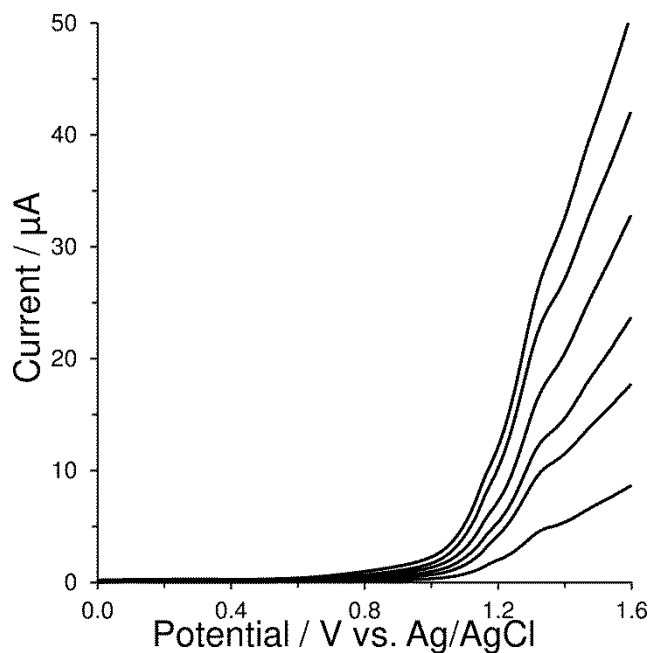


**Figure 1** CV of 0 (dashed line) and  $0.1 \text{ mmol}\cdot\text{L}^{-1}$   $\alpha$ -tocopheryl acetate at CPE/SDS (solid line) performed in 99.8% ACN containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{LiClO}_4$  at  $50 \text{ mV}\cdot\text{s}^{-1}$ .

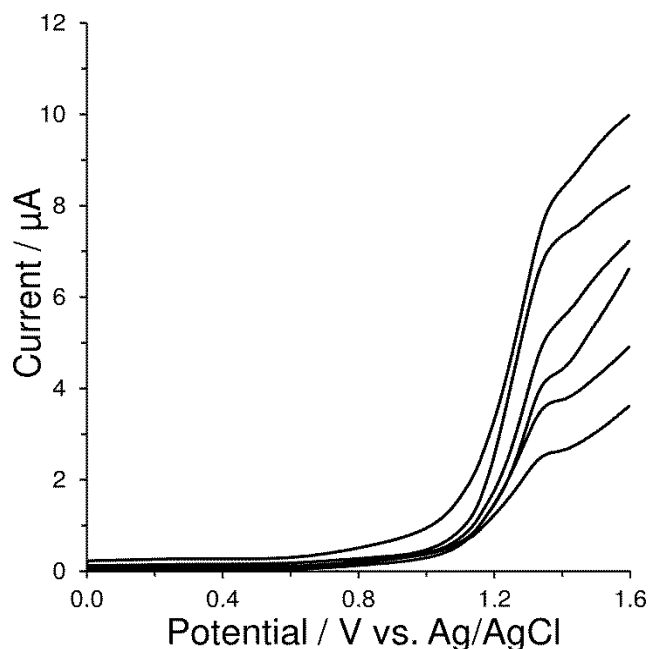
#### Optimization of square wave voltammetry

At the beginning, it was necessary to find optimum working conditions of used pulse voltammetric technique. In the case of the SWV, the sensitivity is affected by two main parameters, namely potential amplitude ( $E_{\text{amp}}$ ) and frequency ( $f$ ). It is generally known that height of peak current usually increases with higher values of these parameters (see Figures 2 and 3). Setting of amplitude higher than 10 mV and frequency 10 Hz significantly worsened the shape of corresponding voltammograms and thus determination their peak heights. For that reason, these values were chosen as optimum. For demonstration, typical voltammetric record with corresponding calibration curve is shown in Figure 4. Thanks to the extremely high base line current from +1.15 V, it was not possible to achieve lower value of detection limit than  $17 \text{ mg}\cdot\text{L}^{-1}$ . All other important analytical parameters together with comparison with already described electroanalytical methods are included in the Table 1. It appears that the

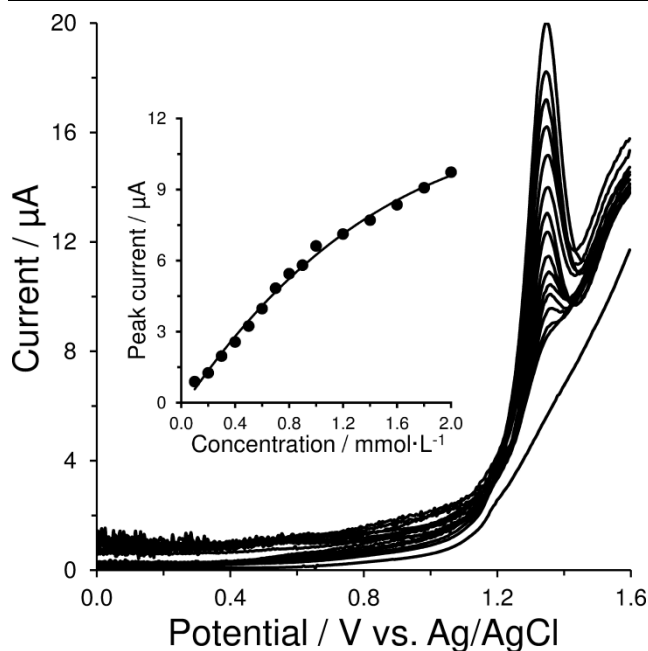
developed voltammetric method does not provide such sensitivity as those based on utilization of glassy carbon electrode (GCE). From scientific point of view, this paper represents the first more detailed work where particular type of CPE was used in the monitoring of  $\alpha$ -TAc.



**Figure 2** SWV of  $0.2 \text{ mmol}\cdot\text{L}^{-1}$   $\alpha$ -tocopheryl acetate at CPE/SDS (solid line) performed in 99.8% ACN containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{LiClO}_4$  at potential amplitudes 5, 10, 15, 20, 25, 30 mV, and frequency 10 Hz.



**Figure 3** SWV of  $0.2 \text{ mmol}\cdot\text{L}^{-1}$   $\alpha$ -tocopheryl acetate at CPE/SDS (solid line) performed in 99.8% ACN containing  $0.1 \text{ mol}\cdot\text{L}^{-1}$   $\text{LiClO}_4$  at potential amplitude 25 mV, frequencies 5, 10, 20, 30, 40, and 50 Hz.



**Figure 4** Voltammograms for 0, 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 mmol·L<sup>-1</sup>  $\alpha$ -tocopheryl acetate with corresponding calibration curve (inserted one) obtained at CPE/SDS. Measured by SWV at  $E_{step} = 5$  mV,  $E_{amp} = 10$  mV, and  $f = 10$  Hz.

**Analysis of cosmetics products**

From chemical point of view, all body/hand creams are always classified as complex emulsion which can be defined as a mixture of oily and watery liquids (the main components). Emulsifiers, fragrances, preservatives can be considered as secondary components (Moravkova and Filip, 2013). The preparation of samples for electroanalysis depends on their solubility in organic solvents.

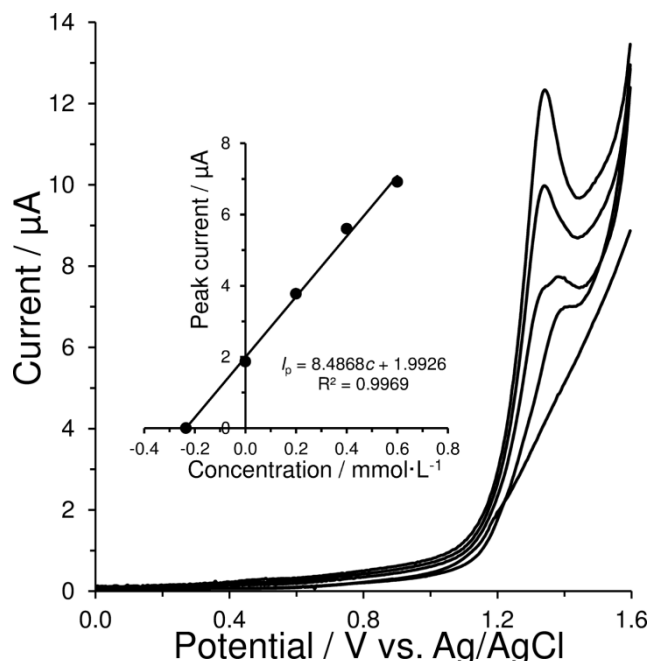
Within this work, three typical examples of cosmetic products were selected for analysis by developed voltammetric method. Herein, it is necessary to mention that presence of the  $\alpha$ -TAc in all selected samples is declared by producers. Unfortunately, its content is not listed on the products label. It is no wonder that this information is not known because the exact composition of body/hand creams is often subject to the production secret.

Generally, content of  $\alpha$ -tocopheryl acetate in cosmetics products usually occurs up to four concentration ranges. The lowest amount from 0.0001 to 25% (w/w) can be found in bath products and bath products like shampoos. Values lower than 0.3% are typical for deodorants, hair products, and after-shave lotion. In the body/hand creams from 0.001 to 25%, suntan gels and creams from 0.05 to 1%, makeup liquids, eye shadows, lipsticks, and face powders from 0.02 to 0.8% represent common values (Thiele and Hsieh, 2005).

Common body/hand creams were well soluble in used supporting electrolyte except of suntan cream, probably due to high content of nonpolar components. Therefore, it has to be counted with a certain error of determination.

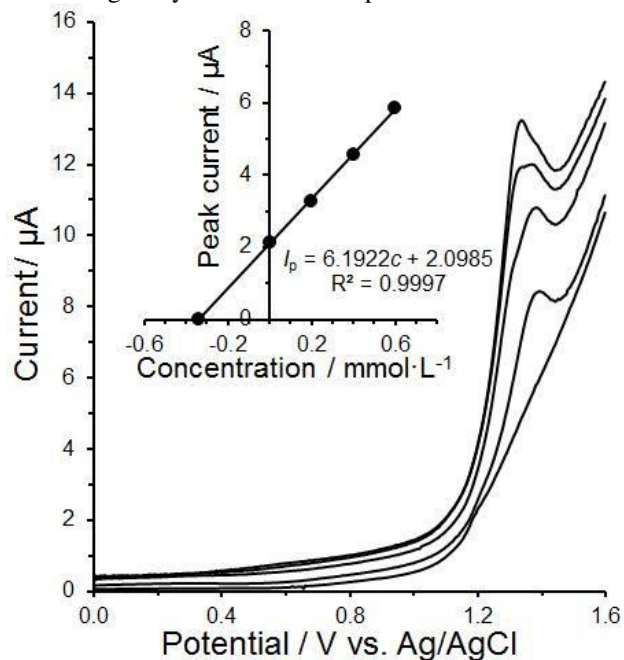
With respect to analytical method selectivity, it should be stated that other accompanying substances, especially esters of all-trans retinol (Tan et al., 2014) may not be oxidized together with the  $\alpha$ -TAc at 1.32 V because

oxidation of retinyl acetate and retinyl palmitate occur at voltages 0.85 and 1.05 V, respectively. Moreover, their presence was not declared by the manufacturers.



**Figure 5** Analysis of refreshing cleansing milk from company Nivea (Germany) by standard addition method.

Figure 5 and Figure 6 show typical voltammograms obtained during analysis of refreshing cleansing milk using standard addition method. Three additions 200  $\mu$ L of 0.01 mol·L<sup>-1</sup>  $\alpha$ -TAc into 10 mL of usually ten times diluted sample solution were performed. Calculated contents of  $\alpha$ -TAc in creams are shown in Table 2. The content ranged from 0.5 to 2% for these samples which is in line with commonly found quantities. Nevertheless, it is necessary to mention that verification of developed method was done only by calculation of the recovery 95.8% using analysis of model sample.



**Figure 6** Analysis of hand cream company Oriflame (Sweden) by standard addition method.



**Table 1** Comparison of conventional voltammetric methods developed for determination of  $\alpha$ -tocopheryl acetate.

Sensor	Technique	Supporting electrolyte	Linear range ( $\mu\text{mol}\cdot\text{L}^{-1}$ )	LOD ( $\mu\text{mol}\cdot\text{L}^{-1}$ )	References
mPtE	LSV	0.1 mol·L <sup>-1</sup> NaClO <sub>4</sub>	90 to 2300	27	(Michalkiewicz et al., 2004)
mPtE	DPV	0.1 mol·L <sup>-1</sup> NaClO <sub>4</sub>	70 to 2200	21	(Michalkiewicz et al., 2004)
mPtE	SWV	0.1 mol·L <sup>-1</sup> NaClO <sub>4</sub>	60 to 2100	18	(Michalkiewicz et al., 2004)
GCE	DPV	0.1 mol·L <sup>-1</sup> NaClO <sub>4</sub> in ACN	—	0.74	(Mikheeva and Anisimova, 2007)
GCE	DPV	0.1 mol·L <sup>-1</sup> BRB (pH 2.8)	0.11 to 8.46	0.03	(Hassan et al., 2008)
CPE/SDS	SWV	0.1 mol·L <sup>-1</sup> LiClO <sub>4</sub> in ACN	100 to 1200	37	(Present work)

ACN; acetonitrile; BRB; Britton-Robinson buffer, CPE/SDS; carbon paste electrode modified by sodium dodecyl sulfate, DPV; differential pulse voltammetry, GCE; glassy carbon electrode, LSV; linear sweep voltammetry, LOD; limit of detection, mPtE; microdisc platinum electrode, SWV; square wave voltammetry.

**Table 2** Analysis of selected cosmetic products.

Sample	Distributor	SWV (g per 100 g)	Declared amount (g per 100 g)	Recovery (%)
Model	—	0.23 ±0.02	0.24	95.8
Refreshing cleansing milk	Nivea, Germany	0.56 ±0.04	—	—
Hand cream	Oriflame, Sweden	1.60 ±0.08	—	—
Suntan cream	Astrid, Czech Republic	2.22 ±0.14	—	—

Note: Values given as arithmetic means with corresponding standard deviations for three analyses. SWV; square wave voltammetry.

## CONCLUSION

Herein, it can be concluded that CPE modified by 30% (w/w) ionic surfactant SDS represents a sophisticated voltammetric sensor suitable for simple and rapid determination of vitamin E acetate in cosmetic products. Unlike very complicated sample preparation in the HPLC as standard reference method usually consisting many consecutive steps (saponification, extraction into organic solvent, and itself separation), only dissolution in the supporting electrolyte and subsequent filtration represented the all steps necessary in the electroanalysis. The developed method provides sufficient sensitivity (LOD = 17 mg·L<sup>-1</sup>) for routine analysis of cosmetics because lipophilic vitamins are present in quantity of units to tens of milligrams per 100 g of sample.

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