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Application of renewable silver amalgam annular band electrode to voltammetric determination of vitamins C, B_1 and B_2

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ABSTRACT

In this work, the design and results of applying silver liquid amalgam film–modified silver solid amalgam annular band electrode (AgLAF–AgSAE), refreshed before each measurement, to voltammetric determination of vitamins C (VC), B_1 (VB1) and B_2 (VB2) are presented. The method is based on adsorptive accumulation of analytes at the AgLAF–AgSAE in a phosphate buffer (VB1), phosphate buffer with Triton X-100 (VB2) and an alkaline borate buffer with Triton X-100 (VC). The analytical parameters and procedure of electrode activation were optimized. The calibration graphs obtained for vitamins C, B_1 and B_2 are linear, respectively, for concentration range 0.05–12, 0.01–0.1 and 0.05–3 mg L^{-1}. The detection limits were calculated and equaled 0.02, 0.003 and 0.009 mg L^{-1}, while repeatability of the peak current was 2%, 1% and 3%, respectively. These results are comparable with results obtained for polarographic determination of the same vitamins using mercury electrodes. Finally, the AgLAF–AgSAE was applied to the determination of vitamins in pharmaceutical samples and fruit juices with satisfactory results.

1. Introduction

Vitamins are essential nutrients that human body needs in small amounts to work properly. They have to be supplied from outside with food and medicines, because organism is unable to synthesize these compounds by anabolic processes [1].

Efficient determination of vitamins in alimentary products, medicines, and also clinical samples is contributed by various analytical methods. In Refs. [2–4] it was proved that using different chromatographic techniques such as ionic, fluidic and HPLC (properly modified), it is possible to fix prosperously vitamins C (ascorbic acid), B_1 (thiamine) and B_2 (riboflavin). Also, stroked works [5–7] concern determination of these vitamins with the use of the fluorescent spectroscopy. For the necessity of marking the peck of samples (as e.g. in pharmaceutical industry), complies also methods of sequence injection analysis (SIA) [8] and flow injection analysis (FIA) [9,10].

Other large group of a practical methods used to determine these vitamins are electrochemical methods. The voltammetric methods are simpler, cheaper and less time-consuming. The vitamin C, B_1 and B_2 were determined, as well, on a metallic electrodes, like: gold [11,12], platinum [13,14], hanging mercury drop electrode, (HMDE) [15,16] and dropping mercury electrode (DME) [17–19]. In voltammetric determination of the VB2 were used different carbon electrodes such a glassy carbon electrodes (GCEs) [20], a carbon paste electrodes (CPEs) [21] and diamond electrode [22]. The overwhelming majority of publications from last years is referred to determination of an VC on a rotating glassy carbon electrode (RGCE) [23], whether on a modified glassy carbon electrodes (m-GCEs) [24].

In respect of validation requirements in routine electroanalysis of vitamins the renewable mercury electrodes are only applied [25,26]. The advantages of usage of electrodes based on mercury are obvious. The exploitation of HMDE has proved their great analytical performance. However, the increased risk associated with the use, manipulation and disposal of metallic mercury has led to seek an alternative sensor. Such an alternative sensor would utilize Hg either in the safe form of an amalgam, or in very small amounts, making it less hazardous. A non-toxic dental amalgam electrode developed by the Trondheim research group [27–29] was found to be suitable for the determination of many heavy metals in stripping voltammetry (SV). Alternative working electrodes based on solid amalgams were also developed by a research group from Prague (the so-called polished solid amalgam electrodes p-SAE or, after modification of their surface by a mercury meniscus, m-SAE) [30,31].

The problem of limiting the amount of mercury or its soluble salts needed for the analytical procedure can be solved with the help of a refreshable mercury film silver based electrode (Hg(Ag)FE) [32]. The electrode is designed in such a way that the thin liquid layer can easily be regenerated before each measurement cycle. Such a procedure ensures good reproducibility of results. A small

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amount of the silver amalgam, tightly sealed inside the electrode body, makes the electrode safe to use both in the laboratory and in on-site conditions.

The aim of the investigation was to examine whether the novel renewable silver liquid amalgam film–modified silver solid amalgam annular band electrode (AgLAF–AgSAE) [33], a very user-friendly electrode, could be used for the determination of vitamins C, B_1 and B_2 by means of the adsorptive stripping voltammetry (AdSV) technique. For that purpose, the composition of the supporting electrolyte, procedure of electrode activation and analytical parameters (i.e., deposition time and deposition potential) have been optimized. The developed methods were successfully applied in studying the synthetic solutions, commercially available pharmaceutical products and fruit juices.

2. Experimental

2.1. Instrumentation

An Electrochemical Analyzer M161 (MTM-ANKO, Poland) was used in this study. The classical three-electrode quartz cell, volume 10 mL, consisting of a homemade renewable silver liquid amalgam film–modified silver solid amalgam annular band electrode with a surface area of 12 mm^2 as the working electrode, Pt wire as the auxiliary electrode, and a self-made Ag/AgCl/3 M KCl as the reference electrode. pH measurements were performed with laboratory pH-meter. All solutions used for analyses were purged with argon. Magnetic Teflon-coated bar was used for stirring (approx. 500 rpm.) during the accumulation period. Glassware was first immersed in 6 M nitric acid, and then rinsed repeatedly with distilled water. The MTM-ANKO *EAGRAPH* software enabled electrochemical measurements, data acquisition and advanced processing of the results [34,35].

2.2. Reagents and materials

All reagents used were of analytical grade. HNO_3 65%, ammonia solution 25%, KNO_3, KCl, and KOH (Merck, Suprapur®). The 1000 mg L^{-1} standard stock solution of vitamin B_1 was prepared by dissolving thiamine hydrochloride (DSM Nutritional Products GmbH) in 0.02 M HCl. The 1000 mg L^{-1} standard stock solution of vitamin B_2 was prepared by dissolving β-riboflavin (Aldrich) in 0.02 M KOH. The 1000 mg L^{-1} standard solution of vitamin C was made from ascorbic acid (Fluka) by dilution in 1 g L^{-1} oxalic acid. All standard stock solutions were prepared freshly before measurements, in volumetric flask were wrapped in aluminum foil and stored in the refrigerator. Triton X-100 (Windsor Laboratories Ltd., UK), 0.1 M phosphate buffer (pH 7.5) and an alkaline 0.1 M borate buffer (pH 9) were applied. All solutions were prepared with quadruply distilled water.

The drug tablets which were used in the experiments were purchased from a local supplier. These were: vitamin C tablets (excipients: lactose monohydrate, polyvidone (PVP), talc, magnesium stearate, starch), product of Pharmaceuticals Poland; vitamin B_2 tablets (excipients: sucrose, lactose, starch, gum arabic, talc, stearic acid, amylum tritici), product of PLIVA, Poland and vitamin B_1 tablets (excipients: lactose monohydrate, starch, polyvidone (PVP), magnesium stearate), product of Polfarmex S.A., Poland. According to the manufacturer, they contained respectively 100 mg VC, 25 mg VB1 and 3 mg VB2.

2.3. Preparation of the AgLAF–AgSAE

The structure of the applied electrode, which allows the silver liquid amalgam film to be refreshed before each measurement and is essential for its performance, is presented in Fig. 1. Fig. 1A shows

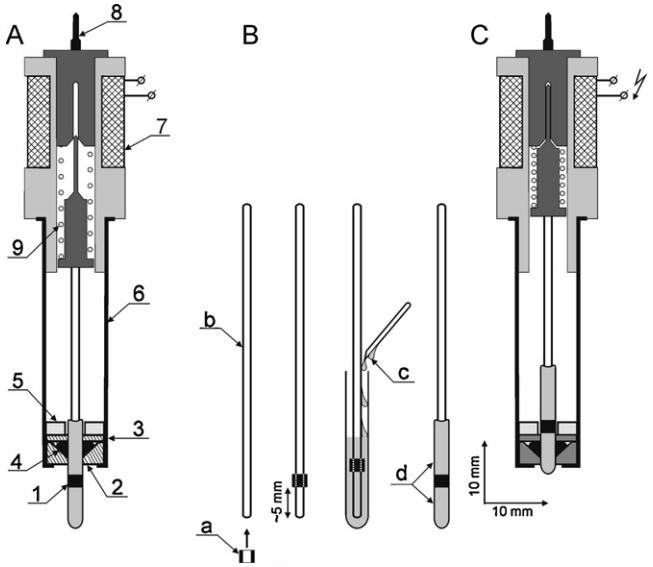

Fig. 1. (A) The AgLAF–AgSAE – ready-for-measurement configuration: (1) silver solid amalgam annular band electrode (AgSAE); (2 and 3) O-rings; (4) 1 wt.% silver liquid amalgam (AgLA); (5) PTFE centering element; (6) electrode body; (7) solenoid; (8) electric contact pin; (9) spring. (B) Construction of the AgSAE: (a) silver tube; (b) stainless steel wire; (c and d) resin. (C) The AgLAF–AgSAE in the position of the AgLAF film refreshing.

the structure of the automatically controlled AgLAF–AgSAE: silver solid amalgam annular band electrode – AgSAE (1); O-rings (2 and 3); 1 wt.% silver liquid amalgam (AgLA) drop, ca. 50 μL, (4); PTFE fastening element (5), fastened together in the polypropylene electrode body (6); linear actuator (solenoid) (7); electric contact pin (8); spring (9).

Fig. 1B shows the preparation of the AgSAE. The polycrystalline silver tube (a) was slid over and mechanically tightened on the stainless steel wire (b). The steel wire below and above the silver tube was covered by resin (c). The excess resin was then mechanically removed (d). After mounting, the electrode surface (resins and silver) was ground by emery papers of decreasing roughness and was finally polished with 0.3 μm Al_2O_3 powder. After thorough rinsing, the electrode was placed for about 2–3 s in 5% HNO_3 solution and afterwards for 1 h in 1 wt.% silver liquid amalgam.

The procedure of refreshing of silver liquid amalgam film (AgLAF) consists of pulling up the AgSAE inside, across the liquid amalgam chamber (Fig. 1C) and then pushing it back outside the electrode body (Fig. 1A). During these movements, the AgSAE makes in contact with the liquid amalgam twice. During the insertion of the AgSAE through the O-rings, the solid and gas contaminants are removed from its surface.

3. Results and discussion

3.1. Characteristic features of the AgLAF–AgSAE

The AgLAF–AgSAE electrode demonstrates many features specific for DME and the time period of the contact of the electrode with the sample solution after film refreshment may be completely controlled. Therefore, AgLAF–AgSAE may be used in the routine electroanalysis of vitamins instead of dropping mercury electrode (DME) [25,26]. The AgLAF–AgSAE maintains perfect repeatability and reproducibility for several thousand cycles (up to ten thousand) under the condition that for AgSAE regeneration, a silver liquid amalgam and not pure mercury should be used [33]. The silver liquid amalgam does not disturb the AgSAE surface; even though it is exposed to constant contact for several weeks, films refreshed

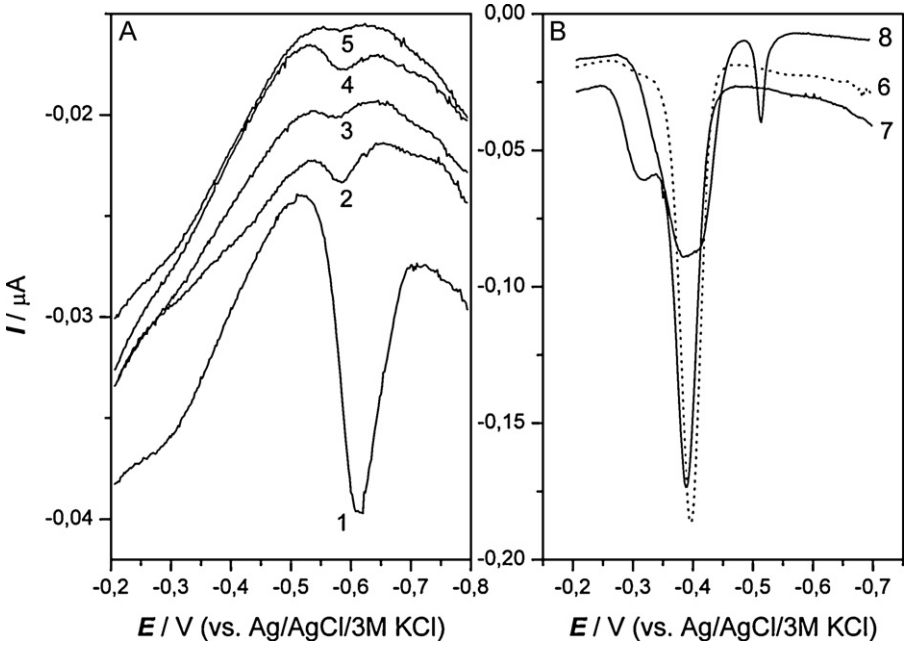

Fig. 2. (A) Background current of AgLAF–AgSAE in 0.1 M phosphate buffer (pH 7.5) after film refreshment and conditioning (1) lack of; (2) by −0.8 V for 5 s; (3) by −0.8 V for 20 s; (4) by −1.1 V for 3 s; (5) by −1.1 V for 8 s. (B) DP voltammograms 0.5 mg L^{-1} vit. B_2 in 0.1 M phosphate buffer (pH 7.5), 5 mg L^{-1} Triton X-100 after film refreshment and conditioning: (6) by −1.1 V for 8 s; (7) by −0.8 V for 20 s and (8) after conditioning (−1.1 V for 8 s) without film refreshment.

using the amalgam do not change their properties for many minutes, and the hydrogen overpotential is comparable to that of the mercury electrode. The applied 1% (in wt.%) silver amalgam was prepared by sinking several silver wires (0.5 mm in diameter) in 0.5 mL of mercury for 2 weeks. The content of silver in the liquid amalgam was determined using atomic absorption spectrometry (AAS) method. After refreshment using the silver liquid amalgam, eventual traces of mercury and silver oxides may remain on the surface of the AgLAF–AgSAE which may interfere with measurements. In such a case, electrode conditioning prior to measurement is necessary.

Fig. 2 illustrates the background current of AgLAF–AgSAE in range of reduction potentials of VB2 for a various electrode conditioning times and potentials after film refreshment. The conditioning of the electrode by the potential −1.10 V for 8 s guaranties properly low background current and disappearance of the characteristic oxygen, mercury and silver oxides reduction (Fig. 2A, curve 5). Similar results ensures conditioning of the electrode by the potential −0.80 V for 20 s (Fig. 2A, curve 3) but the long conditioning times (20 s) are the reason of the deformation and decrease of the VB2 peak (Fig. 2B, curve 7). Vitamin B_2 voltammogram recorded on the electrode which was only conditioned without film refreshment is also presented (curve 8).

Summarizing, MFEs with the non-refreshable surface should not be used in VB2 determination while the time and conditioning potential decide on the quality (i.e., signal-to-background current ratio, peak current) of the recorded signal. In the case of VC and VB1 determination and respecting the range of applied potentials, the conditioning of AgLAF–AgSAE was not necessary.

The appropriate values of the potential and the time of regeneration were inset and modified in the program of the used computer-controlled instrument and regeneration of AgLAF–AgSAE could thus be carried out automatically.

3.2. Influence of the buffer type

AdSV signals are strongly affected by the type and concentration of all components of the measured electrolyte. Therefore supporting electrolytes of a different composition and concentration were investigated for the AgLAF–AgSAE. In the case of VB1 and VB2 determination the best results were obtained for 0.1 M phosphate buffer (pH 7.5) while for the VC 0.1 M borate buffer (pH 9). However, to guarantee the required voltammograms shape, as well as repeatability and reproducibility of the recorded stripping peaks, the addition of Triton X-100 in the amount of 5 mg L^{-1} in the case of VB2 determination (Fig. 3A) and 1 mg L^{-1} in the case of VC (Fig. 3B), was required. Higher concentrations of Triton X-100 are the reason of the considerable decrease of the VC and VB2 peak heights. Our experiments point out that: (a) Triton X-100 addition stabilizes the adsorption (accumulation) processes of the vitamins on the AgLAF–AgSAE surface; (b) the electrode reaction is a one-step process; (c) the vitamin accumulated on the electrode surface is the only source of the signal.

In the case of VB1 (in a measured concentration ranges, i.e., 0.01–0.1 mg L^{-1}) Triton addition of 1 mg L^{-1} suppressed the signal by 30%, while the signal disappears totally at Triton X-100 addition of 2 mg L^{-1}.

3.3. Optimization study

To obtain suitable conditions for the differential pulse adsorptive stripping voltammetry (DP AdSV) determination of VC, VB1 and VB2, the influence of accumulation potential (E_{acc}), accumulation time (t_{acc}), pulse amplitude (ΔE), step potential (E_s) and pulse width ($t_p = t_w$ (waiting time) + t_s (current sampling time)) was investigated.

The influence of the accumulation potential was studied in the range from −0.40 to −0.10 V with alkaline 0.1 M borate buffer (pH 9), 1 mg L^{-1} Triton X-100 spiked with 1 mg L^{-1} VC; −0.90 to −1.30 V with 0.1 M phosphate buffer (pH 7.5) spiked with 0.1 mg L^{-1} VB1; 0.05 to −0.30 V with 0.1 M phosphate buffer (pH 7.5), 5 mg L^{-1} Triton X-100 spiked with 1 mg L^{-1} VB2. The repeatability and the magnitude of the analytical signals were found to be independent of the accumulation potential in tested potential intervals. The accumulation potentials −0.25 V for VC, −1.25 V for VB1 and −0.20 V for VB2 were chosen, respectively.

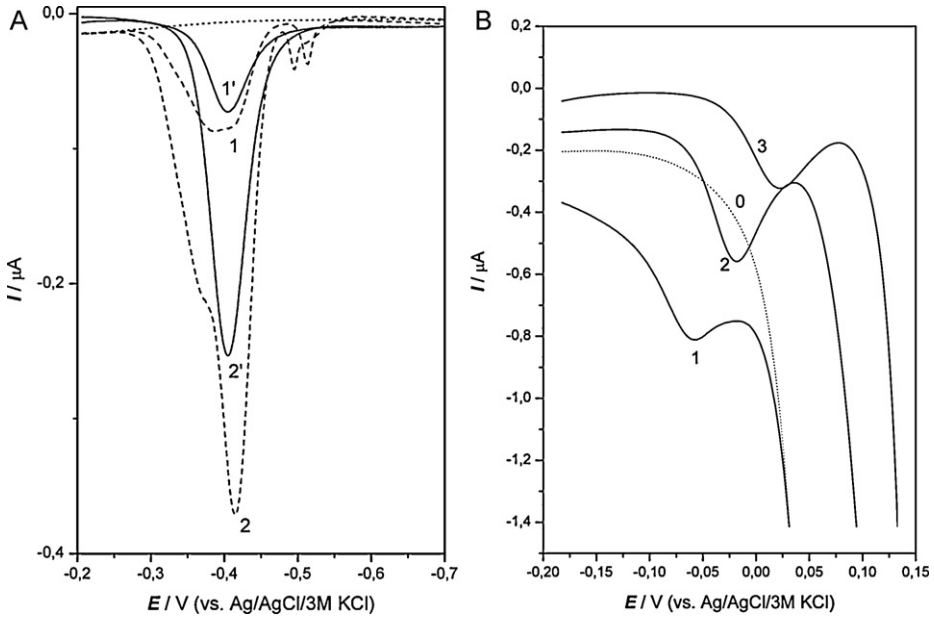

Fig. 3. (A) DP voltammograms of (1) 0.1 and (2) 0.5 mg L^{-1} vit. B_2 in 0.1 M phosphate buffer (pH 7.5) (1′) and (2′) with Triton X-100 addition of 5 mg L^{-1}. (B) DP voltammograms of 1 mg L^{-1} vit. C in 0.1 M borate buffer (pH 9): (0) blank; (1) 0; (2) 1; (3) 5 mg L^{-1} Triton X-100.

The accumulation time was changed from 0 to 120 s. It can be observed, that for VC peak current increased up to 20–30 s of accumulation, after which it decreased. For VB1 the peak current increased up to 20 s of accumulation (ca. 5-times) after which it decreased. For VB2 the peak current increased linearly up to 50 s of accumulation (ca. 14-times) after which it stabilized. For further studies the accumulation time of 20 s for VC and VB1 and 40 s for VB2, were chosen.

It was observed, that VB1 and VB2 peaks potential was not dependent on either the accumulation time and potential. In the case of VC the peak potential was shifted by ca. 40 mV in the direction of positive potentials in conjunction with increase of the accumulation time.

To optimize the conditions for vitamins C, B_1 and B_2 determination, the following DP technique parameters were systematically changed: E_s in the range 1–5 mV; ΔE in the range 10–60 mV (both positive and negative modes) and t_p from 10 to 60 ms. Consequently, these parameters were investigated with supporting electrolyte spiked with vitamins.

Vitamin C. Changes of the step potential caused increase of a peak current of about 80%. For $E_s > 3$ mV increase of the peak current was unnoticeable (<20%) but increase of the background current was observed. In determinations the step potential of 2 mV was applied. For a pulse amplitude of −10 mV the peak current of VC was equal to −0.09 μA and increased up to −30 mV (−0.24 μA) after which it stabilized. The peak heights were similar for both negative and positive amplitude values. For negative amplitude peak potential was shifted by −0.038 V (for −10 mV) and −0.024 V (for −60 mV). For ΔE, in the range 10–60 mV, the width of the peak at half-height was equal to 46 mV. The pulse amplitude of −30 mV was chosen. In each case $t_w = t_s$, the VC peak height decreased with the lengthening of the pulse time, i.e., around 45% for the change from 10 to 60 ms, significantly strongly decreased also the background current. The best result (precision, reproducibility and the signal-to-background current ratio) was obtained for $t_p = 20$ ms, and this was the value chosen for further work.

Vitamin B_1. For a step potential of 1 mV the VB1 peak current was equal to −0.53 μA and quasi linearly increased with increasing step potential (−3.07 μA for 5 mV). However significantly increased also background current, therefore in determinations the step potential of 3 mV was applied. For a pulse amplitude of −10 mV the peak current VB1 was equal to −0.66 μA and quasi linearly increased up to −50 mV (−2.98 μA). The peak heights were similar for both negative and positive amplitude values. For ΔE, in the range 10–60 mV, the width of the peak at half-height was equal to 45 mV, the peak potential was constant and equals −1.445 V. For negative amplitude peak potential was shifted by 34 mV (for −10 mV Ep = −1430 mV) in the direction of positive potentials. The pulse amplitude of −50 mV was chosen. In each case $t_w = t_s$, the VB1 peak height decreased with the lengthening of the impulse time, i.e., around 4-times for the change from 10 to 60 ms, significantly strongly decreased, also the background current. The best result was obtained for $t_p = 20$ ms, and this was the value chosen for further work.

Vitamin B_2. For a step potential of 1 mV the VB2 peak current was equal to −0.38 μA and was almost constant with increasing step potential (−0.43 μA for 5 mV). The step potential of 2 mV was applied. For a pulse amplitude of −10 mV the peak current VB2 was equal to −0.27 μA and linearly increased up to −30 mV (−0.72 μA). For ΔE, in the range 10–60 mV, the width of the peak at half-height was equal to 64 mV. The peak heights were similar for both negative and positive amplitude values. The peak potential was −0.416 V (for −10 mV) and −0.394 V (for −60 mV). The pulse amplitude of −30 mV was chosen. In each case of $t_w = t_s$, the VB2 peak height decreased with the lengthening of the impulse time, i.e., around 3-

Table 1
Parameters of calibration model for determination of VB1, VB2 and VC.

	Concentration range [mg L^{-1}]	Detection limit [mg L^{-1}]	Calibration equation ip [μA] c [mg L^{-1}]	Correlation coefficient r	RSD [%] ($n = 5$)
Ascorbic acid (VC)	0.05–12	0.02	$ip = 0.043 + 0.366c$	0.9998	2
Thiamine (VB1)	0.01–0.1	0.003	$ip = 0.014 + 20.8c$	0.9991	1
Riboflavin (VB2)	0.05–3	0.009	$ip = -0.0016 + 0.168c$	0.9992	2.5

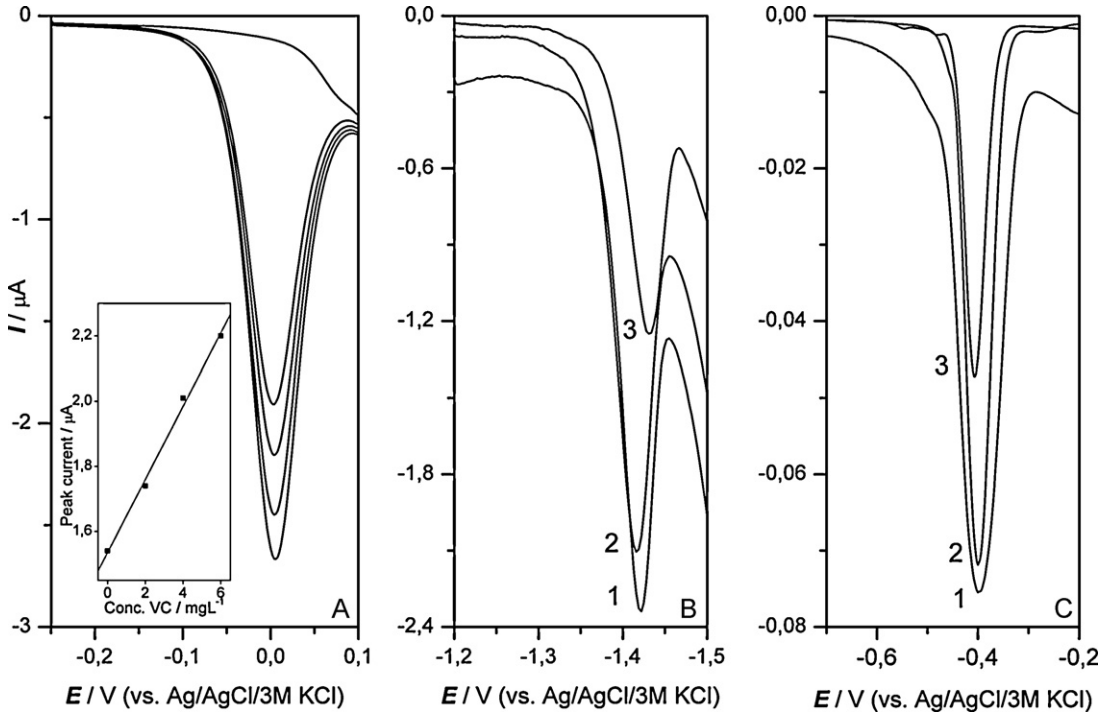

Fig. 4. DP typical voltammograms: (A) quantification of vit. C in juice "Tarczyn"; (B) vit. B_1 (1) in vitamin B_1 tablets (PLIVA), (2) in juice "Tarczyn-Multiwitamina-z-zielony" (Agros Nova), (3) in juice "Tymbark-Multiwitamina-classic" (Tymbark S.A.); (C) vit. B_2 (1) in vitamin B_2 tablets (PLIVA), (2) in juice "Tarczyn-Multiwitamina-z-zielony" (Agros Nova), (3) in juice "Tymbark-Multiwitamina-classic" (Tymbark S.A.).

times for the change from 10 to 60 ms. The best result was obtained for t_p = 20 ms, and this was the value chosen for further work.

3.4. Calibration graphs

Voltammograms at different concentrations of VC, VB1 and VB2 were recorded using the optimal conditions. Analyses were performed in solutions of supporting electrolyte: 0.1 M borate buffer (pH 9), 1 mg L^{-1} Triton X-100 (VC); 0.1 M phosphate buffer (pH 7.5) (VB1); 0.1 M phosphate buffer (pH 7.5) and 5 mg L^{-1} Triton X-100 (VB2). The parameters of calibration model and the evaluation of precision expressed as RSD were presented in Table 1.

The short-term reproducibility of the analytical response for the AgLAF–AgSAE was excellent. The long-term stability of the electrode was tested by measuring the current response at a 1 mg L^{-1} VC, VB1 and VB2 over a period of one week. The experiment results shown that the signal fluctuates by about 5%, suggesting that the AgLAF–AgSAE reported in this work has long-term stability. The electrode used in synthetic solutions containing up to 5 mg L^{-1} Triton X-100 did not require mechanical pretreatment for over 1000 measurements.

3.5. Analysis of vitamin C, B_1 and B_2 in the tablets and fruit juices

The electrode AgLAF–AgSAE was used to determine the amount of vitamins C, B_1 and B_2 in tablets using the standard addition method (three additions). At first, they were carefully pulverized and dissolved in distilled water. This was filtered into 100 mL standard flask and made up to the mark. This stock solution was diluted as appropriate for analysis. In Table 2, the analysis results are summarized for 90 analyzed tablets (for 30 of each product). These data were obtained by using AgLAF–AgSAE at ten tablets and each measurement was repeated five times. They gave an average VC content of 100.4 mg (result of the analysis – 5.02 mg, dilution of 20 times); VB1 content of 24.9 mg and VB2 content 2.88 mg; in the 100, 25 and 3 mg/tablet quoted by the manufacturer.

Table 2
Vitamin C, B_1 and B_2 content of analyzed tablets.

Tablet number	VC [mg]	VB_1 [mg]	VB_2 [mg]
1	4.92	26.8	2.87
2	5.10	24.3	2.84
3	5.04	23.8	2.92
Average	5.02 ± 0.09	25 ± 2	2.88 ± 0.04

The proposed procedure using the AgLAF–AgSAE for vitamins determination was applied also for analysis of fruit juices. Juice samples were analyzed with no previous preparation. To 0.1 – 0.5 mL of juice samples, the relevant volume of adequate supporting electrolyte was added to make up the final volume of solution in the cell of 5 mL. The data obtained are shown in Table 3. The precision of the measurements was determined from the mean values of three replicates of each sample.

Fig. 4 shows typical voltammograms for VC quantification in fruit juice "Tarczyn-Multiwitamina-z-zielony" (Agros Nova Sp. z o.o., Poland) (Fig. 4A), further VB1 (Fig. 4B) and VB2 (Fig. 4C)

Table 3
Vitamin C, B_1 and B_2 content of analyzed fruit juices.

Juices	VC [mg L^{-1}]		VB1 [mg L^{-1}]		VB2 [mg L^{-1}]	
	Declared	Measured	Declared	Measured	Declared	Measured
Tymbark	90	96 ± 3	2.1	1.9 ± 0.4	2.4	2.3 ± 0.3
Tarczyn	120	119 ± 3	2.8	2.5 ± 0.3	3.2	2.7 ± 0.2

determination in Vitamin B_1 and B_2 tablets (PLIVA, Poland), fruit juices "Tarczyn-Multiwitamina-z-zielony" (Agros Nova, Poland) and "Tymbark-Multiwitamina-classic" (Tymbark S.A., Poland).

4. Conclusions

The renewable silver liquid amalgam film–modified silver solid amalgam annular band electrode (AgLAF–AgSAE) of prolonged analytical applicability is a useful sensor for adsorptive stripping voltammetry. The simple, mechanical system of film refreshment provides excellent electrode surface repeatability (~1%) and reproducibility (2–5%) and long-term stability (more than ten thousand measurement cycles) even without any additional pre-treatment. The amalgam chamber inside of the electrode body contains only 50 μL of 1 wt.% silver amalgam, and the electrode can be used for several months, providing stable operation for a great number of regeneration cycles without replenishing the amalgam reservoir. Moreover, the thickness of amalgam film amounts to ca. 50 nm, and the AgLAF–AgSAE does not introduce any mercury into the analyzed solution. Therefore, the use of AgLAF–AgSAE does not cause significant problems with the disposal and toxicity of mercury, in opposition to liquid mercury electrodes. The results of the investigation also demonstrate that the AgLAF–AgSAE can be applied successfully for sensitive determination of vitamins C, B_1 and B_2, by means of adsorptive stripping voltammetry. The peaks of vitamins are well defined. The estimated limits of detection are at satisfactory levels and comparable to those obtained using mercury electrodes. The AgLAF–AgSAE electrode was found to be stable towards the determination of vitamins C, B_1 and B_2 because it was not poisoned during the reduction/oxidation of vitamins.

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