CATIONIC SURFACTANTS AS MODIFIERS FOR CARBON PASTE ELECTRODES. APPLICATION TO THE DETERMINATION OF IODIDE

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This article reports on applicability of carbon paste electrodes modified "in situ" with a surfactant in voltammetry to selected inorganic anions. A new method for the determination of iodide is proposed based on ion-pairing of iodide with 1-ethoxycarbonylpentadecyl-trimethylammonium bromide (Septonex). The procedure developed has been tested and verified by means of analyzing both model and real samples.

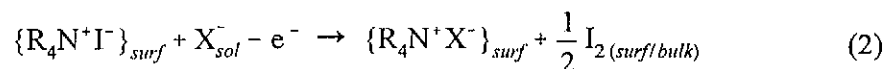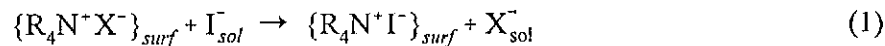[1] To whom correspondence should be addressed.

Introduction

Cationic surfactants represented by various types of tetraalkylammonium salts with long lipophilic chain and a positively charged active site ($R_4N^+A^-$), are applicable in various fields of analytical chemistry [1]. In electrochemistry, these substances have often been used as effective extractants, anion exchangers, or ion-pairing agents [2,3]. For example, their ability to form ion-pairs which are insoluble in water but extractable in the organic phase is utilized in the so-called two-phase potentiometric titrations for the determination of various substances, including the surfactants themselves [1–3]. Cationic surfactants are being occasionally used as special electrode modifiers, e.g., for carbon paste-based electrodes [4–6].

Carbon paste electrodes (CPEs) are usually prepared in laboratories by manual homogenization of powdered graphite with a suitable liquid or low melting solid binder. The mixture obtained in this way, i.e., carbon paste, acts as electrode material which can easily be modified; either *in situ* or directly — by mechanical admixing the modifier into the paste [5,6]. Carbon paste electrodes modified with surfactants and related lipophilic compounds offer some attractive applications thanks to rather specific properties of the carbon paste [5,6].

Already Adams — the inventor of CPEs [4] — and his research group showed first the usefulness of such a CPE [7]. Their electrode containing solid anionic surfactant admixed into the paste could be operated even in non-aqueous media where common bare carbon paste mixtures undergo rapid disintegration [7,8]. The stability of CPE modified with surfactant was explained by its repelling effect towards the solvent [7]. Another interesting effect of anionic and non-ionic surfactants on the properties of CPEs has been demonstrated by Albahadily and Mottola [9] who applied these substances as *in situ* modifiers to prepare carbon paste-based electrochemical detectors with substantially lowered ohmic resistance and improved detectability; both being a consequence of effective removal of the lipophilic binder layer from the carbon paste surface. In 1994, Kauffmann *et al.* presented a detailed study [10] in which one can find an interpretation of ion-pairing processes with some surfactants immobilized onto the carbon paste surface (e.g., ion-pairing of sodium hexadecylsulfonate with some protonated organic compounds) and, for the first time, a more general insight into the behavior of surfactant-modified CPEs. Ion-pairing at CPEs modified with surfactants has also been extensively studied by our group [11–15]; predominantly, with voluminous lipophilic inorganic analytes such as $[Fe(CN)_6]^{3-}/^{4-}$ [11], $TlCl_4^-$ [12,13] or I^- [14,15]. These investigations have demonstrated the usefulness of ion-pairing employed as the accumulation process in voltammetric analysis. Due to non-electrolytic and purely physico-chemical nature of ion-pairing processes, the preconcentration step can be performed with high efficiency, allowing one to determine the analyte of interest even in samples with substantially complex matrix such as wine [11], alloys [13], or table salts [15]. When suitably coupled with some special electrode pre-

treatments, ion-pairing may also effectively assist in electrolytic accumulation of an analyte, thus providing a way to achieve very low detection limits as shown, e.g., on the determination of Ag^+ ions [16].

Iodide, I^-, is a typical example of an anion readily forming very stable ion-pairs with tetraalkyl(or tetraaryl)ammonium salts according to the following general scheme

$$\{R_4N^+X^-\}_{surf} + I^-_{sol} \rightarrow \{R_4N^+I^-\}_{surf} + X^-_{sol} \tag{1}$$

$$\{R_4N^+I^-\}_{surf} + X^-_{sol} - e^- \rightarrow \{R_4N^+X^-\}_{surf} + \frac{1}{2}I_{2\,(surf/bulk)} \tag{2}$$

$$\frac{1}{2}I_{2\,(surf/bulk)} + e^- \rightarrow I^-_{sol} \tag{3}$$

where the reaction (1) represents the formation of the ion-associate at the electrode and its preconcentration, (2) denotes anodic oxidation of this ion-associate during the voltammetric equilibration step and the scheme (3) corresponds to the voltammetric reduction of released iodine to iodide. Indexes "sol", "surf", and "surf /bulk" identify the phase in which the corresponding species act (the latter indicating the extraction of elementary iodine to the carbon paste bulk [15]). Voltammetric methods for the determination of iodide employing ion-pairing agents such as ion-exchanger *Dowex 1* [14], Friedel's salt (anion-exchanging clay from the family of layered double hydroxides [17]), cetyltrimethylammonium bromide [18], and cinchonine [19] have been successfully applied in analytical practice; e.g., to analysis of mineral waters [15], table salts [15,18] or disinfectant solutions [19].

The article presented herein is devoted to the basic characterization of different types of CPEs modified *in situ* with cationic surfactants. The observations and results obtained in this fundamental study have then been exploited in proposing a simple and inexpensive method for the determination of iodide in mineral waters.

Experimental

Apparatus

A polarographic analyzer (Model PAR 174, Princeton Applied Research, U.S.A.) was connected to a personal computer *via* an interface card for A/D conversion of the data (PC ADDA-14, Model FPC-011; Flytech Technology Co., U.S.A.). This assembly was combined with an SMDE electrode stand (Laboratorní přístroje, Prague, the Czech Republic) adapted for measurements with CPEs. A Pt-plate served as auxiliary electrode and a Ag/AgCl electrode (0.1 M KCl; type RAE 111, Crytur, the Czech Republic) as the reference. Stirring was performed with a Teflon-coated magnetic bar at 600 rpm.

The pH values were measured using a digital pH meter (Radelkis, Hungary) equipped with a combined glass pH sensor (glass vs Ag/AgCl electrode; Model OP-0808P, Radelkis).

Working Electrodes

According to previously recommended procedure [20,21] and using a pestle and mortar, three types of carbon pastes (denoted as shown below) were made by thoroughly hand-mixing of 0.5 g of RW-B spectroscopic graphite powder (Ringsdorff Werke, Germany) with 0.2 ml of the corresponding liquid binder : (a) silicone oil (*Lukooil MV-15 500*, Lučební závody, the Czech Republic); "C/SO" carbon paste type, (b) paraffin oil (*Uvasol*; Merck); "C/Uv" type, and (c) tricresyl phoshate (mixture of isomers, Fluka); "C/TCP" type. The carbon pastes were packed into piston-like electrode holders [5]. The carbon paste electrode surface (2 mm in diameter) was renewed by smoothing with a wet filter paper.

Chemicals and Reagents

All chemicals used were of analytical reagent grade and purchased from Lachema (The Czech Republic) except sodium chloride which was of Suprapur quality (Merck, Germany). The stock solutions for the preparation of the supporting electrolytes were made 1 M in concentration; standard solution of iodide being prepared as 0.01 mol l^{-1}. Fresh diluted standard solutions (0.001 M or 1×10^{-4} M, resp.) were prepared before each use. The surfactants selected for *in situ* modification of CPEs included: (1-ethoxycarbonylpentadecyltrimethylammonium bromide (*Septonex*), cetyltrimethylammonium bromide (CTAB), cetylpyridinium bromide (CPyB), dodecyldimethylbenzylammonium bromide (*Ajatin*), and diisobutylfenoxyethoxyethyl-dimethylbenzylammonium chloride (*Hyamine 1622*).

All the above-mentioned modifying agents were made as 0.001 M stock solutions.

All solutions to be analyzed were deaerated with argon (purity: 99.996%, Linde Technoplyn, the Czech Republic). Redistilled water was used throughout.

Samples

Model Samples: Synthetic solutions were prepared by dissolving the accurately weighed amount of NaCl in 80 ml of re-distilled water. This solution was then spiked with the appropriate amount of iodide, acidified with 35% HCl to pH 1.5, and made up with water to the desired volume. The concentration of iodide in model solutions was chosen as 50, 500, and 5000 mg $I^- l^{-1}$.

Real Samples: In accordance with previous experience [15], two different types of commonly marketed mineral waters were chosen for analysis; the first one containing a relatively high content of I^- represented by *Vincentka* mineral water (Helios Ltd., Prague, the Czech Republic) and the second one being a product with a "usual" content level of iodide (Hanácká kyselka mineral water; Hanácká kyselka Ltd., Horní Moštěnice, the Czech Republic). To degase mineral water samples prior to analyses, a Sonorex TK-52 sonication bath (Model UO 405 BJ-1; Tesla Vráble, Slovakia) was used.

Procedures

Voltammetry: The accumulation (in stirred solution) was performed at accumulation potential (E_{ACC}) of +0.7 V vs Ag/AgCl for a period (t_{ACC}) of 3 min., unless stated otherwise. After equilibration, t_{EQ}, for 20 s (in quiet solution), the cathodic scan was recorded from the initial potential (E_{INIT}, always identical with E_{ACC}) to the final potential (-0.5 V) in differential pulse mode. The scan rate was 20 mV s^{-1}, the pulse height -50 mV, and the sampling rate 5 data s^{-1}.

Determination of Iodide

To a 19 ml sample, 1 ml 1 M HCl and 200 µl 0.001 M *Septonex* were added. After deaerating with argon gas for ca 5 min, this solution was used directly for voltammetric analysis. In the case of real samples, the proper analysis was preceded by degasing mineral water in sonication bath for approx. 10 min.

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Data Processing and Evaluation of the Results

The computerized measuring apparatus described above enabled also a complete evaluation of the voltammetric data by self-made software (ADDA 174-A [22]). For evaluating the concentration, addition of at least two iodide standards was used. The signals were evaluated as peak areas. The results of determinations were evaluated using either the recovery rate (%) or with the aid of conventional statistics for small sets of data [23]. As the reference method for the determination of iodine in real samples, ICP-MS technique was selected.

Results and Discussion

Effect of Surfactants on the Signal-to-Noise Characteristics of Carbon Paste Electrodes

Investigations described in this section have been focused predominantly on defining the accumulation capabilities of the carbon paste surface modified with a surfactant *in situ*, i.e., directly in the solution to be analyzed. The accumulation process at surfactant-modified CPEs was studied with selected inorganic anions, which is the reason why the set of surfactants chosen had included cation-active substances (see Experimental).

Figure 1 depicts schematically "ion-pairing function" of the carbon paste surface modified with either (a) cationic or (b) anionic surfactant. Anionic surfactants have not, in fact, been included in this work; nevertheless, it seems to be useful to describe herein their function as well, since there are some analogies in their behavior with respect to the counterions. In both cases, the modifying substance is firmly immobilized at the electrode surface thanks to a strong interaction between the hydrophobic pasting liquid binder and highly lipophilic moiety of surfactant. The active part of surfactant bearing the respective charge is thus exposed to the solution and attracts a species with opposite polarity that then participates in the ion-pairing process.

In order to utilize the accumulation effect at the carbon paste surface modified with a surfactant, it was necessary to check whether the presence of modifying agent itself did not give rise any unwanted signal within the potential range of interest, affecting negatively the response for voltammetric reduction of accumulated species and thus deteriorating the overall signal-to-noise characteristics of a CPE. Figure 2 shows the base-line of three CPEs in dependence on the concentration of surfactant in the solution when using *Septonex* as a model type of cationic surfactant modifying agent.

As can be seen, the base-line of both C/SO and C/Uv are influenced by the presence of *Septonex* only at its higher concentrations whereas the base-line of the
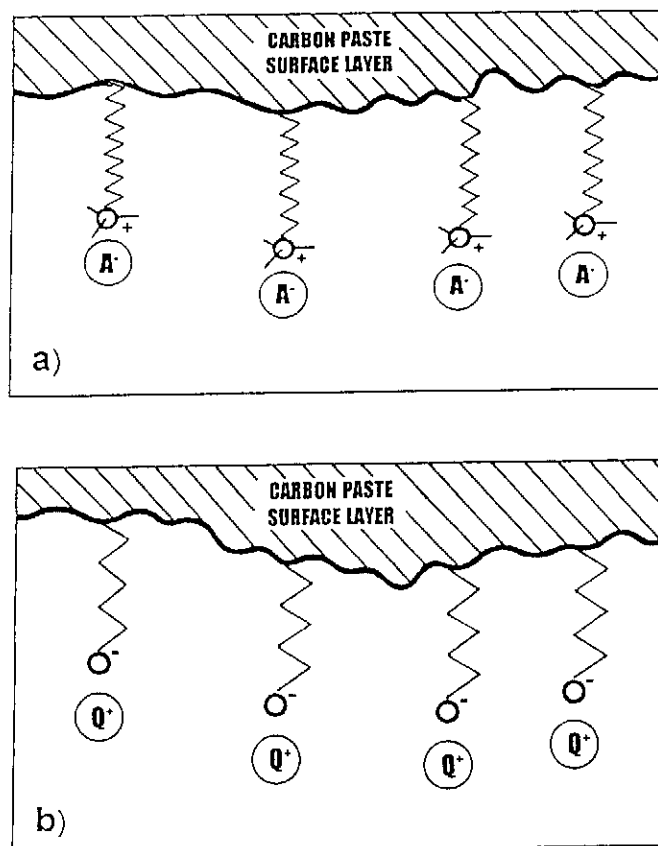
Fig. 1 Carbon paste modified with surfactants (a schematic view showing the anchoring of lipophilic chain of surfactant at the carbon paste surface): a) cationic surfactant [e.g., tetraalkyl(tetraaryl)ammonium salt]; b) anionic surfactant [sodium alkylsulfonate]
Note: A^- represents an anion and Q^+ a cation to be paired

C/TCP electrode exhibits completely opposite trend. This can be explained by a special nature of the C/TCP carbon paste that contains tricresyl phosphate whose protonated molecules in acidic media [15] may interact with modifying agent, in this case with *Septonex*. With respect to both C/SO and C/Uv, their deteriorated base-line due to the presence of *Septonex* at higher concentrations (see peaks in Fig. 2) may be caused — similarly to Adams's observations [7] — by a repelling effect of surfactant towards liquid binder in the paste. This binder linking and coating the graphite particles is then stripped off, which usually results in enhanced background currents or even a parasitic signal of the "naked" graphite surface [20]. The voltammograms in Fig. 2 document that an adequate amount of modifier in the supporting electrolyte does not affect the base-line of both C/SO and C/Uv. Nearly identical relations were observed even for the other cationic surfactants (i.e., CTAB,
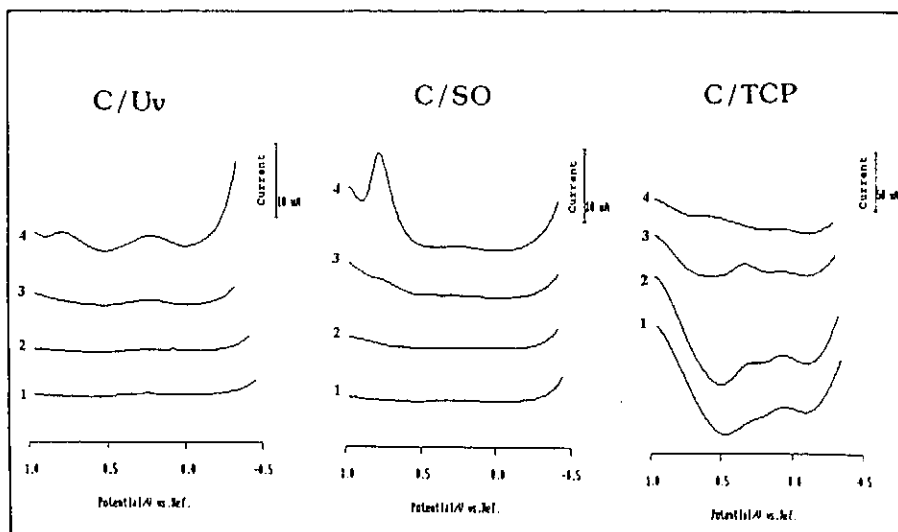
Fig. 2 Effect of *Septonex* upon the base-line of three different carbon paste electrodes: 1) base-line in the supporting electrolyte (0.5 M NaCl + 0.1 M HCl); c(*Septonex*) = 2) 1×10^{-6}; 3) 1×10^{-5}; 4) 5×10^{-5} mol l^{-1}. Experimental conditions: DPCSV; accumulation potential, E_{ACC} = +1.0 V vs Ag/AgCl; accumulation time, t_{ACC} = 1 min; equilibrium time, t_{EQ} = 15 s; scan rate, v = 20 mV s^{-1}; pulse height, ΔE = -50 mV

CPyB, and *Ajatin*); but, they had caused a more pronounced base-line deformation compared to that noticed for *Septonex*. Owing to this, *Septonex* was chosen for all further studies when its total concentration of 1×10^{-5} mol l^{-1} in the supporting electrolyte being ascertained to be optimal.

Accumulation of Some Inorganic Anions onto Carbon Paste Electrodes Modified "In Situ" with Septonex

Figure 3 illustrates the sets of voltammograms obtained by analyzing model solutions of four typical inorganic anions that have been selected as potentially active species for ion-pairing and, at the same, readily reducible voltammetrically in a way analogous to the previous scheme (1a-c). This study has revealed that the accumulation of MnO_4^-, CrO_4^{2-} and $AuCl_4^-$ is not very effective and solely higher concentrations of these anions could be detected.

In contrast to this, the preconcentration of iodide *via* ion-pairing with *Septonex* was found to be fairly efficient, allowing to determine even trace amounts of iodide. The latter statement is also evident when one compares the voltammograms in Fig. 3 together with the corresponding data given in the caption.
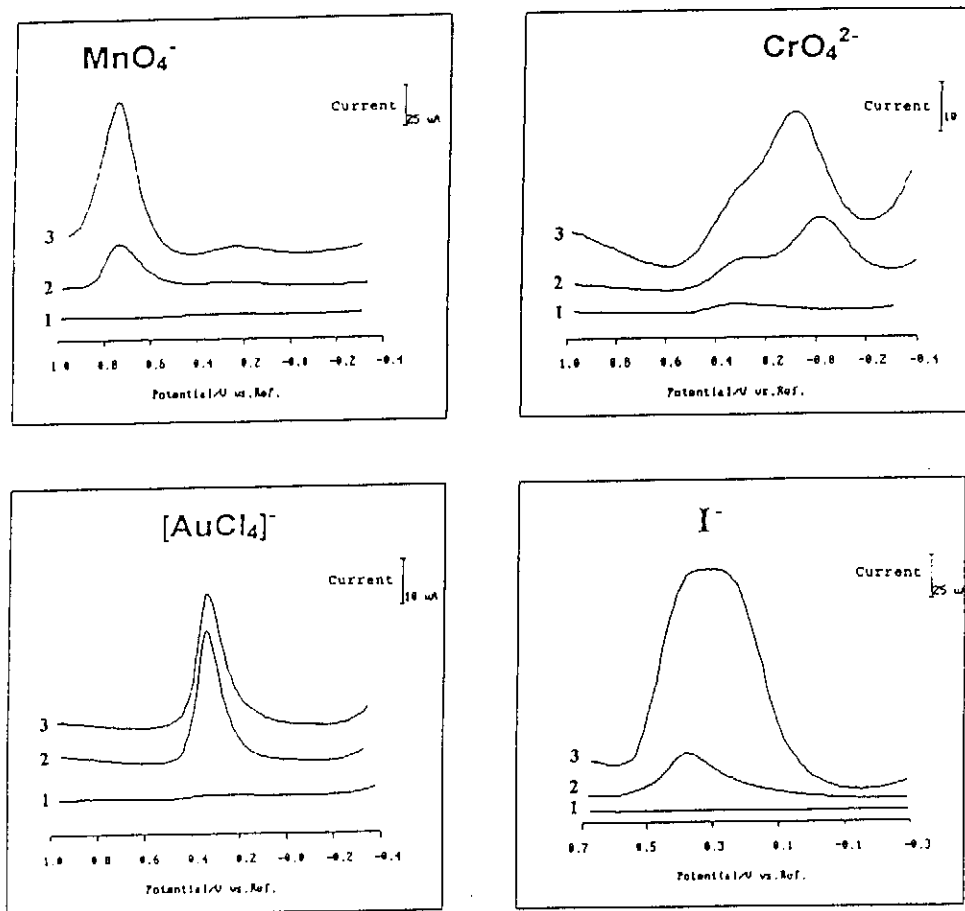
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Fig. 3 Study on the accumulation of some selected inorganic anions at the C/SO carbon paste electrode modified *in situ* with *Septonex*: 1) base-line in the corresponding electrolyte; 2) c(anion) = 1×10^{-5} mol l^{-1}; 3) c(*Septonex*) = 2.5×10^{-5} mol l^{-1}. Experimental conditions: DPCSV, C/SO, 0.1 M HCl (for analysis of AuCl$_4^-$), 0.5 M NaCl + 0.1 M HCl (CrO$_4^{2-}$, I$^-$), 0.1 M Na$_2$SO$_4$ + 0.1 M H$_2$SO$_4$ (MnO$_4^-$); E_{ACC} = +1.0 V, t_{ACC} = 1 min, t_{EQ} = 15 s, v = 20 mV s^{-1}, ΔE = -50 mV

During testing individual CPEs modified with *Septonex*, it was found that the C/SO electrode had povided the most satisfactory performance for accumulating anionic species which was mainly thanks to very favourable signal-to-noise characteristics of this electrode [20,21].

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Cathodic Stripping Voltammetry of Iodide at the C/Uv Electrode Modified with Septonex. Characterization of the Method and Its Application in Practical Analysis.

Basic principles of a stripping voltammetric method for the determination of iodide employing ion-pairing-based accumulation were already mentioned in the Introduction. Detailed theoretical background on the mechanism of preconcentrating the iodide species *via* ion-pairing at modified carbon pastes, comments on the strategy of optimizing experimental conditions as well as discussion on possible interferences are beyond the scope of this article and can be found elsewhere [15]. This paragraph concerns rather practical aspects of the method, including practical consideration of its applicability.
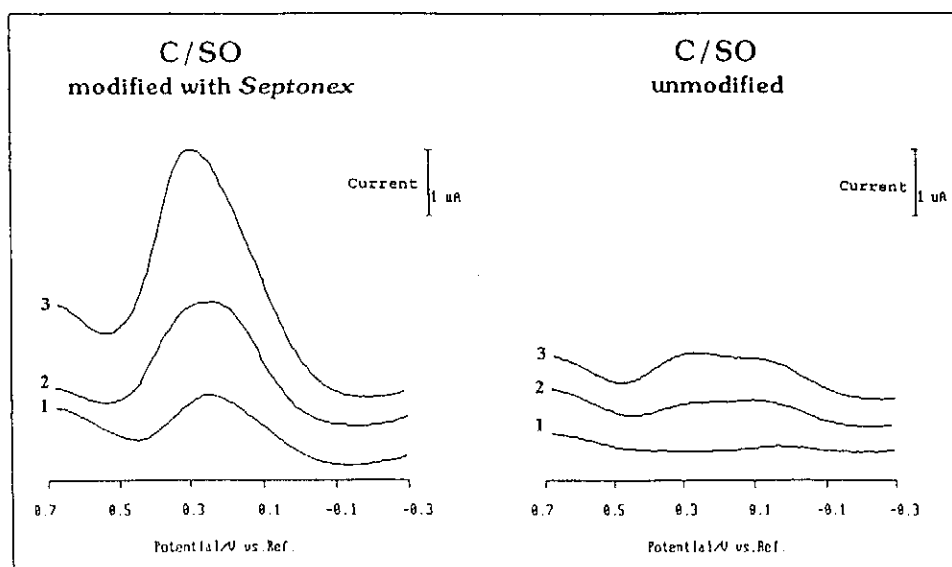

Fig. 4 Voltammetric responses for iodide after its accumulating at modified and unmodified C/SO carbon paste electrode: 1) base-line + 4×10^{-6} M I⁻; 2) + 8×10^{-6} M I⁻; 3) + 1.2×10^{-5} M I⁻. Experimental conditions: DPCSV, C/SO, 0.05 M NaCl + 0.05 M HCl (pH 1.5), c(*Septonex*) = 1×10^{-5} mol l⁻¹, E_{ACC} = +0.7 V, t_{ACC} = 2 min, t_{EQ} = 15 s, v = 20 mV s⁻¹, ΔE = −50 mV

Figure 4 makes a comparison between the responses for reduction of iodide after its accumulating as the Septonex | iodide ion-pairs and between the signals obtained at unmodified CPE. The respective voltammograms illustrate clearly the efficiency of ion-pairing accumulation at modified CPE. Small and plateau-like responses recorded with unmodified electrode can be attributed to extractive

accumulation. (Iodine released at the electrode at the positive potential applied is extractable onto pasting liquid and can therefore yield a response during voltammetric reduction scanning [24].) In accordance with previous results [15], the main constituent of the supporting electrolyte was sodium chloride; however, its concentration had to be lowered in order to ensure the optimum function of surfactant which — when being immobilized *in situ* — requires a medium with a relatively low salinity [10]. Also, a majority of other experimental parameters and their choice were similar to those described previously (see [15]) and they will not be further commented here.

For ion-pairing of iodide, the C/SO electrode offered again the most favorable properties among three *Septonex*-modified CPEs tested and therefore silicone oil-based CPE was chosen for all practical analyses.

Table I summarizes the results of determination of iodide in model solutions, including important experimental data and parameters. Acceptable recovery rate was calculated for both model solutions with 500 and 5000 μg I^- I^{-1} whereas the analysis of model solution No. 3 yielded somewhat higher value, indicating a limited applicability of the method to samples with a very low concentration of iodide.

Table I   Voltammetric determination of iodine in model solutions. Survey of the results and some parameters of the method

Model solution spiked with, μg I^- I^{-1}	Number of analyses	Found, μg I^- I^{-1} [1)]	Recovery rate, %	Reproducibility, % [2)]	Background current level, nA [3)]
5000	3	4660	93	5.0	30
500	4	439	88	9.3	50
5	3	70	140	14.4	120

signal proportional to concentration: $50 - 10\,000$ $\mu g I^-$ I^{-1} (i.e., $4 \times 10^{-7} - 8 \times 10^{-5}$ mol I^{-1}); detection limit (3:1 signal-to-noise criterion, $t_{ACC} = 15$ min.): 25 μg I^- I^{-1} (2×10^{-7} mol I^{-1})

[1)]   given as the arithmetic mean;
[2)]   calculated as the relative standard deviation of 5 replicates;
[3)]   orientation value indicating the average noise at the base-line of C/SO within the potential range of interest (from +0.5 to 0.0 V vs Ag/AgCl)

Table II surveys the results of analysis of mineral water samples together with those obtained with the reference ICP-MS method. The data in the table show a good agreement between both instrumental techniques and correspond also to the values declared by producers of both mineral waters.

Table II Determination of iodine in real samples. Survey of the results obtained by voltammetric method with C/SO modified with *Septonex* and using ICP-MS

Mineral water sample		Found, $\mathrm{mgI^- \, l^{-1}}$ [1]	
Product	Declared content, $\mathrm{mg \, I^- \, l^{-1}}$	Voltammetric method with $(\mathrm{C/SO})_{Septonex}$	Reference determination by ICP-MS
Vincentka	6.59	6.77 ± 0.65	7.00 ± 0.20
Hanácká kyselka	0.155	0.14 ± 0.09	0.137 ± 0.007

[1] given as intervals $\bar{x} \pm s$ (for $\alpha = 0.05$) where $\bar{x}$ is the arithmetic mean and s the relative standard deviation

It can be concluded that the method for voltammetric determination of iodide at a CPE modified with cation-active surfactants offers satisfactory performance. The method is simple, rapid and requires only minimal expenses with respect to chemicals and reagents. Furthermore, practically no sample pretreatment is needed. Advantageous seems to be also the fact that the method utilizes a well-established carbon paste mixture together with *in situ* modification, both simplifying significantly the preparation of the electrode, its eventual surface pretreatments or storage prior to (or after) being used for analysis. Especially the latter was found quite problematic when considering the pros and cons of a recently proposed method employing tricresyl phosphate-containing carbon paste electrode [15]. (This special CPE exhibits rather specific behavior due to ageing effects and usually requires special pre-treatments before use [20].) In comparison with this recently published method, a certain drawback of the approach employing *Septonex*-modified C/SO electrode should be noticed: due to specific nature of *in situ* modification, the C/SO with *Septonex* cannot be applied to analyses of samples with too high ionic strength and salinity [10]. This means that the method is practically inapplicable to determination of iodide, e.g., in table salts which are easily analyzable with tricresyl phosphate-based CPE [15]. Otherwise, both voltammetric methods discussed herein are comparable with respect to their analytical parameters such as the selectivity, reproducibility, the signal-to-concentration linear proportionality or detection limit.

As shown by analysis of real samples, the methodical approach based on *Septonex*-modified C/SO can be recommended for the determination of iodide in mineral waters and related samples; but, there are still some improvements needed to make this method more widely applicable. For instance, its detection limit is not yet low enough in order to achieve the concentration level of iodide typical of common natural waters ($< 1 \times 10^{-7} \, \mathrm{mol \, l^{-1}}$ [25]).

Acknowledgements

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