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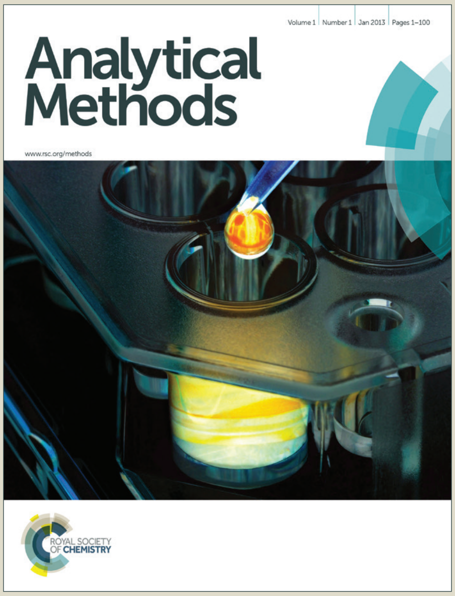

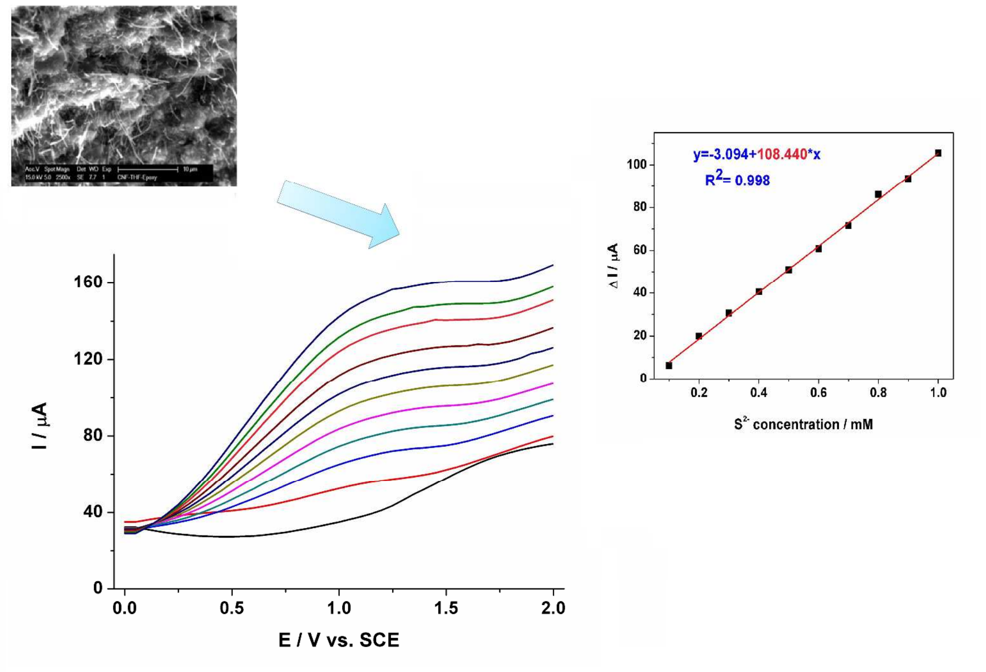

Detection results obtained for sulfide detection in real water at CNF electrode using square-wave voltammetry
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Electrochemical detection of sulphide in water/seawater using nanostructured carbon-epoxy composite electrodes

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In this study, the performances of the carbon nanofibres-epoxy composite (CNF) electrode in comparison with the boron-doped diamond (BDD) electrode were assessed comparatively for the voltammetric/amperometric direct detection of sulphide from water and seawater using cyclic voltammetry (CV), differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV). Both electrodes allowed detecting directly the sulphide from aqueous solutions and carbon nanofibres exhibited the catalytic effect towards sulphide oxidation, which lead to the best sensitivity. The best electranalytical parameters were achieved using pulsed voltammetric techniques, thus, the optimized square-wave voltammetry allowed to achieve the best sensitivity of 347.899 μA mM^{-1} for sulphide detection. However, chronoamperometry (CA) results in real water without supporting electrolyte adding are very promising for practical use of CNF electrode for *in-field* direct detection of sulphide from water and seawater.

1. Introduction

Free sulphide (H_2S, HS^-, S^{2-}) is an exceedingly important substance in the aquatic environment. They are found widely in natural water samples and wastewater and serve as a very important pollution index for water, especial due to its potential to poison many aquatic organisms, even at the micromolar concentrations[1-3]. The presence of sulphide in water as hydrogen sulphide can cause undesirable taste and odour as well as toxic effects on aquatic life. Sulphide can release into aquatic environments through the anaerobic degradation of sulphur containing proteins, amino acids, or other types of organic components. Sulphide salts are frequently used in industrial waste streams to minimize the transport of several toxic metals, *e.g.*, mercury and lead into environment through precipitation reaction.[4] The total level of sulphide in waste discharges has been limited because of its toxicity, oxygen depletion, and production of H_2S. Clinical cases of sulphide poisoning typically present at levels from 30 to 3000 μg L^{-1} and its lethal doses depending on exposure to H_2S, which can be varied in the range of 300–1000 μg L^{-1}.[5] Dissolved sulphide plays an important role within bio-geochemical processes and it is released into aquatic environments by the mining of sulphide-containing minerals and by their mobilization by bacteria.[3,5] In aqueous media function of pH, sulphide can be found in different forms, *i.e.*, dissolved H_2S, bisulfide ion (HS^-, $pKa_1 = 6.88$) and sulphide ion (S^{2-}, $pKa_2 = 14.15$). The determination of sulphide species or total sulphide in waters has received a great importance for environmental chemists.[5]

Sulphur cycling and speciation has been studied in various seawater matrices, *e.g.*, Black Sea[6,7] and Adriatic Sea[8]. The sulphide maximum concentration of 423 μM was determined and three distinct zones of water in the central basin of Black Sea were found: the oxic (0-65 m), the anoxic/non-sulfidic (65-100 m) and the sulfidic zone (>100 m).[6]

Various methods have been developed for measuring sulphide in aqueous and seawater samples. A comprehensive review on the analytical methods related with the detection of sulphide was reported by Lawrence et al.[5] and Pandey et al.[9] Titrimetric,[10] colorimetric,[11,12] spectroscopic,[13] chromatographic[14] and electrochemical[2,15-22] methods have been successfully used for sulphide determination.

Among other sulphide measurement methods, electrochemical techniques exhibit some advantages including their easy application, low cost, and direct, sensitive and fast detection even at low concentrations of sulphide species. Three main electrochemical methods have been reported for sulphide determination, the potentiometry using Ag/Ag_2S ion-selective electrode,[23] the voltammetry[24,25] and the amperometry.[26] For sulphide determination below 1 μM, a preconcentration step (stripping technique) is required. As example, anodic stripping voltammetry (ASV) associated with a mercury film electrode has been reported,[27] but the toxicity of mercury limits its application. A stripping chronopotentiometry procedure have been developed using vibrating gold micro-wire electrode for sulphide determination in hydrothermal seawater samples.[2]

The advantages of the electrochemical methods can be better achieved by modified electrodes eliminating the interference species for the amperometric detection of sulphide in accordance with its electrocatalytic oxidation. The direct electrochemical oxidation of sulphide is highly irreversible with a high overpotential at the bare and common electrodes. Therefore, the oxidation products of sulphide can be adsorbed on the electrode surface resulting fouling and passivation of the electrode surface, which cause poor sensitivity and selectivity as well as unstable analytical signals.

To overcome the interferences, the electrode activity loss and to assure reproducibility, the electrode surface can be modified with redox mediators. Approaches based on redox mediators such as ferrocene sulfonates,[28] cobalt pentacyanonitrosylferrate,[3] and calix[4]arene[11] were employed as amperometric sensors for determining dissolved sulphide in aqueous media.

Carbon-based electrodes are very promising in electroanalysis due to several advantages, *i.e.*, low background current and wide potential window suitable for occurring direct electrochemical oxidation process, chemical inertness, low-cost, and suitability for various sensing and detection application.[29,30] Boron-doped diamond (BDD) electrode,[16] carbon nanotubes-modified glassy carbon and carbon fibre for indirect detection of sulphide[17] have been reported. The suitability of BDD electrode was examined through the electrocatalytic oxidation of ferrocyanide to ferricyanide in the presence of sulphide.

Recently, carbon based materials, such as: graphite, carbon fibres etc. have been used most often as the conductive phase in preparing composite working electrode. Important advances in analytical electrochemistry, particularly in sensor devices have led to the development of composites based on conductive phases dispersed in polymeric matrices. These new materials combine the electrical properties of carbon with the ease of processing of plastics (epoxy, Teflon etc.) and show attractive electrochemical, physical, mechanical and economical features compared to the classic electrodes.[30-32]

This study aimed to examine the direct oxidation of sulphide in order to detect it in aqueous and seawater samples at a carbon nanofibre-epoxy composite electrode (CNF) in comparison with a boron-doped diamond electrode (BDD). Cyclic voltammetry (CV) was used to test the electrochemical response for sulphide determination both in 0.1 M Na_2SO_4 supporting electrolyte and simulated seawater. Also, some mechanistic aspects in direct relation with the detection purposes were discussed using CV. Differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV) techniques were optimized to enhance the electroanalytical performance for sulphide detection from simulated seawater.

2. Experimental

2.1. Preparation and characterization of CNF composite electrode

The dispersion of carbon nanofibers (CNFs) in tetrahydrofuran, 99.9% (THF, Sigma Aldrich) was achieved by ultrasonication using a Cole-Parmer® 750-Watt Ultrasonic Processor for about 10 min prior to mixing with the polymer resin. After the sonication process, the solution of CNFs/THF was sonicated again with epoxy resin to obtain a more homogeneous mixture. An effective method, two roll mill (TRM) of achieving high levels of dispersion and distribution was used to prepare the electrode composition.

The ratio between the components was chosen to reach 20 weight per cent (w/w) content of CNF. During processing the temperature was kept constant at 70°C, the mixing speed was maintained at 10 and 20 rpm for about 40 min, after then the curing agent (weight ratio of epoxy resin: curing agent was 100:38) was added to CNF- resin mixture and mixing was continued for an additional 20 min to ensure an uniform dispersion within the sample.

The mixture was then poured into PVC tubes and cured in a vacuum oven at 80°C for 24 h, after which it was left to cool down at room temperature, and the composite electrode with disc surface area of 19.63 mm^2 was obtained. The electrical contacts of the electrodes were assured using copper wire.

Morphological characterization of the carbon nanofibre-epoxy composite electrode was carried out using scanning electron microscopy (SEM XL20, Philips) with an acceleration voltage of 15 kV.

The electrical conductivity of the carbon nanofiber-epoxy composite electrode was determined by four-point probe (FPP) method[33] based on DC conductivity measurements.

2.2. Electrochemical measurements

The electrochemical studies were performed using an Autolab potentiostat-galvanostat PGSTAT 302 (Eco Chemie, The Netherlands), controlled by a PC using the GPES 4.9 software and a three-electrode cell. The cell structure included a 3 mm working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). CNF composite and BDD electrodes were used as working electrodes for sulphide detection by cyclic voltammetry (CV), differential-pulsed voltammetry (DPV) and square-wave voltammetry (SWV). The commercial BDD electrode supplied by Windsor Scientific Ltd. for electroanalytical use was a mirror polished doped polycrystalline industrial diamond (microcrystalline; doping degree about 0.1% boron). All measurements were performed at room temperature without further temperature control.

The working electrode was cleaned mechanically by polishing on 0.2 μm Al_2O_3 powder, washed in water and then, in ethanol. Before the electrochemical measurements, an electrochemical pre-treatment by ten repeated cycling in a potential range between 0 and +1 V vs. SCE in 0.1 M Na_2SO_4 or simulated seawater supporting electrolyte was performed for BDD electrode. The electrochemical pre-treatment was performed in a potential range between -0.5 and +1.1 V for the CNF electrode.

The electroactive surface area of CNF composite electrode was determined using CV and the classical ferro/ferricyanide–based method.[34] It is well-known that ferro/ferricyanide is one-electron reversible redox system and its electrochemical behavior provides information about the electroactive surface area based on the diffusion coefficient determined based on Randles-Sevcik equation (1):

$$I_p = 2.69\times10^5 AD^{1/2}n^{3/2}v^{1/2}C \qquad (1),$$

where: A represents the area of the electrode (cm^2), n is the number of electrons participating in the reaction and is equal to 1, D is the diffusion coefficient of the molecule in solution, C is the concentration of the probe molecule in the solution (4 mM), and v is the scan rate ($V\ s^{-1}$).

Sodium sulphide was provided by Merck (Germany) and 0.1 M stock solution was prepared using distilled water. The supporting electrolyte was 0.1 M Na_2SO_4 solution, prepared using Na_2SO_4 of analytical purity (Merck, Germany) with distilled water, and simulated seawater consisted of 0.1 M Na_2SO_4 and 1 M NaCl in according with the real seawater composition.

3. Results and discussion

3.1. Morphological and electrical characterization of CNF composite electrode

The qualitative information about the distribution of carbon nanofibers within the epoxy matrix for CNF composite electrode was provided by SEM imaging. Figure 1 shows SEM image of CNF composite electrode and reveals a uniform distribution of carbon nanofibers within epoxy matrix, which assured a good electrical conductivity. Thus, the four-point probe resistance measurement (FPP) has been provided the electrical conductivity for CNF composite of 0.247 Scm^{-1}, which is suitable for the electrochemical application.

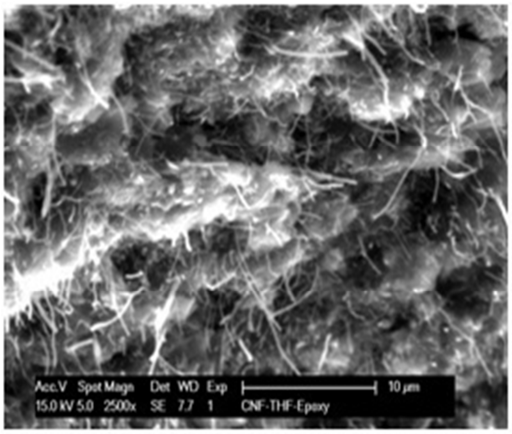

Fig. 1 SEM image of CNF composite electrode surface

3.2. Cyclic voltammetry measurements

The electrochemical behaviors of the commercial boron-doped diamond (BDD) and carbon nanofibre-epoxy composite (CNF) electrodes were tested in 0.1 M Na_2SO_4 and simulated seawater supporting electrolytes. Figures 2 and 3 show cyclic voltammograms recorded with BDD and respective, CNF electrodes in 0.1 M Na_2SO_4 supporting electrolytes and in the presence of various sulphide concentrations ranged between 0.1 and 1 mM.

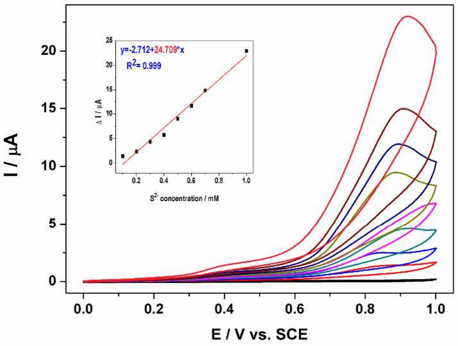

Fig. 2 Cyclic voltammograms recorded on BDD electrode in 0.1 M Na_2SO_4 supporting electrolyte in the presence of 0.1-0.7, 1 mM sulphide, potential scan rate: 0.05 Vs^{-1}; potential range: 0 to +1 V/SCE; Inset: the calibration plots of the current vs. sulphide concentration for the CVs recorded at E= +0.92 V vs. SCE;

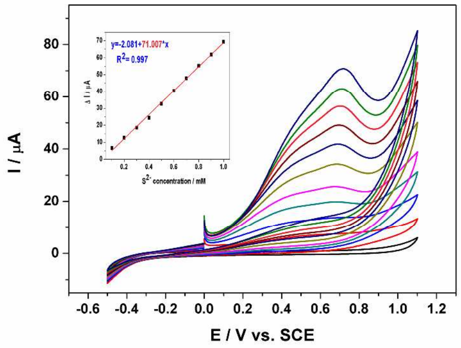

Fig. 3 Cyclic voltammograms recorded on CNF electrode in 0.1 M Na_2SO_4 supporting electrolyte in the presence of 0.1-1 mM sulphide, potential scan rate: 0.05 Vs^{-1}; potential range: -0.5 to +1.1 V/SCE; Inset: the calibration plots of the current vs. sulphide concentration for the CVs recorded at E= +0.715 V vs. SCE;

For both electrodes, the oxidation process of sulphide started at about +0.2 V/SCE, and two oxidation peaks appeared at about +0.4 and respective, +0.8V/SCE suggesting that the sulphide oxidation to the elemental sulphur occurred in two steps, with the formation of S_x^{2-} polysulfide intermediates[35]. The electrochemical oxidation of sulfide occurred in according with the reactions:

$$xS^{2-} \rightarrow S_x^{2-} + (2x-2)e^- \quad (2)$$
$$S_x^{2-} \rightarrow xS + 2e^- \quad (3)$$

The higher peak was reached at the potential value of +0.7 V/SCE for CNF and +0.9V/SCE for BDD electrode, which was selected further for calibration. The lower potential value of the second oxidation peak informed about better electrocatalytic effect of CNF towards sulfide oxidation in comparison with BDD electrode. The oxidation peak currents increased linearly with sulphide concentrations for both electrodes with the correlation coefficient better than 0.99 (insets of Figures 2 and 3).

In order to apply these electrodes in seawater, a different composition of the supporting electrolyte consisting of 0.1 M Na_2SO_4 +1 M NaCl was tested and named simulated seawater. The question that arises is if the high concentration of chlorine affects or not the sulphide detection.

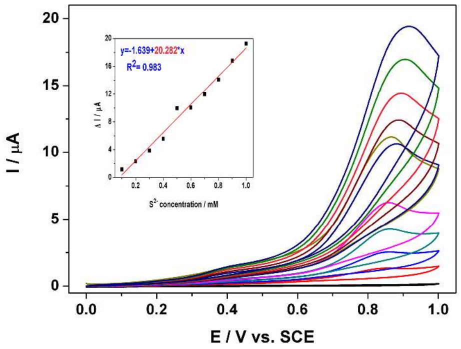

Fig. 4 Cyclic voltammograms recorded on BDD electrode in simulated seawater supporting electrolyte in the presence of 0.1-1 mM sulphide, potential scan rate: 0.05 Vs^{-1}; potential range: 0 to +1 V/SCE; Inset: the calibration plots of the current vs. sulphide concentration for the CVs recorded at E= +0.915 V vs. SCE;

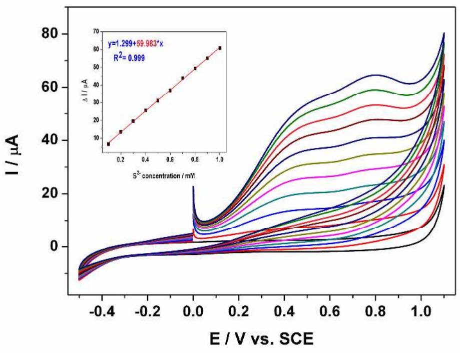

Fig. 5 Cyclic voltammograms recorded on CNF electrode in simulated seawater supporting electrolyte in the presence of 0.1-1 mM sulphide, potential scan rate: 0.05 Vs^{-1}; potential range: -0.5 to +1.1 V/SCE; Inset: the calibration plots of the current vs. sulphide concentration of the CVs recorded at E= +0.8 V vs. SCE;

Figures 4 and 5 show cyclic voltammograms recorded with these electrodes in the simulated seawater as supporting electrolytes and in the presence of various sulphide concentrations (the same range as previous). No significant changes of the voltammogram shapes were noticed and the oxidation peaks were not affected by the chlorine presence. This promising behavior makes it suitable for testing in seawater for direct anodic detection of sulphide. Also, the large potential window and implicit, the high overpotential for chlorine and oxygen evolution are found and desired for direct anodic detection of sulphide on BDD electrode without the interference of the chlorine evolution. Also, in this system a good linearity between anodic peak current and sulphide concentration is achieved (with a correlation coefficient higher than 0.95).

Even if the anodic peaks seem to be more pronounced for BDD, the values of the background currents are very low and as consequence, the sensitivity is low. The higher background current the higher sensitivity is achieved. Thus, the sensitivity for sulphide detection using CV at CNF electrode was higher in comparison with the one reached for BDD electrode, which can be attributed to the catalytic effect of CNFs towards the sulphide oxidation.

In order to elucidate some aspects regarding the electrooxidation process of sulphide, the effect of the scan rate was studied for both electrodes using simulated seawater supporting electrolyte for a sulphide concentration of 0.5 mM, the results being presented in Figures 6 and 7.

From the insets presented in both figures it can be noticed the linear dependences of the anodic peak currents versus the square root of the scan rates, suggesting that the oxidation reaction of sulfide is a diffusion-controlled process at both electrodes, which is very desired for the detection application. The electrode potential for the sulfide oxidation shifted towards positive value with increasing the scan rate indicates that the electrooxidation process is irreversible, which is supported also, by the lack of the cathodic peak corresponding to the anodic one.

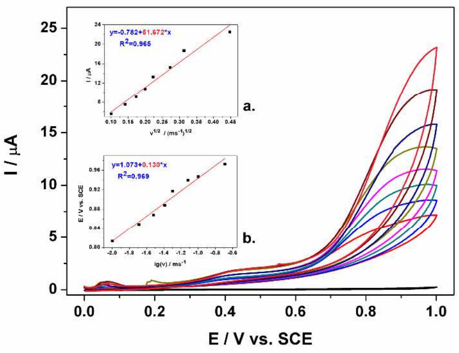

Fig. 6 Cyclic voltammograms recorded on BDD electrode in simulated seawater supporting electrolyte in the presence of 0.5 mM sulphide in a potential range: 0 to +1 V/SCE, at different scan rates: 0.01, 0.02, 0.03, 0.04, 0.05, 0.075, 0.1, 0.2 V/s; Insets: **a)** The calibration plots of the anodic peak current vs. square root of the scan rate; **b)** The calibration plot of the peak potential E vs. log (v);

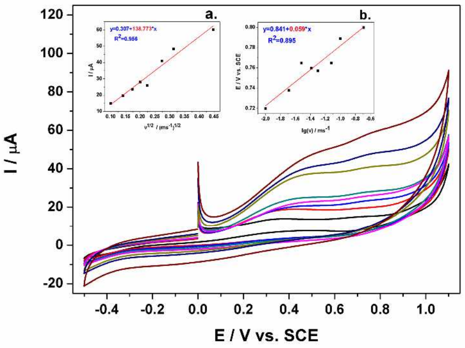

Fig. 7 Cyclic voltammograms recorded on CNF electrode in simulated seawater supporting electrolyte in the presence of 0.5 mM sulphide in a potential range: -0.5 to +1.1 V/SCE, at different scan rates: 0.01, 0.02, 0.03, 0.04, 0.05, 0.075, 0.1, 0.2 V/s; Insets: **a)** The calibration plots of the anodic peak current vs. square root of the scan rate; **b)** The calibration plots of the peak potential E vs. log (v);

3.3. Detection measurements

3.3.1. Differential-pulsed voltammetry

In comparison with CV, it is well-known that differential-pulsed technique (DPV) is more sensitive and promising for detection experiments. Due to the operating parameters are responsible for electroanalytical performance, the effects of DPV parameters on the response of CNF electrode have been studied. Pulse amplitude (a), step potential (ΔE_s) and scan rate (v) were optimized in direct relation to the sensitivity and the results are presented in Table 1. The best sensitivity for sulfide detection was achieved for pulse amplitude of 0.2 V, a step potential of 0.05 V and a scan rate of 0.05 Vs^{-1}, those conditions being considered more suitable for further studies. The DP voltammograms recorded under these parameters in a potential range from -0.2V to +1V are presented in Figure 8.

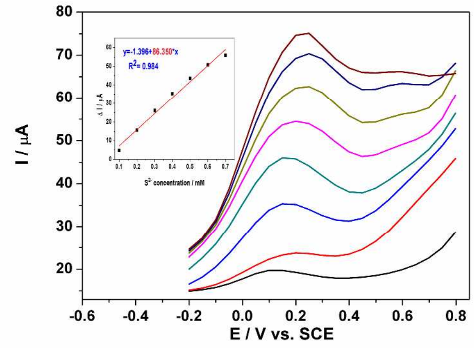

Fig. 8 Differential- pulsed voltammograms recorded on CNF electrode in simulated seawater supporting electrolyte under optimized conditions: a=0.2V; ΔE_s=0.05V; v=0.05Vs^{-1}, in the potential range -0.2 to +1 V/SCE in the presence of 0.1-0.7 mM sulphide concentrations. Inset: The calibration plots of the currents recorded at E = 0.22 V/SCE vs. sulphide concentration;

Also, during the optimization process it was observed that the oxidation peak shifted towards more negative values, a very desirable condition in electroanalysis. For these operating conditions, the first oxidation step is more activated, and the detection potential is about +0.2 V/SCE.

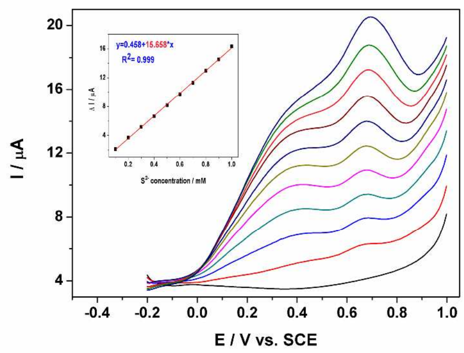

Fig. 9 Differential- pulsed voltammograms recorded on CNF electrode in simulated seawater supporting electrolyte under the following conditions: a=0.05V; ΔE_s=0.01V; v=0.05Vs^{-1}, in the potential range -0.2 to +1 V/SCE in the presence of 0.1-1 mM sulphide concentrations. Inset: The calibration plots of the currents recorded at E =0.7 V/SCE vs. sulphide concentration;

For a pulse amplitude of 0.05V, a step potential of 0.01V and a scan rate of 0.05 Vs^{-1}, the oxidation peak occurred at about + 0.7 V/SCE (Figure 9) in comparison with +0.22V/SCE occurred under the above-specified optimized conditions (Figure 8). Under these conditions, the second oxidation step is activated and the higher detection potential was selected.

As it was expected, the oxidation peak appeared at the lower potential value versus CV (+0.22 V/SCE vs. +0.8 V/SCE) and better sensitivity was achieved (86.350 μAmM^{-1} vs. 59.983 μAmM^{-1}).

Table 1 The dependence of the sensitivity on the operating DPV parameters: modulation amplitude (**a**), step potential (**ΔE_s**) and scan rate (**v**);

a (V)	ΔE_s (V)	v(Vs^{-1})	Sensitivity(μA mM^{-1})
0.05	0.01	0.05	15.658
0.1	0.01	0.05	32.496
0.1	0.02	0.05	35.838
0.1	0.05	0.05	58.570
0.2	0.01	0.05	61.124
0.2	0.02	0.05	71.782
0.2	0.02	0.1	75.858
0.2	**0.05**	**0.05**	**86.350**
0.2	0.05	0.1	75.555
0.2	0.1	0.1	68.750

3.3.2. Square-wave voltammetry

Under the optimized operating conditions established for DPV, another comparative voltammetric technique was employed. Using a pulse amplitude of 0.2 V and a step potential of 0.05 V, the frequency was varied in order to improve the electroanalytical parameters. The results are presented in Table 2.

Table 2 The dependence of sensitivity and correlation coefficient on square-wave voltammetry frequency applied under the optimized operating conditions: modulation amplitude of 0.2 V and step potential of 0.05 V

f (Hz)	Sensitivity(μA mM^{-1})	R^2
10	171.957	0.983
25	267.860	0.973
50	347.899	0.958

For all the studied frequencies (10, 25 and 50 Hz) it was observed a good liniarity between the anodic peak current and sulfide concentration, which supported also the difussion-controlled process for sulfide electrooxidation. However, the best sensitivity with the good correlation coefficient was achieved for SWV frequency of 50 Hz selected as optimum.

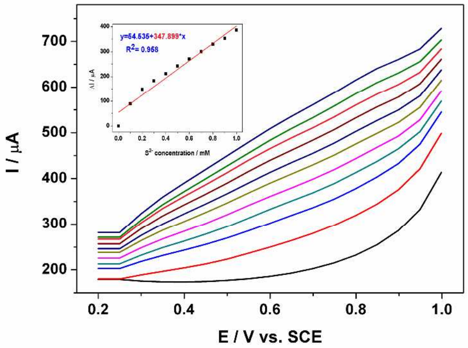

Fig. 10 Square-wave voltammograms recorded on CNF electrode in simulated seawater supporting electrolyte under optimised conditions at a frequency of 50 Hz in the potential range +0.2 to +1 V/SCE in the presence of 0.1-1 mM sulphide concentrations. Inset: The calibration plots of the currents recorded at E = 0.855 V/SCE vs. sulphide concentration.

Figure 10 shows the square-wave voltammograms recorded at various sulphide concentrations in the simulated seawater in a potential range between +0.2 and +1V vs. SCE.

In comparison with CV and DPV, SWV technique operated at 50 Hz frequency allowed to achieve the best electroanalytical performance regarding sensitivity of sulphide on CNF electrode (Table 3).

3.3.3. Chronoamperometry

Considered one of the easiest electrochemical techniques, chronoamperometry was employed based on the existing well-established essential point of reference provided by the voltammograms. Figure 11 presents the current-time profiles recorded after 100 seconds, obtained by setting the working electrode at +0.9 V/SCE for the established concentration range. The linear dependence between current and concentration is also valid, although the sensitivity is lower than in voltammetric techniques. (17.027 µA mM^{-1} vs. 59.983 µA mM^{-1}). The lower sensitivity is due to a possible adsorption process of sulfide on the electrode surface and as consequence, a fouling effect occurred.

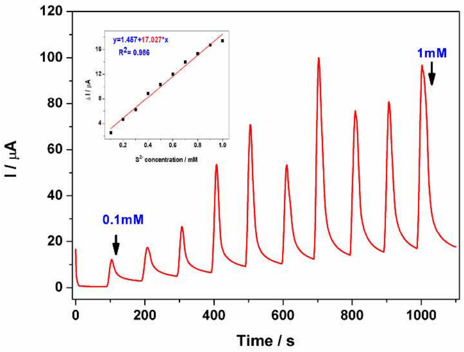

Fig. 11 Chronoamperogram recorded on CNF electrode in simulated seawater supporting electrolyte at E =0.9 V vs. SCE in the presence of 0.1-1 mM sulphide concentrations. Inset: The calibration plots of the currents vs. sulphide concentrations.

The electroanalytical parameters achieved by each applied electrochemical technique are gathered in Table 3. The SWV technique allowed reaching the best sensitivity but at high potential value (+0.85V/SCE), while using DPV the best LOD and respective, LQ were reached at low potential value (+0.22 V/SCE). Also, CA results are promising for practical *in-field* detection application.

3.3.4. Application on real water sample

The three of previous-discussed techniques, *i.e*, CV (Figure 12), SWV (Figure 13) and CA (Figure 14) were applied on a real surface water sample (Bega river, Timisoara, Romania). This test aims two approaches, the first refers to use of this electrode in the detection application without supporting electrolyte adding, which represents a major advantage especial for *in-field* applications. Also, the interference of the real water matrix in the sulphide detection is studied. The electroanalytical results are gathered in Table 4.

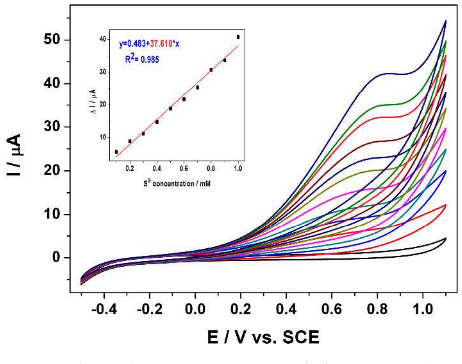

Fig. 12 Cyclic voltammograms recorded on CNF electrode in a real water sample in the presence of 0.1-1 mM sulphide, potential scan rate: 0.05 Vs^{-1}; potential range: -0.5 to +1.1 V/SCE; Inset: the calibration plot of the current vs. sulphide concentration of the CVs recorded at E= +0.85 V vs. SCE.

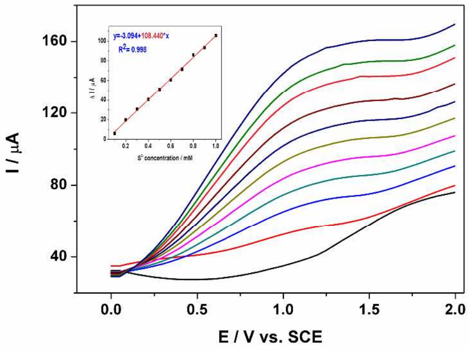

Fig. 13 Square-wave voltammograms recorded on CNF electrode in a real water sample under optimised conditions at a frequency of 50 Hz in the potential range 0 to +2 V/SCE in the presence of 0.1-1 mM sulphide concentrations. Inset: The calibration plots of the currents recorded at E = 1.435 V/SCE vs. sulphide concentration;

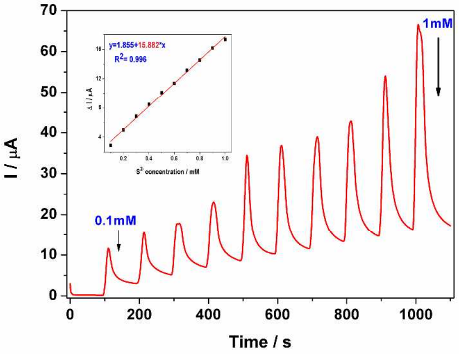

Fig. 14 Chronoamperogram recorded on CNF electrode in a real water sample at E =+0.9 V vs. SCE in the presence of 0.1-1 mM sulphide concentrations. Inset: The calibration plot of the currents vs. sulphide concentrations.

The best sensitivity was obtained under SWV technique (108.44 µA mM^{-1}), although there is a significant difference between this value and the one achieved for the simulated water. This can be explained by the lower value of ionic strength of the real water in comparison with the supporting electrolyte.

Also, the lowest limit of detection and respective, the lowest limit of quantification was obtained for CA technique (statistical computation of the small values of the blank led to this result), which is in direct relation with the background current. These results, especial CA behavior proved that this electrode exhibited a great potential for the real *in-field* direct detection of sulphide from water and seawater without any supporting electrolyte adding. This electrochemical behavior is specific to the microelectrode array, which has been already reported by our group for other carbon-based composite electrode.[36]

Table 3 The electroanalytical parameters obtained for sulphide detection in simulated seawater at CNF electrode by applying electrochemical techniques

Electroanal. Techniques	E /V vs. SCE	Sensitivity (µA mM^{-1})	R^2	RSD (%)	LOD (mg L^{-1})	LQ (mg L^{-1})
CV	0.8	59.983	0.997	2.32	0.141	0.470
DPV	0.22	86.350	0.984	0.22	**0.048**	**0.161**
SWV	0.85	**347.899**	0.958	3.40	0.941	3.139
CA	0.9	17.027	0.986	12.91	0.401	1.337

Table 4 The electroanalytical parameters obtained for sulphide detection in a real water sample at CNF electrode by applying electrochemical techniques

Electroanal. Techniques	E /V vs. SCE	Sensitivity (µA mM^{-1})	R^2	RSD (%)	LOD (mg L^{-1})	LQ (mg L^{-1})
CV	0.85	37.619	0.985	6.95	0.288	0.963
SWV	1.435	108.44	0.998	0.24	0.117	0.390
CA	0.9	15.882	0.996	4.94	0.056	0.187

Conclusions

Both carbon nanofibre-epoxy (CNF) and boron-doped diamond (BDD) electrodes exhibited the useful peculiarities for the anodic oxidation and the voltammetric detection of sulphide from the aqueous solutions. The diffusion-controlled anodic oxidation of sulphide on these electrodes is much desired for the electroanalysis application.

Cyclic voltammetry results obtained in the presence of various sulfide concentrations showed that CNF electrode exhibited superiority regarding the sensitivity of sulphide detection in comparison with BDD electrode, due to the electrocatalytic effect of CNF electrode towards the sulphide detection.

In comparison with CV, pulsed voltammetric techniques allowed enhancing the sulphide detection performance. The best sensitivity in simulated seawater was achieved under optimized square-wave voltammetry technique with modulation amplitude of 0.2 V, step potential of 0.05 and frequency of 50 Hz. The lowest limit of detection and lowest limit of quantification were achieved under optimized differential pulsed voltammetry technique (0.048 mg/L and respective, 0.161 mg/L).

The promising application results on a real water sample using chronoampeormetry technique reclaim the carbon nanofibre-epoxy composite electrode for its use for the practical *in-field* direct detection of sulphide in water/seawater.

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Notes and references

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