

Investigation and elimination of surfactant-induced interferences in anodic stripping voltammetry for the determination of trace amounts of cadmium

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Abstract: This article aims to investigate in detail to what extent surfactants affect the determination of cadmium by anodic stripping voltammetry. In recent years, the production and use of surfactants have been steadily increasing, so that their concentration in environmental water samples is rising. At the same time, it is known that organic compounds, such as surfactants, often hinder the voltammetric determination of trace elements by stripping. Non-ionic (Triton X-100, Brij 35, Tween 20, Tween 60, Tween 80), cationic (CTAB, CTAC, DTAB, HPC) and anionic (DSS, SDS) compounds were selected to investigate the effect of surfactants on the voltammetric signal of cadmium. At the same time, the extent to which the addition of Amberlite resins to the analysed solution eliminates the interfering effect of surfactants was tested. Three types of Amberlite resins XAD-2, XAD-7 and XAD-16 were selected for the study and the ratio of resin weight to solution volume was determined. Finally, the determination of cadmium in surfactant-enriched environmental samples was carried out. The recoveries obtained between 95.5 and 107%, with RSD between 3.4 and 6.2%, confirm the validity and correctness of the proposed procedure. All measurements were carried out by anodic stripping voltammetry using a CNTs/SGC electrode modified with a bismuth film as the working electrode.

Keywords: cadmium, stripping voltammetry, surfactants, Amberlite resins

1. Introduction

Contaminants in environmental water samples can have different chemical characteristics and, in a preliminary classification, they can roughly be divided into organic, inorganic and metal species pollutants (Bruzzoniti et al., 2000). Monitoring each of them is necessary for full control and estimation of the quality of natural water samples. Unfortunately, the determination of one of them is very often disturbed by another one. In this paper attention will be focused on the influence of surface active substances on trace cadmium determination.

Cadmium is one of the most serious metallic threats to the environment and humans. It is found in all components of the environment, including natural waters, soils, and plant and animal organisms. To make matters worse, this element has a long half-life and once it enters the environment, it is not degraded and remains in constant circulation. It is highly toxic even at low concentrations due to its rapid movement in the trophic chain, soil-plant-human, easy absorption and bioaccumulation in living organisms (Hasanuzzaman et al., 2019). Cadmium poisoning is a very common and serious problem. It causes cardiovascular dysfunction as well as damage to human organs such as the kidneys, liver, lungs, pancreas and testes. This element impairs the functioning of the immune system and is also a cause of oxidative stress and inflammation, so it can promote the development of cancer. It increases the risk of lung, kidney, liver, testicular and prostate cancer. In extreme cases, poisoning by this metal leads to respiratory failure and death (Genchi et al. 2020; Satarug et al., 2003). According to the recommendations of the FAO/WHO, the tolerable consumption of cadmium by an adult is 25 µg/kg of body weight per

month, and the permissible dose is 0.8 $\mu\text{g}/\text{kg}$ of body weight per day (WHO 2011) (WHO Technical Report Series 960, 2011).

Not surprisingly, the determination of cadmium is one of the most important issues in analytical chemistry. This is also reflected in the number of procedures described in the literature and dedicated to the determination of cadmium by various methods. One of the first-choice methods for cadmium analytics is voltammetry, which offers a number of advantages such as, first and foremost, a low detection limit and, at the same time, relatively low instrument cost, as well as speed and simplicity of measurement. This is confirmed by the number of publications devoted to the development of newer and better voltammetric cadmium determination procedures [Abdel and Mahmoud, 2023; Ahmed et al., 2023; Bu et al., 2020; Karazan and Roushani, 2023; Rahim and Mahmoud, 2023; Rojas-Romo et al., 2020; Tapia et al., 2023; Thanh et al., 2019; Wang et al., 2022; Zarei et al., 2022]. And the number of such publications is constantly increasing, demonstrating voltammetry as the method of first choice and the need for further improvements. Unfortunately, one of the main disadvantages of voltammetric methods is the interference associated with the presence of surfactants, which can cause a reduction or complete loss of signal of the labelled ion, making analysis impossible [Grabarczyk and Koper, 2022; Hoyer and Jensen, 2003; Kubiak and Wang, 1989].

Surfactants are characterized by a specific structure consisting of hydrophobic elements and a hydrophilic part thanks to which they reduce the surface tension of liquids. Owing to this property, surfactants exhibit many useful functions as washing agents, wetting agents, dispersing agents, foaming agents, solubilizing agents, emulsifying agents and others. The diversity of the structure of surfactants determines the wide range of their applications. They are compounds used, for example, as ingredients in detergents and cosmetics, including personal care products such as liquid soaps, shower gels, shampoos and toothpastes. Thanks to their remarkable properties, surfactants are also widely used in the production of paper, food products, paints and varnishes, as well as in the metallurgical, agrochemical, pharmaceutical, mining, textile, construction and many other industries [Chen et al., 2005; Haiyan, 1997; Li, 2007; Liu et al. 2009; Schramm et al., 2003]. Such widespread use of surfactants is linked to their ubiquity in environmental waters. This, in turn, as mentioned earlier, can contribute to making voltammetric determination of cadmium difficult or impossible [Batley and Florence, 1976; Mackay, 1994; Maleki et al., 2005; Wang and Den-Bai 1984].

The problem of interference in voltammetry caused by surfactants is well known, but nevertheless often overlooked in the determination procedures described in the literature. Also in the case of the voltammetric determination of cadmium, the influence of surfactants was not investigated in the vast majority of procedures, while as regards the determination of environmental samples, a time-consuming mineralization of real samples before the actual measurement is often recommended. One important factor influencing the extent to which surfactants interfere with voltammetric determination is the type of electrode acting as the working electrode. Mercury-based electrodes are very sensitive to the presence of surfactants in the sample, as surfactants readily adsorb to the mercury surface blocking the surface. In addition, mercury as a toxic material is being eliminated from voltammetric procedures and replaced by other more environmentally friendly materials. One of the most common replacements for mercury electrodes in voltammetric analysis today are bismuth electrodes, which were introduced by Wang in 2000 [Adamczyk et al., 2022; Bobrowski et al., 2010; Królicka et al., 2014; Wang et al., 2000; Wasąg and Grabarczyk, 2016; Węgiel et al. 2017]. Since then, a number of procedures using bismuth electrodes as working electrodes for cadmium accumulation have also been developed in anodic stripping voltammetric (ASV) analysis of cadmium. Unfortunately, none of these works examined how the cadmium signal is affected by surfactants [Grabarczyk et al., 2023; Karazan and Roushani, 2023; Rojas-Romo et al., 2020; Thanh et al., 2019; Wang et al., 2022].

Therefore, the aim of the research carried out in this work is to investigate in detail to what extent surfactants affect the cadmium signal in a voltammetric procedure using a bismuth based electrode. A wide range of anionic, cationic and non-ionic surfactants was used in the research, such as anionic surfactants: 1-dodecanesulfonate (DSS), sodium dodecyl sulfate (SDS), cationic surfactants: dodecyltrimethylammonium bromide (DTAB), cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), and hexadecylpyridinium chloride (HPC), and non-ionic

surfactants: Triton X-100, Brij 35, Tween 20, Tween 60, and Tween 80, to obtain the widest possible spectrum of research.

Another aim of this study was to propose a simple and quick procedure for the determination of trace amounts of cadmium in the presence of high concentrations of surfactants. For this purpose, three types of Amberlite type resins (XAD-2, XAD-7, XAD-16) were tested, which, introduced directly into the measuring cell, remove surfactants from the sample solution, increasing the sensitivity of cadmium determinations in the presence of even high concentrations of surfactants. The permissible concentrations of different surfactants that do not interfere with the cadmium signal were investigated as a function of the mass of resin introduced into the sample solution. The adsorptive properties of microreticular adsorbents, especially Amberlite XAD resins to collect organic substances are commonly known [Lepane 1999; Estevez et al. 1995]. XAD resins adsorb organic matter mainly by hydrophobic bonding, however, the exact mechanism of adsorption is unknown. Most XAD resins are nonpolar and XAD-7 is the only "moderately polar" XAD resin now available. [Janos 2003].

The study was carried out using the ASV method with a CNTs/SGC electrode modified with a bismuth film. The electrode was based on spherical glassy carbon (SGC) microparticle powder and multiwall carbon nanotubes (CNTs), which gave it unique properties mainly related to the lowering of the detection limit due to the use of carbon nanomaterials with a large specific surface area [Ahammad et al., 2009; Britto et al., 1996; Kaliyaraj Selva Kumar et al., 2022; Nemcova et al., 2012; Wang and Yue, 2017]. The novel CNTs/SGC electrode was in situ modified with a bismuth film with simultaneous accumulation of cadmium in metallic form on it. As demonstrated in the paper [Grabarczyk et al., 2023], the procedure for the determination of Cd(II) based on this electrode, in addition to its low detection limit, is characterized by a wide range of linearity and high selectivity to many foreign ions. In our study, we investigated in detail the effect of a wide range of surfactants on the voltammetric cadmium signal obtained by the ASV method using the electrode described above.

2. Materials and methods

2.1. Instrumentations

The voltammograms were recorded using a μ Autolab analyzer (Utrecht, The Netherlands) with a personal computer operated by GPES 4.9 software. The electrochemical cell consisted of a carbon nanotubes/spherical glassy carbon (CNTs/SGC) electrode as the working electrode, Ag/AgCl (saturated NaCl) as a reference electrode and a platinum wire as an auxiliary electrode. The CNTs/SGC was fabricated as described in the paper [Grabarczyk et al., 2023]. Each day before measurements, the electrode was polished with a 0.3 μ m aluminum oxide suspension on a Buehler polishing pad for 30 s and then immersed in an ultrasonic bath for 30 s.

2.2. Reagents

A stock standard solution of Cd(II) with a concentration of 10^{-5} mol L⁻¹ was prepared from a standard solution of 1 g L⁻¹ acquired from Fluka (Buchs, Switzerland). The 1 mol L⁻¹ acetate buffer pH = 3 ± 0.1 (1 mol L⁻¹) was prepared from Suprapur CH₃COOH and NaOH obtained from Merck. Triton X-100, sodium dodecyl sulfate (SDS) and cetyltrimethylammonium bromide (CTAB) were purchased from Fluka (Buchs, Switzerland). Dodecyltrimethylammonium bromide (DTAB) was obtained from Sigma. Cetyltrimethylammonium chloride (CTAC) and sodium 1-dodecanesulfonate (DSS), Brij 35 and hexadecylpyridinium chloride (HPC), Tween 20, Tween 60 and Tween 80 were obtained from Sigma-Aldrich (St. Louis, USA). Amberlite XAD-2, XAD-7 and XAD-16 obtained from Sigma was washed four times in water and dried at a temperature of 50 °C. All solutions were made using triply distilled water.

2.3. Procedure

The voltammetric measurement parameters were adopted as in literature data [Grabarczyk et al., 2023]. The analyzed sample or the standard solution containing 50 μ L of 1×10^{-5} mol L⁻¹ Cd(II), and optionally a surface active substance, was pipetted into a voltammetric cell containing 1 mL of 1 mol L⁻¹ acetate buffer pH=3, 313 μ L of 1 g L⁻¹ Bi(NO₃)₃ and the total volume of the solution was finally made up to 10 mL. The voltammetric measurement was carried out according to the following scheme: activation of

the electrode at a potential of -2.0 V for 3 s followed by an accumulation stage at -0.9 V for 50 s. During this time, the formation of a bismuth film and the simultaneous accumulation of cadmium as a result of its reduction to metallic form take place. Then, after a 5 s rest time, a voltammogram was recorded, as a result of the potential change from -1.0 V to -0.4 V, and the peak visible on the voltammogram at a potential of approximately -0.75 V, corresponding to the oxidation of Cd(0) to Cd(II), was directly proportional to the content of Cd(II) ions in the solution. After each measurement, an electrochemical cleaning process of the CNTs/SGC electrode was carried out by applying a potential of 0.2 V to the electrode for 20 s to remove residual metals. To eliminate interference from surfactants, 0.3 g of resin was additionally introduced into the prepared solution in the voltammetric cell, as described above, and the sample was stirred for 3 minutes before voltammetric measurement.

2.4. Preparation of real samples

Real samples, such as Lake Zemborzyce and Ciemiega river water from the outskirts of Lublin, were collected into clean polypropylene bottles and analyzed after minor pretreatment consisting of successive filtration through the Whatman filter No 1 (Sigma-Aldrich) and a 0.45 μm cellulose acetate membrane filter in the Sartorius device. Tap water and rain water were analysed with no pretreatment. Recovery tests were carried out for samples spiked with standard solutions of Cd(II) and different surfactants, which were added to the water samples approximately two hours before analysis.

3. Results

Studies of the influence of surfactant substances on the voltamperometric cadmium signal were carried out using more than a dozen surfactants divided into anionic, cationic and non-ionic species. In addition, in the case of surfactants causing interference by suppressing the cadmium signal, a procedure was used to lessen the interference. For this purpose, the addition of Amberlite type resin to the voltammetric cell was used and the effects of the mass of resin were investigated to ensure the most effective elimination of these interferences.

3.1. Effect of non-ionic surfactants

Triton X-100, Brij 35 and three kinds of Tween (Tween 20, Tween 60, Tween 80), as representatives of non-ionic surfactants, were chosen. Triton X-100 (mixture of octylphenol ethoxylates) is a high-purity liquid, water-soluble non-ionic surfactant, available commercially, which has come to be recognized as a standard among similar products. Triton X-100 is widely used in many commercial and industrial products as a detergent substrate, in textile and fiber production due to its superior wetting ability and excellent grease and oil removal from hard surfaces. Given its widespread use, Triton X-100 is released into the environment in relatively large quantities [Chen et al., 2005; Haiyan, 1997; Li, 2007; Liu et al. 2009]. Brij 35, which is a non-ionic surfactant, is the commercial name for dodecyl-poly-ethylene-oxide-ether containing poly-ethylene-oxide chains as the hydrophilic part and *n*-alkyl chains as the hydrophobic part forming micelles in water. If another solvent (e.g. alcohol) is added to the binary Brij 35/water system, then microemulsions with many interesting properties are obtained. The system has practical applications in cosmetics, pharmaceuticals, paints, cleaning, and biotechnology [Gergely and Madarasz, 2006]. Non-ionic surfactants Tweens, due to their stability and comparative non-toxicity, are often used as detergents and emulsifiers in many household and pharmacological applications. They are used in cosmetics to solubilize essential oils into water-based products and in the pharmaceutical and food industry [Cortes et al., 2021]. Taking this into account, Triton X-100, Brij 35 and Tweens were chosen to study the effect of non-ionic surfactants on the voltammetric cadmium signal.

At the beginning, the impact of these non-ionic surface active substances on the Cd(II) voltammetric signal was studied using a standard procedure, as described in Section 2.3, and the obtained results are presented in Fig. 1. The action of surface active substances is accepted to correspond to the action of Triton X-100 in the concentration range from 0.2 to 2 mg kg⁻¹ [Cosovic and Vojvodic, 1982]. Therefore, in this study investigating the effect of individual surfactants on the voltamperometric cadmium signal, their concentrations in this range were used, while in some cases even above 2 mg L⁻¹. It could be seen that in the presence of 2 mg L⁻¹ of Triton X-100, Tween 80, Tween 60 and Tween 20, the signal of

cadmium was suppressed to about 20%, 40%, 55% and 65%, respectively, relative to the signal recorded in the absence of surfactants (Fig. 2). In the case of Brij 35, its concentration of 1 mg L⁻¹ did not interfere with the cadmium signal and only at its concentration of 2 mg L⁻¹ did the cadmium signal decrease to 85%. To summarize the effect of the non-ionic surfactants on the cadmium signal, it can be concluded that none of the tested non-ionic surfactants affects the cadmium signal in concentrations up to 0.1 mol L⁻¹, while at a concentration of 2 mg L⁻¹, its value decreases in the range of 85 to 15%.

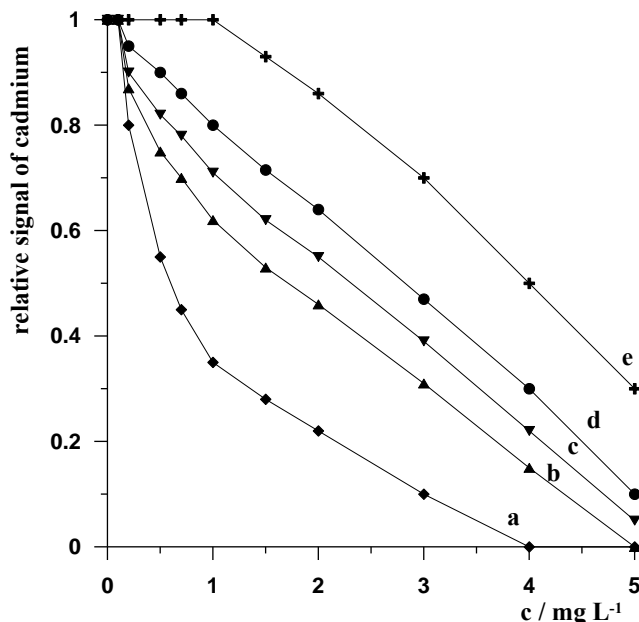


Fig. 1. The relative signal of 1×10^{-5} mol L⁻¹ Cd(II) in the presence of non-ionic surface active substances: Triton X-100 (a), Tween 80 (b), Tween 60 (c), Tween 20 (d), Brij 35 (e)

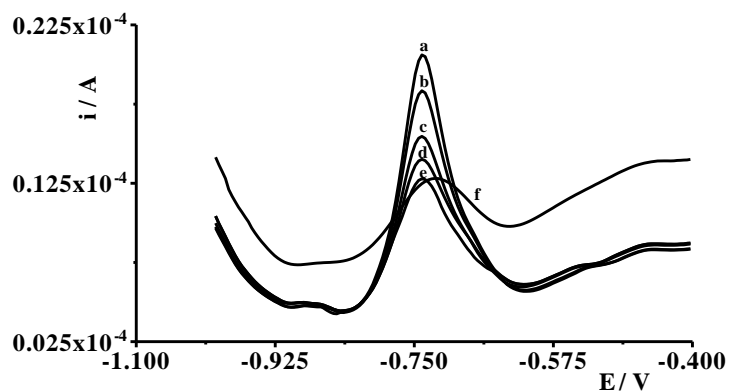


Fig. 2. The voltammograms of 1×10^{-5} mol L⁻¹ Cd(II) recorded in the absence (a) and presence of 2 mg L⁻¹ non-ionic surface active substances: Brij 35 (b), Tween 20 (c), Tween 60 (d), Tween 80 (e), Triton X-100 (f)

3.1.1. Reduction of interferences from non-ionic surfactants

In order to reduce interference from the non-ionic surfactants, it was proposed to use the adsorption properties of Amberlite resins. Three types of Amberlite resins, XAD-2, XAD-7 and XAD-16, were chosen for the study. As demonstrated in preliminary experiments, Cd(II) ions present in the samples at acetate buffer pH=3 do not adsorb onto these types of resins, so these resins could be added directly to the voltammetric cell. Surfactants, on the other hand, readily adsorb onto resins under these conditions and their amount in the solution is thus significantly reduced. As a result, they interfere much less with the analytical cadmium signal. In order to select the optimum mass of resin to be introduced into the voltammetric vessel, the following experiments were carried out. 10 mL standard solutions containing 5×10^{-8} mol L⁻¹ Cd(II), 0.1 mol L⁻¹ acetate buffer pH=3, 1.5×10^{-4} mol L⁻¹ Bi(NO₃)₃

and the following different masses of resins: 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g, were prepared. Subsequently, 5 mg L^{-1} of the surfactants Triton X-100, Brij 35, Tween 20, Tween 60 or Tween 80 was introduced into these solutions, a voltammetric measurement was carried out for each of them after 3 min of stirring, and it was observed how the cadmium signal changed. The results obtained are presented in Figs. 3A-E, which show the relative cadmium signals (calculated relative to the cadmium

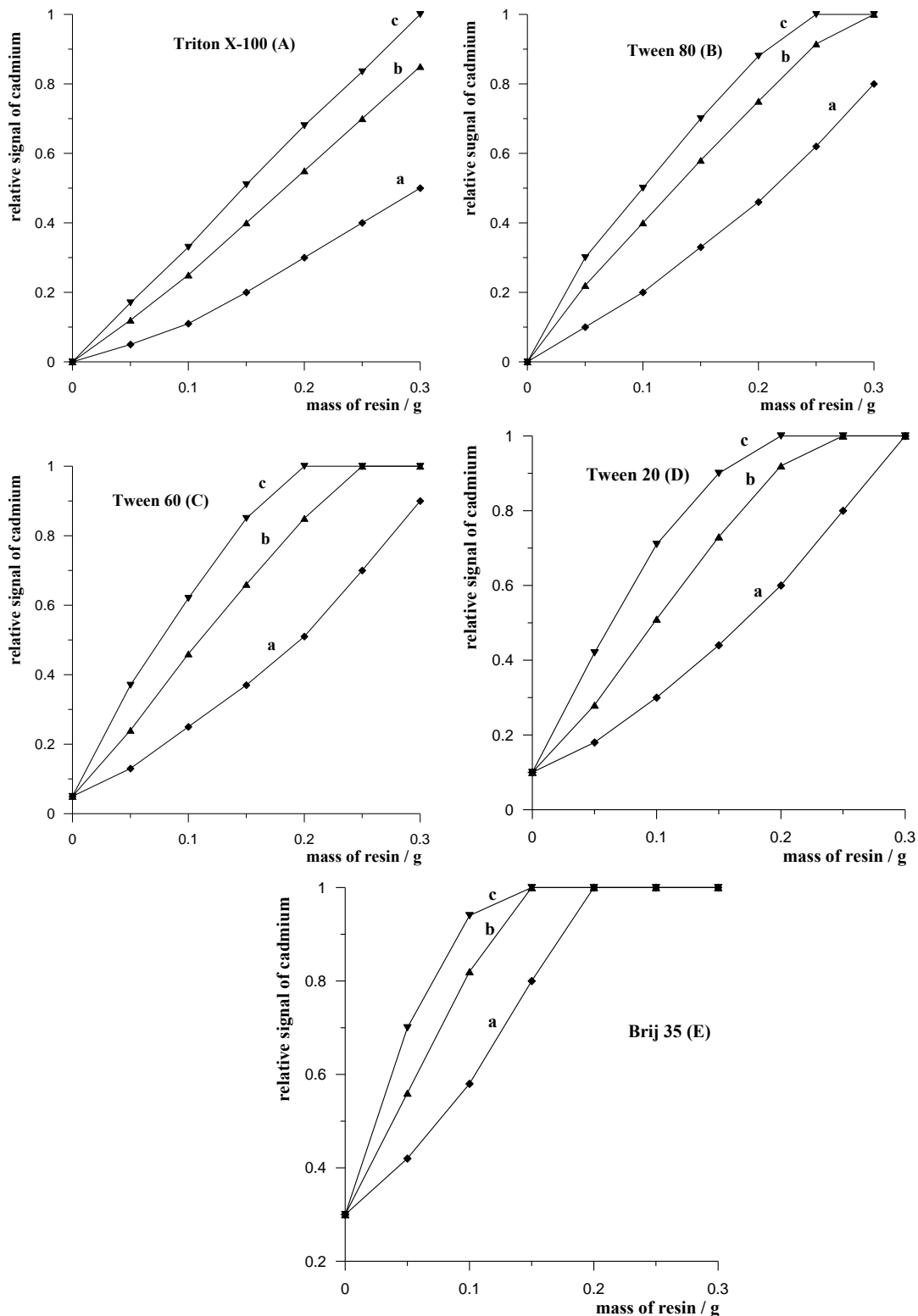


Fig. 3. The relative signal of $1 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd(II)}$ in the presence of 5 mg L^{-1} Triton X-100 (A), Tween 80 (B), Tween 60 (C), Tween 20 (D), Brij 35 (E) after mixing with different masses of resins: XAD-2 (a), XAD-16 (b), XAD-7 (c)

signal obtained in the absence of surfactants) as a function of the mass and type of resin introduced into the voltammetric cell. As can be seen, the cadmium signal increases with increasing resin weight in the cell, indicating that surfactant-induced interference is eliminated to a greater extent with increasing resin weight. For all the non-ionic surfactants tested, the best results in interference elimination were obtained using Amberlite XAD-7 resin, as in the presence of even 5 mg L^{-1} of these surfactants the introduction of 0.3 g of Amberlite XAD-7 resin into the solution completely eliminates interference and the cadmium signal obtains its appropriate value. A slightly weaker efficiency in interference removal was obtained for XAD-16 resin; the addition of 0.3 g of this resin ensures that the cadmium peak obtains its correct magnitude in the presence of 5 mg L^{-1} Brij 35, Tween 20, Tween 60 and Tween 80, while in the case of Triton X-100 the cadmium peak is only reduced by 15%. The weakest performance in interference removal was observed for XAD-2 resin since in the presence of 0.3 g of this resin, the correct cadmium peak is obtained in the presence of 5 mg L^{-1} Brij 35, Tween 20, whereas in the case of Tween 60, Tween 80 and Triton X-100 the cadmium peak is decreased by 10%, 20% and 50%, respectively.

3.2. Effect of cationic surfactants

As regards cationic surfactants, they are widely used in cosmetic chemistry products such as soaps, hair conditioners, shampoos and other hair products. Due to the fact that they are effective antimicrobial agents, cationic surfactants are also widely used as disinfectants and antiseptics as well as in germicidal and disinfectant products. Owing to their positive charge, cationic surfactants strongly adsorb onto negatively charged slurry, soil and sediment surfaces, which is also used in practice. Such widespread use of cationic surfactants demonstrates that these substances should be present in many elements of the environment [Rhein, 2007]. Well-known synthetic cationic surfactants such as cetyltrimethylammonium bromide (CTAB), cetyltrimethylammonium chloride (CTAC), dodecyltrimethylammonium bromide (DTAB) and hexadecylpyridinium chloride (HPC) are one of these, and it is for this reason that they were chosen to study the effect of cationic surfactants on the voltammetric signal of cadmium.

The effect of these cationic surfactants on the voltammetric signal of Cd(II) was investigated using a standard procedure and the results are shown in Figure 4. The measurements were carried out without adding resin to the solution. It could be seen that the cadmium signal disappears in the presence of already 1 mg L^{-1} CTAB, 1.5 mg L^{-1} CTAC and 2 mg L^{-1} DTAB. For HPC, the cadmium signal decreases to about 20% in its presence at a concentration of 2 mg L^{-1} .

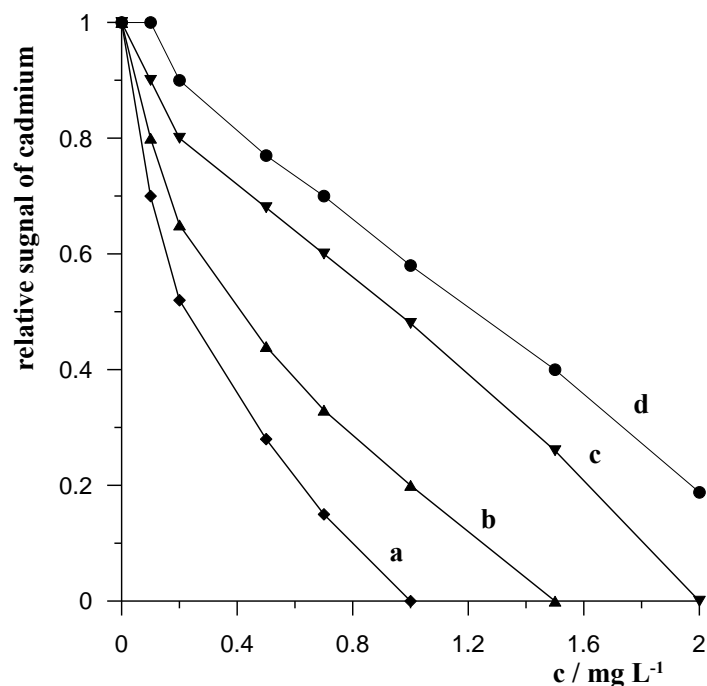


Fig. 4. The relative signal of $1 \times 10^{-5} \text{ mol L}^{-1}$ Cd(II) in the presence of non-ionic surface active substances: CTAB (a), CTAC (b), DTAB (c), HPC (d)

3.2.1. Reduction of interferences from cationic surfactants

In order to reduce interference from the cationic surfactants, identically to the non-ionic ones, the addition of Amberlite type resins, that is, XAD-2, XAD-7 and XAD-16, to the voltammetric cell was used. A series of measurements were carried out using different masses of the resins (0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 g) introduced into solutions containing $5 \times 10^{-8} \text{ mol L}^{-1} \text{ Cd(II)}$, 0.1 mol L^{-1} acetate buffer $\text{pH}=3$, $1.5 \times 10^{-4} \text{ mol L}^{-1} \text{ Bi(NO}_3)_3$ and 2 mg L^{-1} of the surfactant CTAB, CTAC, DTAB or HPC. For each of the surfactants introduced into the solution, a voltammetric measurement was carried out after 3 min of stirring and it was observed how the cadmium signal changed. The results obtained are presented in Figure 5A-D. It is clear that, as with the non-ionic surfactants, the cadmium peak increases with increasing resin mass in the solution and for 0.3 g of resin (both XAD-2, XAD-7 and XAD-16) in the presence of 2 mg L^{-1} DTAB and HPC, the cadmium peak reaches the value as in the absence of surfactants. This means that in this case the interference was completely eliminated by mixing the sample with the resin. In the presence of 2 mg L^{-1} CTAB and CTAC in the solution, the addition of 0.3 g of XAD-7 resin also completely eliminates interferences and the cadmium peak reaches the correct value. In the case of XAD-16 resin, the cadmium peaks are reduced by about 5% and 10% in the presence of CTAC and CTAB, respectively. In the case of XAD-2 resin, on the other hand, the cadmium peaks are smaller by about 25% and 40% in the presence of CTAC and CTAB, respectively. In summary, it can be concluded that, as in the case of interference from the non-ionic substances, in the case of the cationic surfactants the best interference removal is also achieved by mixing the sample with XAD-7 resin, it is slightly weaker in the case of XAD-16 resin, while XAD-2 resin is the least effective in removing interference from cationic surfactants.

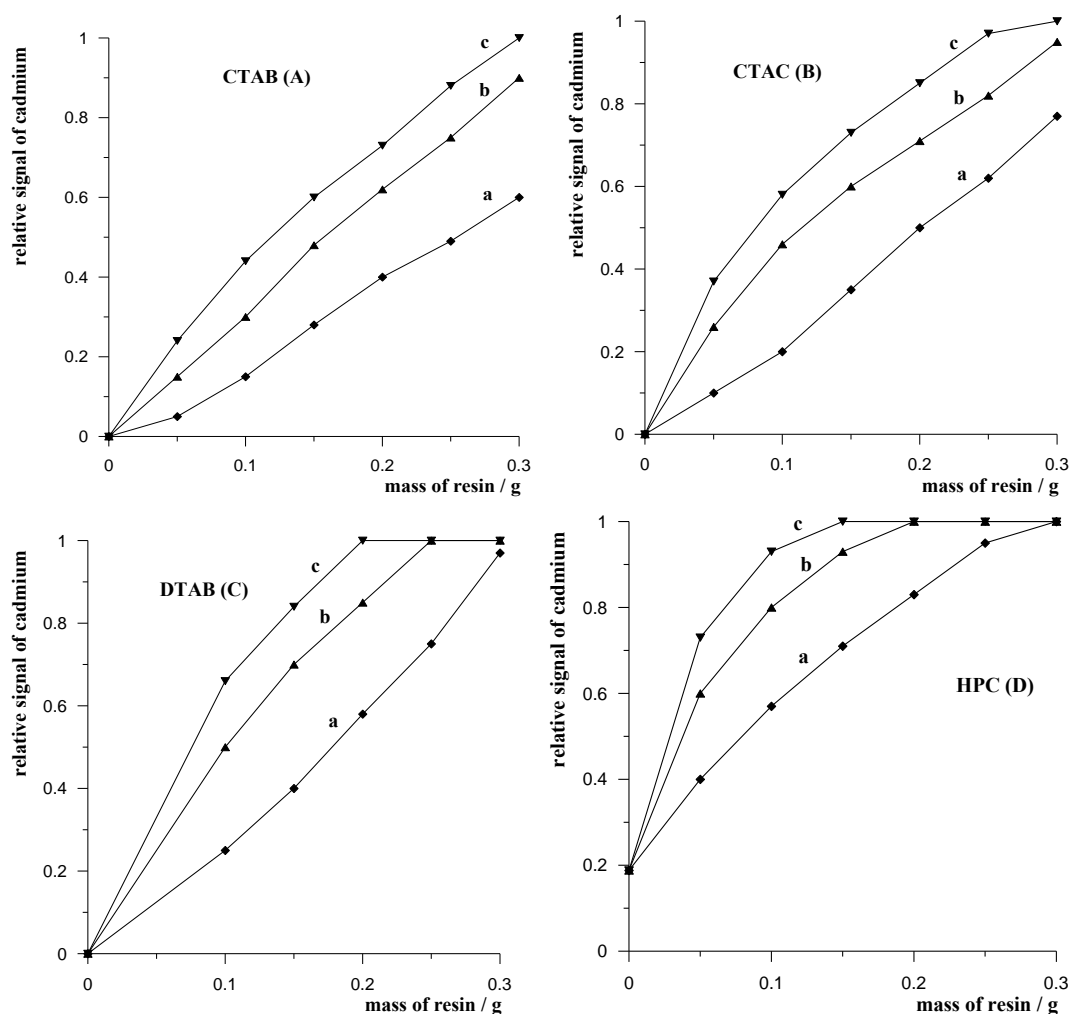


Fig. 5. The relative signal of $1 \times 10^{-5} \text{ mol L}^{-1} \text{ Cd(II)}$ in the presence of 2 mg L^{-1} CTAB (A), CTAC (B), DTAB (C), HPC (D) after mixing with different masses of resins: XAD-2 (a), XAD-16 (b), XAD-7 (c)

3.3. Effect of anionic surfactants

Sodium 1-dodecanesulfonate (DSS) and sodium dodecyl sulfate (SDS) were chosen to investigate the effect of anionic surfactants on the voltamperometric cadmium signal. They were selected for this study because they are well-established commercial anionic synthetic surfactants. They are commonly used as an ingredient in household and personal care products, for example in liquid detergents and concentrated shampoos, as well as in specialized applications such as textile and leather auxiliaries, metal cleaning preparations, steam jets, and pickling bathes [Williams, 2007].

At the beginning, the impact of these anionic surface active substances on Cd(II) voltammetric signal was studied using a standard procedure, as described in Section 2.3. The measurements were carried out without adding resin to the solution. When investigating the effect of DSS and SDS on the voltammetric cadmium signal, it was found that the presence of these surfactants in the analyzed sample at concentrations up to 2 mg L did not affect the peak current of cadmium. Therefore, it was assumed that the anionic surfactants did not cause interference and in this case it was not necessary to add Amberlite resin to the solution.

4. Application

The ASV procedure for cadmium determination using the CNTs/SGC electrode modified with a bismuth film as the working electrode and Amberlite XAD-7 to eliminate surfactant-induced interference was carried out on environmental water samples. The real samples selected for testing were further enriched with cationic, anionic and non-ionic surfactants. Studies on the recovery of cadmium from real water samples were conducted using the standard addition method following prior addition of specific concentrations of Cd(II) to the samples. The recoveries obtained between 95.5 and 107%, shown in Table 1, confirm the validity and correctness of the proposed procedure and the possibility of determining Cd(II) in real samples where anionic, cationic and non-ionic surfactants are present in high concentrations.

Table. 1. Analysis of surfactant-enriched real samples. The samples were examined using the standard addition method and were diluted five times

Sample	added surfactant		Cd(II) added (nmol L ⁻¹)	Cd(II) found (nmol L ⁻¹)	Recovery (%)	RSD (n=3) (%)
	name	concentration (mg L ⁻¹)				
Lake	Triton X-100	3	20.0	21.4	107	4.7
Zemborzyce	CTAB	2	40.0	38.2	95.5	6.2
Ciemiega river water	Tween 20	3	20.0	20.6	103	5.3
	CTAC	2	40.0	41.1	103	4.8
Tap water	Tween 60	3	20.0	19.3	96.5	3.7
	DTAB	2	40.0	40.8	102	5.8
Rain water	Tween 80	3	20.0	20.8	104	3.4
	DSS	2	40.0	39.4	98.5	5.1

5. Conclusions

For the first time, the effect of a wide range of surfactants on the voltammetric cadmium signal was investigated in great detail. All measurements were carried out using the ASV method with a CNTs/SGC electrode modified with a bismuth film as the working electrode. This electrode was selected from among the electrodes used in cadmium determination as one of the electrodes acceptable in the laboratory environment, in contrast to the most commonly used mercury electrodes, at the same time providing a wide range of linearity and a low detection limit for cadmium. The effects of the selected synthetic surfactants were investigated in the range of their concentrations from 0.2 to 2 mg kg⁻¹, which corresponds to the action of surfactants present in real environmental samples. The anionic surfactants were found to have no effect on the cadmium signal, while cationically charged surfactants had the most interfering effect. In the case of the non-ionic and cationic surfactants causing a decrease

in the cadmium peak, a procedure of mixing the analyzed samples with Amberlite resins, such as XAD-2, XAD-7 and XAD-16, was used. It was shown that the best effect in removing interference was demonstrated by XAD-7 resin, slightly weaker by XAD-16 resin, while XAD-2 resin exhibited the weakest effect in removing interference. 0.3 g of resin added per 10 ml of solution was chosen as the optimum mass of resin. When 0.3 g of XAD-7 resin was introduced into the analyzed solution, the voltammetric cadmium signal was not affected in the presence of 5 mg L⁻¹ of the non-ionic surfactants and 2 mg L⁻¹ of the cationic surfactants. Cadmium recoveries from surfactant-enriched environmental water samples were investigated to confirm the validity of the proposed procedure and its practical use.

References

- ABDEL RAHIM, A.M., MAHMOUD, E.M.M. 2023. *Recent development of eco-friendly nanocomposite carbon paste electrode for voltammetric determination of Cd(II) in real samples*. Analytical Sciences 39, 179–190.
- ADAMCZYK, M., GRABARCZYK, M., LESZKO W. 2022. *A voltammetric approach to the quantification of tungsten in environmental waters using a solid bismuth microelectrode*. Measurement 194, 111089.
- AHAMMAD, A.J.S., LEE, J.J., RAHMAN, M.A. 2009. *Electrochemical sensors based on carbon nanotubes*. Sensors 9, 2289–2319.
- AHMED, A.S., MOHAMED, M.B.I., BEDAIR, M.A., EL-ZOMRAWY, A.A., BAKR, M.F., 2023. *A new Schiff base-fabricated pencil lead electrode for the efficient detection of copper, lead, and cadmium ions in aqueous media*. RSC Advances 13, 15651-15666.
- BATLEY, G.E., FLORENCE, T.M. 1976. *The effect of dissolved organics on the stripping voltammetry of seawater*. Journal of Electroanalytical Chemistry and Interfacial Electrochemistry 72, 121-126.
- BOBROWSKI, A., KRÓLICKA, A., ZARĘBSKI J. 2010. *Morphology and Electrochemical Properties of the Bismuth Film Electrode Ex Situ Electrochemically Plated from Perchloric Acid*. Electroanalysis 22, 1421-1427.
- BRITTO, P.J., SANTHANAM, K.S.V., AJAYAN, P.M. 1996. *Carbon nanotube electrode for oxidation of dopamine*. Bioelectrochemistry and Bioenergetics 41, 121–125.
- BRUZZONITI, M.C., SARZANINI, C., MENTASTI, E., 2000. *Preconcentration of contaminants in water analysis*. J. Chromatogr. A 902, 289-309.
- BU, L., XIE, Q., MING, H. 2020. *Simultaneous sensitive analysis of Cd(II), Pb(II) and As(III) using a dual-channel anodic stripping voltammetry approach*. New Journal of Chemistry 44, 5739-5745.
- CHEN, H.J., TSENG, D.H., HUANG, S. L., 2005. *Biodegradation of octylphenol polyethoxylate surfactant Triton X-100 by selected microorganisms*. Bioresource Technol. 96, 1483-1491.
- CORTES, H., HERNANDEZ-PARRA, H., BERNAL-CHAVEZ, S.A., DEL PRADO-AUDELO, M.L., CABALLERO-FLORAN, I.H., BORBOLLA-JIMENEZ, F.V., GONZALEZ-TORRES, M., MAGANA, J.J., LEYVA-GÓMEZ, G., 2021. *Non-Ionic Surfactants for Stabilization of Polymeric Nanoparticles for Biomedical Uses*. Materials 14, 3197.
- COSOVIC, B., VOJVODIC, V., 1982. *The application of a.c. polarography to the determination of surface-active substances in seawater*. Limnology and Oceanography 27, 361-369.
- ESTEVEZ, V.I., CORDEIRO, N.M.A., DA COSTA DUARTE, A., 1995. *Variation on the adsorption efficiency of humic substances from estuarine waters using XAD resins*. Marine Chemistry 51:61-66
- GENCHI, G., SINICROPI, M. S., LAURIA, G., CAROCCI, A., CATALANO, A., 2020. *The Effects of Cadmium Toxicity*. Int. J. Environ. Res. Public Health 17, 3782 (1-24).
- GERGELY, T., MADARASZ, A., 2006. *Structure of BRIJ-35 Nonionic Surfactant in Water: A Reverse Monte Carlo Study*. Langmuir 22, 590–597.
- GRABARCZYK, M., KOPER A. 2011. *How to determine uranium faster and cheaper by adsorptive stripping voltammetry in water samples containing surface active compounds*. Electroanalysis 23, 1442-1446.
- GRABARCZYK, M., WARDAK, C., PIECH, R., WAWRUCH A. 2023. *An Electrochemical Sensor for the Determination of Trace Concentrations of Cadmium, Based on Spherical Glassy Carbon and Nanotubes*. Materials 16, 3252.
- HAIYAN, G., 1997. *Review of the application of non-ionic surfactants*. Chin. J. Prac. Tech. 1997, 24-25.
- HASANUZZAMAN, M., NARASIMHA M., PRASAD, V., FUJITA, M. 2019. *Cadmium Toxicity and Tolerance in Plants*. Elsevier Inc. London, UK.

- HOYER, B., JENSEN, N. 2003. *Suppression of surfactant interferences in anodic stripping voltammetry by sodium dodecyl sulphate*. *Electrochemistry Communications* 5, 759-764.
- JANOS, P., 2003. *Separation methods in the chemistry of humic substances*. *Journal of Chromatography A* 983, 1-18.
- KALIYARAJ SELVA KUMAR, A., LU, Y., COMPTON, R.G. 2022. *Voltammetry of carbon nanotubes and the limitations of particle-modified electrodes: are carbon nanotubes electrocatalytic?* *The Journal of Physical Chemistry Letters* 13, 8699–8710.
- KARAZAN, Z.M., ROUSHANI, M. 2023. *Selective determination of cadmium and lead ions in different food samples by poly (riboflavin)/carbon black-modified glassy carbon electrode*. *Food Chemistry* 423, 136283.
- KRÓLICKA, A., BOBROWSKI, A., ZARĘBSKI, J., TESAROWICZ, I. 2014. *Bismuth Film Electrodes for Adsorptive Stripping Voltammetric Determination of Sunset Yellow FCF in Soft Drinks*. *Electroanalysis* 26, 756-765.
- KUBIAK, W.W., WANG, J. 1989. *Anodic-stripping voltammetry of heavy metals in the presence of organic surfactants*. *Talanta* 36, 821-824.
- LEPANE, V. 1999. *Comparison of XAD resins for the isolation of humic substances from seawater*. *Journal of Chromatography A* 845, 329-335.
- LI, M.H., 2007. *Effects of nonionic and ionic surfactants on survival, oxidative stress, and cholinesterase activity of planarian*. *Chemosphere* 70, 1796-1803.
- LIU, X., LI, A., ZHOU, B., QIU, C., REN, H., 2009. *Chemiluminescence determination of surfactant Triton X-100 in environmental water with luminol-hydrogen peroxide system*. *Chem. Cent. J.* 3, 7.
- MACKAY, R.A. 1994, *Electrochemistry in association colloids*. *Colloids and surfaces A: physicochemical and engineering aspects*. 82, 1-28.
- MALEKI, N., SAFAVI, A., SHAHBAAZI, H.R. 2005. *Minimizing the Interferences from Adsorption of Substances onto Cell Components in Stripping Voltammetry*. *Analytical Letters* 38, 1769-1781.
- NEMCOVA, L., BAREK, J., ZIMA, J. 2012. *A voltammetric comparison of the properties of carbon paste electrodes containing glassy carbon microparticles of various sizes*. *Journal of Electroanalytical Chemistry* 675, 18–24.
- RAHIM, A.M.A., MAHMOUD, E.M.M. 2023. *Recent development of eco-friendly nanocomposite carbon paste electrode for voltammetric determination of Cd(II) in real samples*. *Analytical Sciences* 39, 179-190.
- RHEIN, L. 2007. *Surfactant Action on Skin and Hair: Cleansing and Skin Reactivity Mechanisms*. *Handbook for Cleaning/Decontamination of Surfaces* 1, 305-369.
- ROJAS-ROMO, C., ALIAGA, M.E., ARANCIBIA, V., GOMEZ, M. 2020. *Determination of Pb(II) and Cd(II) via anodic stripping voltammetry using an in-situ bismuth film electrode. Increasing the sensitivity of the method by the presence of Alizarin Red S*. *Microchemical Journal* 159, 105373.
- SATARUG, S., BAKER, J.R., URBENJAPOL, S., HASWELL-ELKINS, M., REILLY, P.E., WILLIAMS, D.J., MOORE, M.R., 2003. *A global perspective on cadmium pollution an toxicity in non-occupationally exposed population*. *Toxicol. Lett.* 137, 65–83.
- SCHRAMM, L.L., STASIUK, E.N., GERRARD MARANGONI, D.G. 2003. *Surfactants and their applications*. *Annual Reports on the Progress of Chemistry, Section C* 99, 3-48.
- TAPIA, M.A., PEREZ-RAFOLS, C., OLIVEIRA, F.M., GUSMAO, R., SERRANO, N., SOFER, Z., DIAZ-CRUZ, J.M. 2023. *Antimonene-Modified Screen-Printed Carbon Nanofibers Electrode for Enhanced Electroanalytical Response of Metal Ions*. *Chemosensors* 11, 219.
- THANH, N.M., LUYEN, N.D., THANH TAM TOAN, T., HAI PHONG, N., VAN HOP, N. 2019. *Voltammetry determination of Pb(II), Cd(II), and Zn(II) at bismuth film electrode combined with 8-hydroxyquinoline as a complexing agent*. *Journal of Analytical Methods in Chemistry* 2019, 4593135.
- WANG, J., DEN-BAL, L. 1984. *Effect of surface-active compounds on voltammetric stripping analysis at the mercury film electrode*. *Talanta* 31, 703-707.
- WANG, J., LU, J., HOCEVAR, S.B, FARIAS, P.A.M., OGOREVC, B. 2000. *Bismuth-coated carbon electrodes for anodic stripping voltammetry*. *Analytical Chemistry* 72, 3218-3222.
- WANG, T., YUE, W. 2017. *Carbon nanotubes heavy metal detection with stripping voltammetry: a review paper*. *Electroanalysis* 29, 2178–2189.

- WANG, Y., WU, X., SUN, J., WANG, C., ZHU, G., BAI, L.P., JIANG, Z.H., ZHANG, W. 2022. *Stripping voltammetric determination of cadmium and lead ions based on a bismuth oxide surface-decorated nanoporous bismuth electrode*. *Electrochemistry Communications* 136, 107233.
- WASAŁ, J., GRABARCZYK M. 2016. *Adsorptive stripping voltammetry of In(III) in the presence of cupferron using an in situ plated bismuth film electrode*. *Analytical Methods* 8, 3605-3612.
- WEĞIEL, K., GRABARCZYK, M., KUBIAK, W.W., BAŚ, B. 2017. *A reliable and sensitive voltammetric determination of Mo(VI) at the in situ renovated bismuth bulk annular band electrode*. *Journal of the Electrochemical Society* 164, H352-H357.
- WHO Technical Report Series 960, *Evaluation of certain food additives and contaminants: seventy-third report of the Joint FAO/WHO Expert Committee on Food Additives*. World Health Organization; 2011. https://apps.who.int/iris/bitstream/handle/10665/44515/WHO_TRS_960_eng.pdf?sequence=1&isAllowed=y [accessed 11 May 2023]
- WILLIAMS, J.J. 2007. *Formulation of Carpet Cleaners*. *Handbook for Cleaning/Decontamination of Surfaces* 1, 103-123.
- ZAREI, E., IZADYAR, A., ASGHARI, A., RAJABI, M. 2022. *Development of 2-aminobenzoic Acid as a Complexing Ligand for Simultaneous Adsorptive Cathodic Stripping Voltammetric Determination of Trace Copper, Lead and Cadmium*. *Portugaliae Electrochimica Acta* 40, 325-335.