Combination of PbFE as an electrochemical sensor and cupferron as a complexing agent for the rapid determination of Mo(VI)

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Abstract

An analytical procedure regarding the trace determination of molybdenum in natural water samples by adsorptive stripping voltammetry (AdSV) using the in situ plated lead film electrode (PbFE) was described. The method is based on adsorptive accumulation of the Mo(VI)-cupferron complex at the PbFE surface. The optimum analytical conditions include the supporting electrolyte containing 0.2-mol L⁻¹ acetic buffer pH = 5.3, 1.45 × 10⁻⁴-mol L⁻¹ Pb(II), and 2.0 × 10⁻⁴-mol L⁻¹ cupferron. A linear response of Mo(VI) in the concentration range of 3.0 × 10⁻⁸ to 1.0 × 10⁻⁶ mol L⁻¹ ($r = 0.997$) was obtained with detection limit of 9.0 × 10⁻⁹ mol L⁻¹ using accumulation time of 50 s. The selectivity of the method was determined by investigating how the presence of foreign ions affects the determination of molybdenum. The interferences of surface-active substances and humic substances on the molybdenum voltammetric signal were precisely examined and effectively minimized by preliminary mixing with Amberlite XAD-7 resin. The application of the proposed procedure to the analysis of natural water samples was validated by the determination of molybdenum in certificate reference materials SPS-SW1 surface water, Bystrzyca river, tap, and mineral water.

Keywords Electrochemical sensors · Molybdenum · Cupferron · Voltammetry · Resin

Introduction

Molybdenum is a relatively rare heavy trace element found in the soil. It belongs to essential microelements which play an important role in a variety of biochemical and physiological functions in plants, animals, and humans. Molybdenum is a transition element which can exist in several oxidation states ranging from 0 to VI, where VI is the predominant form (MoO₄²⁻) found in the environment. Similarly to most metals required for plant growth, molybdenum is utilized by specific plant enzymes to participate in reduction and oxidation reactions. It takes part in the uptake of nitrogen from both nitrogen gas and nitrate [1, 2]. This element is an important constituent of several key enzymes and plays a major role in various oxidation-reduction reactions [3]. Molybdenum is utilized by

selected enzymes to carry out redox reactions. Enzymes that require molybdenum for activity include nitrate reductase, xanthine dehydrogenase, aldehyde oxidase, and sulfite oxidase [4]. Although small amounts of molybdenum are essential to human health, large amounts can be toxic. High doses of molybdenum have been found to produce cellular and tissue damages leading to a variety of adverse effects and human diseases [5]. There is a very narrow range of concentrations between beneficial and toxic [6], so the evaluation of molybdenum level in environmental samples with various matrices, especially in soil and natural water, is needful and highly recommended.

To date, various methods for the determination of molybdenum in environmental samples have been described. Among the available measurement techniques are located cloud point extraction coupled with flame atomic absorption spectrometry [7], graphite furnace atomic absorption spectrometry [8, 9], cloud point extraction connected with graphite furnace atomic absorption spectrometry [10], inductively coupled plasma-atomic emission spectrometry [11], inductively coupled plasma-mass spectrometry [12], spectrophotometry [13, 14], and neutron activation analysis [15]. These methods have a number of advantages, first of all,

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excellent sensitivity and good selectivity, but they also have serious drawbacks which include expensive apparatus, pre-treatment of real samples, and complicated procedures. The viable alternative to these techniques are electrochemical methods, especially adsorptive stripping voltammetry (AdSV) which provides very low detection limit, good selectivity, and above all, direct determination without the need for application of additional procedures of separation and preconcentration. In the last years, multiple AdSV procedures have been developed for the determination of molybdenum using different complexing agents such as alizarin S [16–18], chloranilic acid [19–24], cupferron [20, 24, 25], 1,10-phenanthroline [26], oxine [27, 28], α -benzoinoxime [29], morin [30], quercetin [31], tiron [32], pyrogallol red [33], pyrocatechol violet [34], chromoxane cyanine R [35], 2-(2-benzothiazolylazo) p-cresol [36], dihydroxynaphthalene [37], and methyl thymol blue [38].

Previous articles showed that in the majority of voltammetric procedures of molybdenum determination, the hanging mercury drop electrode (HMDE) [16, 17, 20, 21, 24, 26–29, 31–37, 39] was used as a working electrode because of its excellent properties. The comparison of parameters of adsorptive stripping voltammetric procedures for molybdenum determination in which hanging mercury drop electrode (HMDE) was used as a working electrode is presented in Table 1. However, in view of mercury toxicity, over the years, HMDE electrodes have been replaced by other more environmentally friendly electrodes. According to literature data, in the case of voltammetric procedures for Mo(VI) determination, some other types of electrochemical sensors have recently been proposed, among them are lead film electrode [18], renewable mercury film silver based electrode [19], bismuth film electrode [22], bismuth bulk annular band electrode [23], screen printed carbon electrode [25], and modified carbon paste electrode [30].

One of the most common problems of voltammetric techniques is their susceptibility to disturbances related to the presence of organic substances in environmental samples. The main reason for this problem is associated with the adsorption of organic substances such as surface-active compounds onto a sensor, which causes peak reduction or even complete disappearance. Since surface-active substances are an integral part of environmental samples, it is indispensable to develop procedures making it possible to determine Mo(VI) in environmental samples containing surfactants. Reviewing the hitherto published articles on molybdenum determination by the AdSV method, it was concluded that in many works dealing with this issue, the influence of organic substances on Mo(VI) determination was not studied at all [2, 16, 17, 22, 30, 31, 34, 39]. In the works in which the problem related to the presence of organic substances was taken into account, it was suggested that in order to eliminate interferences from organic substances, pre-mineralization of the samples by UV

irradiation or acid etching in combination with heating before the determination should be performed [18, 19, 35–37]. The authors of some other works proposed the use of Amberlite XAD-7 resin for the same purpose [20, 23].

Up to now, only one AdSV procedure has been developed for the determination of trace molybdenum using lead film electrode (PbFE) sensor as a working electrode. In that work, molybdenum was determined as a complex with alizarin S [18]. In the present article, a new adsorptive stripping voltammetry procedure was applied for the trace molybdenum(VI) determination which was based on adsorptive accumulation of the complexes of molybdenum with cupferron onto the surface of PbFE. This arrangement was proposed for the first time in this work. The most notable advantages of lead film electrodes are lower toxicity and lower background current in the presence of dissolved oxygen as compared with mercury film electrodes. Although lead is toxic too, to test solution was introduced only insignificant amount of this element. Such low concentrations (in our procedure $1.45 \times 10^{-4} \text{ mol L}^{-1}$) are safe for the laboratory environment. In the case of mercury electrodes, there are volatile mercury vapors that are very harmful and toxic. The use of lead film electrodes is not associated with such a problem.

In order to minimize the negative impact of organic compounds on the molybdenum signal, XAD-7 resins were used. This method of removing organic matter from the sample was used in our previous works and as compared with other methods such as UV irradiation; it seems to be the most effective procedure for eliminating interferences. The developed method was successfully applied to the analysis of natural water samples without their prior preparation.

Materials and methods

Apparatus

The measurements were performed using a μ Autolab analyzer (Utrecht, The Netherlands). A conventional three-electrode system consisting of a modified glass carbon (GC) with the inner diameter of 1 mm as the working electrode, a platinum auxiliary electrode, and an Ag/AgCl reference electrode (in saturated NaCl) was used in all experiments. The GC electrode was polished on silicon carbide paper (SiC-paper, #2500, Buehler, Denmark) and using 0.3- μm alumina slurry on a Buehler polishing pad. After polishing, the electrode was washed and sonicated for 30 s in an ultrasonic bath. The pH measurements were made on an Elmetron pH meter CI-316. A mechanical stirrer (type RZR 2021, Heidolph, Germany) was used during preliminary mixing analyzed sample with resin.

Table 1 The comparison of parameters of adsorptive stripping voltammetric procedures for trace molybdenum determination in which hanging mercury drop electrode (HMDE) was used as a working electrode. The procedures are arranged according to the growing detection limit

Complexing reagent	Supporting electrolyte	Linear range (nmol L ⁻¹)	Detection limit (nmol L ⁻¹)	Accumulation time (s)	Application	Ref.
Oxine	0.05-M acetate buffer pH 3.5	0.01–5.0	0.0017	60	Plant foodstuffs	[27]
Pyrocatechol violet	0.08-M H ₂ SO ₄	0.01–1000	0.002	30	Mineral water, analytical grade acids	[34]
Dihydroxynaphthalene	0.01-M acetate buffer pH 4.7	0.01–1.0	0.006	60	Lake water, river water	[37]
Methylthymol blue	0.1-M phosphate buffer pH 2.5	0.1–1500	0.02	60	Mineral water, analytical grade salts	[38]
Tiron	0.02-M KNO ₃	0.1–200	0.06	60	River water, tap water, certified steel references materials (BS XCCS, BS 2932, IRON 464, IRON 467), foodstuffs	[32]
α-benzoinoxime	0.1-M acetate buffer pH 3.0	25–100	0.10	300	Mineral water, river water, sea water,	[29]
Chloranilic acid	0.01-M HCl	1.7–625	0.16	60	certified reference surface water, extracts of fly ashes	[21]
Chloranilic acid	0.1-M acetate buffer pH 3.0	1.0–100	0.30	30	Certified reference material–seawater NASS-5	[20]
Alizarin red S	-	1.5–50	0.48	20	Drinking water	17
Cupferron	0.05-M acetate buffer pH 3.0	1.0–200	0.60	60	River water, tap water, alloy	[24]
1,10-phenanthroline	0.5-M NaCl in 0.01-M HCl pH 2	2.5–500	0.60	1200	-	[26]
2-(2-benzothiazolylazo) p-cresol (BTAC)	0.2-M acetate buffer pH 3.5	10–100	0.60	240	Spex mix and Bovine liver (SRM 1777-b) certified standard	[36]
Chromoxanecyanine R	0.1-M acetate buffer pH 3.6	1.0–300	0.80	60	River water, tap water, plant foodstuffs	[35]
Quercetin	Britton–Robinson buffer 0.4 M pH = 3.7	0.9–100	0.90	60	Synthetic sea water (ASTM D665), tap water, mineral bottled water	[31]
Oxine	0.1-M HCl	5.0–1500	1.0	60	Certified reference seawater samples (CASS-2 and NASS-2)	[28]
Pyrogallol red	0.06-M Briton–Robinson buffer solution pH 2.5	8.0–800	1.0	90	River water, tap water, alloy	[33]
Alizarin red S	0.01-M acetate buffer pH 4.0	10–260	2.6	60	Tap water seawater, effluent samples	16

Reagents

All solutions were prepared using ultra-purified water (> 18 MVcm) supplied by the Milli-Q system (Millipore, UK). All chemicals used were of analytical reagent grade or Suprapur. The working solutions of Mo(VI) and other foreign ions solutions such as Zn(II), Cd(II), Bi(III), Ni(II), Co(II), Cu(II), Hg(II), Cr(III), Fe(III), Ge(IV), Mn(II), Sb(III), Au(III), Ga(III), Pt(IV), V(V), and W(VI) at a concentration of 1×10^{-4} mol L⁻¹ were prepared by appropriate dilution of 1-g L⁻¹ stock standard solutions in 0.01-mol L⁻¹ HNO₃ (Merck). The solution of cupferron at concentrations of 1×10^{-2} mol L⁻¹ was prepared weekly by dissolving 0.0155 g of the reagent in deionized water in a 10-mL volumetric flask and was stored in a refrigerator at a temperature of 6 °C. The solutions of 1 mol L⁻¹ of the acetate buffers were prepared from Suprapur CH₃COOH and NaOH obtained from Merck. A stock standard solution of 1-g L⁻¹ Pb(II), polyethylene

glycol tert-octylphenyl ether (Triton X-100), cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS), and Rhamnolipid was purchased from Fluka (Buchs, Switzerland). Humic acid sodium salt (HA) was obtained from Aldrich. The river fulvic acid (FA) and natural organic material (NOM) were obtained from the Suwannee River and purchased from the International Humic Substances Society. Certified reference material SPS-SW1 was obtained from the National Research Council, Canada. Amberlite XAD-7 resin was obtained from Sigma, washed four times with ultrapure water, and dried up at a temperature of 50 °C.

General procedure

Standard measurements were performed using differential pulse adsorptive stripping voltammetry (DP-AdSV) in the following manner. A total of 3 mL of 1-mol L⁻¹ acetate buffer

(pH = 5.3), 300 μL of 1×10^{-2} -mol L^{-1} cupferron, 450 μL of 1-g L^{-1} Pb(II), different concentration of Mo(VI), and an adequate volume of ultrapure water were transferred to the voltammetric cell in order to obtain a 15-mL solution containing 0.2-mol L^{-1} acetate buffer, 2.0×10^{-4} -mol L^{-1} cupferron, and 1.45×10^{-4} -mol L^{-1} Pb(II), respectively. The measurements were carried out from underaerated solutions.

Before each measurement, electrochemical cleaning of the GC electrode was performed in the following way: -1.3 V for 15 s and 0.2 V for 15 s. During the potential of -1.3 V , the remains from the previous measurement were reduced to the metallic state, and then at 0.2 V potential, they were stripped from the electrode.

The standard measurement of Mo(VI) determination was carried out, while the potential of the electrode was changed in the following sequence:

- (1) -1.1 V for 30 s.
- (2) -0.6 V for 20 s.
- (3) -0.6 V for 5 s (equilibration time)
- (4) scan from -0.6 to -0.9 V .

During the first step, a lead film electrode was plated, while during the second step, the Mo(VI)-cupferron complex was accumulated on the electrode. During those steps, the solution was stirred using a magnetic stirring bar. Then after a period of 5 s without mixing the solution, a differential pulse stripping voltammogram was recorded, while the potential was scanned from -0.6 to -0.9 V , with the intensity of the obtained peak directly proportional to the concentration of Mo(VI) in the sample. The scan rate, pulse time, and pulse height were 80 mVs^{-1} , 2 ms, and 50 mV, respectively.

Procedure of elimination of organic substances interferences

One-milliliter sample solution, 4 mL of 1-mol L^{-1} acetate buffer (pH = 5.3) and an adequate volume of ultrapure water, so the final volume of the solution was 10 mL, were added to a glass vial, and finally, 0.5 g of XAD-7 resin was inserted. Then, a magnetic stirring bar was put into the vial, and the solution was mixed for 5 min at room temperature. During that time, the organic substances were adsorbed on the resin, while molybdenum (VI) ions remained in the solution. Finally, after sedimentation of the resin, 7.5 mL of the solution was pipetted into the 15-mL electrochemical cell. Next 300 μL of 1×10^{-2} -mol L^{-1} cupferron and 450 μL of 1-g L^{-1} Pb(II) were inserted into the electrochemical cell, so that the desired concentrations were obtained (0.2-mol L^{-1} acetate buffer pH = 5.3, 1.45×10^{-4} -mol L^{-1} Pb(II), and 2.0×10^{-4} -mol L^{-1} cupferron).

Results and discussion

In order to obtain the optimum conditions for molybdenum(VI) determination, the following parameters (affecting the height and shape of the peak) were examined:

- pH and concentration of the supporting electrolyte,
- the concentration of cupferron,
- the concentration of lead,
- the potential and time of formation of lead film at the electrode surface,
- the potential and time of adsorption of the molybdenum-cupferron complex at the electrode surface.

Effect of pH and concentration of supporting electrolyte

The supporting electrolyte acetate buffer was studied in the pH range of 4.0–6.2 for molybdenum determination. Based on literature data, acetate buffer was widely used for the adsorptive stripping voltammetry metal determination using cupferron as a complexing agent [24, 25, 38–40]. The measurements were performed for the samples containing a constant concentration of Mo(VI) equal to $5.0 \times 10^{-7}\text{ mol L}^{-1}$, 2.0×10^{-4} -mol L^{-1} cupferron, 1.45×10^{-4} -mol L^{-1} Pb(II), and 0.2-mol L^{-1} acetate buffer with different pH values. The peak current increased with the increase in pH to 5.3, and above pH equal to 5.4, the peak current slightly decreased. Because the maximum peak current was observed for acetate buffer pH = 5.3, this supporting electrolyte was chosen for further research.

The effect of acetate buffer of pH = 5.3 concentration on the voltammetric peak current of molybdenum was also taken into account. The measurements were performed for the standard solution changing the concentration of acetate buffer in the range from 0.1 to 0.4 mol L^{-1} . It was observed that the peak current was growing up with the increase of buffer concentration to 0.2 mol L^{-1} . A concentration higher than 0.2 mol L^{-1} did not cause significant changes in the peak height, but the signal was distinctly widened with increasing concentration.

Effect of cupferron concentration

To choose the optimum quantity of cupferron in the sample, the effect of its concentration on the peak current was studied in the range from $1.0 \times 10^{-5}\text{ mol L}^{-1}$ to $7.0 \times 10^{-4}\text{ mol L}^{-1}$. The measurements were performed for solutions containing 5.0×10^{-7} -mol L^{-1} Mo(VI), 0.2-mol L^{-1} acetate buffer of pH = 5.3, and 1.45×10^{-4} -mol L^{-1} Pb(II). The results showed that the peak of molybdenum appeared at a concentration of

cupferron equal to $5.0 \times 10^{-5} \text{ mol L}^{-1}$, then it linearly increased with the increasing concentration of the complexing agent up to $2.0 \times 10^{-4} \text{ mol L}^{-1}$, and finally decreased at higher concentrations. So the concentration of $2.0 \times 10^{-4} \text{ mol L}^{-1}$ was adopted as the optimum one for further experiments (Fig. 1).

Effect of lead concentration

The concentration of Pb(II) in the tested solution is the main chemical factor that determines morphology of the in situ plated lead film and consequently the analytical results. Therefore, this parameter was precisely studied. The AdSV peak current of $5.0 \times 10^{-7} \text{ mol L}^{-1}$ Mo(VI) in the presence of 0.2 mol L^{-1} acetate buffer of pH = 5.3 and $2.0 \times 10^{-4} \text{ mol L}^{-1}$ cupferron was measured in the function of Pb(II) concentration over the range 5.0×10^{-6} to $4.0 \times 10^{-4} \text{ mol L}^{-1}$. It was found that the peak of molybdenum appeared at a concentration of Pb(II) equal to $2.5 \times 10^{-5} \text{ mol L}^{-1}$. At Pb(II) concentration ranging from $2.5 \times 10^{-5} \text{ mol L}^{-1}$ to $1.45 \times 10^{-4} \text{ mol L}^{-1}$, the peak current of molybdenum increased linearly and finally reached a maximum, and next with the increase of lead concentration, the molybdenum signal progressively decreased. On the basis of these results, the Pb(II) concentration of $1.45 \times 10^{-4} \text{ mol L}^{-1}$ was chosen as the optimum one for further research (Fig. 2).

Fig. 1 The influence of cupferron concentration on $5.0 \times 10^{-7} \text{ mol L}^{-1}$ Mo(VI) voltammetric signal. Concentration of Pb(II) $1.45 \times 10^{-4} \text{ mol L}^{-1}$ and acetate buffer 0.2 mol L^{-1} (pH = 5.3)

Fig. 2 The influence of lead concentration on $5.0 \times 10^{-7} \text{ mol L}^{-1}$ Mo(VI) voltammetric signal. Concentration of cupferron $2.0 \times 10^{-4} \text{ mol L}^{-1}$ and acetate buffer 0.2 mol L^{-1} (pH = 5.3)

Effect of potential and time of lead film formation and Mo(VI)-cupferron accumulation

The effect of the electrode potential on lead film formation and Mo(VI)-cupferron accumulation was studied for a solution containing $5.0 \times 10^{-7} \text{ mol L}^{-1}$ Mo(VI). On the basis of the performed measurements, it was found that the best signal of molybdenum was obtained by applying a combination of two successive steps: -1.1 V for 30 s followed by -0.6 V for 20 s. The optimization of these parameters was carried out by changing the second potential while the first potential was fixed, and then the second potential was fixed while the first potential was modified.

So at first, the potential of Mo(VI)-cupferron accumulation was fixed and was equal to -0.6 V and 20-s accumulation time, while the potential of lead film formation was changed in the range from -1.2 to -0.7 V at 30 s. It was stated that for the potential of lead film formation in the range from -1.2 to -1.0 V , the peak of molybdenum was maximum and constant; for less negative potentials, the peak height slightly decreased. So the potential of -1.1 V was chosen as an optimum value. The effect of lead film formation time was tested by changing from 10 to 50 s using the potential of -1.1 V . The peak current of molybdenum increased as the film formation time increased to 30 s, and then it was constant.

Next, the potential -1.1 V and 30-s accumulation time were selected for lead film formation, while the potential of Mo(VI)-cupferron accumulation was changed in the range from -0.8 to -0.4 V and accumulation time of 20 s. It was

found that with the changing potential from -0.8 to -0.6 V, the peak current increased, while further changing the potential towards a less negative value caused a decrease of the peak current. Therefore, the potential of -0.6 V for Mo(VI)-cupferron accumulation was selected as the optimum one. The influence of Mo(VI)-cupferron accumulation time was tested from 10 to 50 s using the accumulation potential of -0.6 V. It was observed that the peak current increases with prolongation of accumulation time up to 20 s, and then it is nearly stable.

Characteristics of the analytical procedure

The linear range and detection limit of the AdSV response for molybdenum were determined for the solution under the optimum experimental conditions: 0.2-mol L^{-1} acetate buffer pH = 5.3, $1.45 \times 10^{-4}\text{-mol L}^{-1}$ Pb(II), and $2.0 \times 10^{-4}\text{-mol L}^{-1}$ cupferron using deposition potential -1.1 V for 30 s followed by -0.6 V for 20 s. The calibration graph for Mo(VI) was linear in the range from 3.0×10^{-8} to $1.0 \times 10^{-6}\text{ mol L}^{-1}$ and obeyed the equation $y = 9.22x + 0.24$, where y and x are the peak current (μampere) and concentration of Mo(VI) ($\mu\text{mol per liter}$), respectively. The linear correlation coefficient was $R^2 = 0.997$. Dependence of the stripping peak current on Mo(VI) concentration is shown in Fig. 3 with the corresponding calibration curve. The detection limit estimated from three times the standard deviation at low Mo(VI) concentration was about $9.0 \times 10^{-9}\text{ mol L}^{-1}$. The stability of the proposed method was evaluated by examining the repeatability and reproducibility by performing differential pulse voltammetric measurements for $1.0 \times 10^{-7}\text{ mol L}^{-1}$ Mo(VI) under the optimized parameters. The repeatability of the measurements was evaluated from ten subsequent measurements using various solutions as relative standard deviation (RSD) of the highest molybdenum peak values and was equal to 3.5%. The reproducibility was evaluated from the measurements performed in five subsequent days as RSD and was 4.0%.

Effect of foreign ions

The next stage of the measurements was to study the effect of different metal cations and different inorganic anions on the Mo(VI) analytical signal. The aim of this stage was to show which of the tested ions cause interference, contributing to the reduction of the molybdenum signal, and in some cases even resulting in its complete disappearance.

The effects of co-existing ions were tested using a fixed concentration of Mo(VI) equal to $5.0 \times 10^{-7}\text{ mol L}^{-1}$ and different concentrations of several foreign ions. An ion was considered to interfere when its presence produced a variation in the molybdenum peak current $> 5\%$. The results showed that up to a 100-fold excess of Au(III), Co(II), Cd(II), Cr(VI), Cu(II), Fe(III), Ga(III), Ge(IV), Hg(II), In(III), Mn(II), Ni(II), Pb(II), Pt(IV), Sb(III), Ti(IV), W(VI), Zn(II), Cl^- , NO_3^- , and SO_4^{2-} , and 50-fold excess of Tl(I) and Bi(III) did not have a significant effect on the Mo(VI) peak. The most interfering ions were Cr(III), Sn(II), and V(V), whose 50-fold excess caused a decrease of the molybdenum peak to 40%, 70%, and 80% of its original value, respectively.

Effect of organic substances

Because the aim of the proposed procedure was the determination of molybdenum in environmental water samples, investigation of the influence of organic matter was required. The most important components of organic matter present in natural water samples are surface-active substances such as typical industrial pollutants as well as humic substances such as the major components of natural organic matter. All kinds of surfactants, anionic (SDS), cationic (CTAB), non-ionic (Triton X-100), and biosurfactant (Rhamnolipid), were examined in this research. The measurements were performed using General Procedure and Procedure with using Amberlite XAD-7 resin for each surfactant separately.

Based on literature data reporting that natural waters contain surfactants with the surface-active effect similar to the

Fig. 3 The voltammograms obtained at the PbFE in the supporting electrolyte containing increasing concentrations of Mo(VI). Concentration of Mo(VI). 0 (a), 0.05 (b), 0.2 (c), 0.3 (d), 0.5 (e), 0.7 (f),

0.9 (g), 1 (h) $\mu\text{mol L}^{-1}$. Supporting electrolyte 0.2-mol L^{-1} acetate buffer (pH = 5.3), $2.0 \times 10^{-4}\text{-mol L}^{-1}$ cupferron, and $1.45 \times 10^{-4}\text{-mol L}^{-1}$ Pb(II). Inset the corresponding calibration plots

Fig. 4 The influence of Rhamnolipid (a), SDS (b), Triton X-100 (c), and CTAB (d) concentration on the relative signal of molybdenum. Fixed concentration 5.0×10^{-7} -mol L⁻¹ Mo(VI), 0.2-mol L⁻¹ acetate buffer pH = 5.3, 2.0×10^{-4} -mol L⁻¹ cupferron, and 1.45×10^{-4} -mol L⁻¹ Pb(II)

effect induced by 0.2 to 2 ppm of Triton X-100 [41], we carried out our research using such concentrations of the examined surfactants. Figure 4 presents the influence of SDS, CTAB, Triton X-100, and Rhamnolipid on the voltammetric signal of Mo(VI) obtained using the *General Procedure* (without elimination of interferences). As can be seen in the case of SDS, Triton X-100, and Rhamnolipid, their concentrations of 2 mg L⁻¹ caused a reduction of the voltammetric signal of molybdenum by about 80, 90, and 45%, respectively. Meanwhile, CTAB at a concentration of 1.5 mg L⁻¹ caused a total loss of the Mo(VI) signal. Using the *Procedure with using Amberlite XAD-7 resin* (with elimination of interferences), all tested surfactants did not affect the analytical signal in the whole range of concentrations (from 0.2 to 2 mg L⁻¹).

Application of proposed procedure

The proposed method has been validated through Mo(VI) determination in the certified reference material SPS-SW1 surface water (batch 127). This material contains besides molybdenum other trace elements such as Al, As, B, Ba, Ca, Cd,

Fig. 5 Differential pulse voltammograms obtained during Mo(VI) determination in the Bystrzyca river water. Diluted ten-fold (a), as (a) + 1.0×10^{-7} -mol L⁻¹ Mo(VI) (b), as (a) + 2.0×10^{-7} -mol L⁻¹ Mo(VI) (c), as (a) + 3.0×10^{-7} -mol L⁻¹ Mo(VI) (d). Fixed concentration. 0.2-mol L⁻¹ acetate buffer pH = 5.3, 2.0×10^{-4} -mol L⁻¹ cupferron, 1.45×10^{-4} -mol L⁻¹ Pb(II)

Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Gd, Ho, K, La, Lu, Mg, and Mn. The results of determination ($n = 3$) show that the certified value (10.0 ± 0.1 ng mL⁻¹) and found value (9.67 ± 0.20 ng mL⁻¹) correspond well. Because solution of certified reference material SPS-SW1 contains nitric acid, a proper quantity of sodium hydroxide was added directly to the solution in voltammetric cell in order to neutralize pH.

To confirm the accuracy of the proposed procedure, three fresh natural water samples from the Bystrzyca river water, tap water, and mineral water were collected from eastern part of Poland, and Mo(VI) determination by the proposed procedure was performed. The voltammograms recorded for those samples did not exhibit any signal of Mo(VI), which indicated that the concentrations of molybdenum were below the detection limits of the proposed procedure. So, the analyzed samples were spiked with Mo(VI) at different concentration levels and the molybdenum content was determined by the standard addition method. The obtained results are listed in Table 2. The typical recorded voltammograms obtained in the course of Mo(VI) determination in Bystrzyca river are presented in the Fig. 5.

Table 2 Analytical results of Mo(VI) determination in water samples by proposed standard procedure in the presence of 0.5 g Ambertite XAD-7 resin. The samples were analyzed after ten-fold dilutions using standard addition methods

Sample	Mo(VI) added (nmol L ⁻¹)	Mo(VI) found (nmol L ⁻¹)	Recovery (%)	RSD ($n = 5$) (%)
Bystrzyca river water	100.0	98.8	98.8	4.6
	200.0	204.8	102.4	5.2
Tap water	100.0	100.7	100.7	3.2
	200.0	204.0	102.0	3.5
Mineral water	100.0	99.4	99.4	4.3
	200.0	196.0	98.0	6.1

Conclusions

The main novelty of the proposed procedure is the application of a new system consisting of an electrochemical sensor, which was PbFE used as a working electrode and cupferron as a complexing agent. The PbFE in situ electrochemically deposited onto a glassy carbon substrate in acid medium occurred to be the right approach to molybdenum determination. The proposed adsorptive stripping voltammetric method offers the advantages of accuracy as well as simplicity of reagents and apparatus. It should be noted that the described procedure is also insensitive to high concentrations of surface-active substances and humic substances thanks to the use of Amberlite XAD-7 resin. To prove its practical applicability, the procedure was successfully tested for the detection of molybdenum in different real water samples.

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