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Selective, sensitive and economical method for the adsorptive voltammetric determination of trace amounts of Mo(VI) in organic matter rich environmental samples

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ABSTRACT

A differential pulse adsorptive stripping voltammetric method has been developed for molybdenum trace determination in environmental water samples containing organic compounds. It was proved that interferences from the organic matrix such as surface active substances and humic substances could be removed by the addition of resin to the analysed sample prior to voltammetric measurement. The parameters for Mo(VI) determination in the presence of resin, using a hanging mercury drop as the working electrode, were examined systematically for two complexing agents: cupferron and chloranilic acid. The detection limits estimated from 3 times the standard deviation for a low Mo(VI) concentrations were equal to 5×10^{-11} and 3×10^{-10} mol L^{-1} for cupferron and chloranilic acid, respectively. At the optimized conditions the quantitative Mo(VI) determination in the presence of even 50 mg L^{-1} of surface active compounds can be performed. The proposed procedures were validated in the course of Mo(VI) determination in certified reference material NASS-5 and in the course of studying recovery of Mo(VI) from spiked river water samples.

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1. Introduction

Molybdenum can exist in five oxidation states (II–VI) but its predominant form occurring in soil and natural waters is the molybdate anion, MoO_4^{2-} [1,2]. This transition element is found naturally in soil and is used in the manufacture of special steels and in the production of tungsten and pigments [3]. Molybdenum is an essential trace element for both plants and animals, including humans, first of all because it plays an important role in enzymatic redox reactions. Nevertheless, it is harmful at higher contents, so monitoring the molybdenum content in environmental samples is desirable and highly recommended [2,3]. There is a strong need for the methods of molybdenum speciation analysis in order to evaluate its actual risk for the environment in connection with its biological availability and toxicity. The variety of different analytical procedures can be possibly employed using masking, separation or preconcentration steps as a general rule [2,4–12]. However, a wide range of possible difficulties still exists. For example, mass or atomic spectrometry techniques are limited by the problems related to their sensitivity and selectivity [2,7–12]. Thus the development of satisfactory sensitive, selective and economical methods for Mo(VI) trace amount quantitative determination is crucial from the analytical point of view. Such advantages as low cost and portable instrumentation, low detection limit and most of all the possibility of direct determination of Mo(VI) with no separation step make the electrochemical techniques, especially adsorptive striping voltammetry (AdSV), suitable for the speciation analysis of molybdenum. In the recent years several AdSV procedures have been developed for this purpose. All of them are based on the adsorptive accumulation of the Mo(VI) complex exploiting different complexing agents such as cupferron [13,14], chloranilic acid [14–17], alizarin S [18,19], 1,10-phenantroline [20,21], oxine [22,23], α-benzoinoxime [24,25] and others [26–32]. It is known that one of the most common problems in the application of stripping voltammetric procedures to the environmental sample analysis are the interference effects caused by organic constituents in the sample matrix. The main reason for this problem is associated with the adsorption of organic substances such as surface active compounds onto a working electrode, which causes peak depression or even complete fouling of the electrode [33–37]. Because surface active substances are commonly present in environmental samples as an effect of their general usage in human activity it is indispensable to develop procedures making it possible to determinate Mo(VI) in environmental samples containing surfactants. Reviewing the literature data in respect of possibilities of molybdenum determination in the presence of organic matter one can conclude that in most of the papers devoted to this subject the influence of organic substances on Mo(VI) determination has not been

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examined [16,17,19–21,25,26,29,32]. Merely in a few papers the problem deriving from the surface active compounds was examined [15,18,22–24]. In the majority of works it was suggested that in order to eliminate the interferences from organic substances, preliminary mineralization of the samples by UV irradiation or acid digestion coupled with heating before determination was recommended [13–16,18,22–24,28,31].

In this work, a highly sensitive adsorptive voltammetric stripping procedure for Mo(VI) determination in the presence of surface active substances is reported. This method is based on the adsorptive accumulation of complexes of molybdenum with cupferron or chloranilic acid onto the surface of a hanging mercury drop electrode (HMDE), while the negative influence of organic matter is eliminated by adsorption of these substances onto the surface of Amberlite XAD-7 resin. A differential pulse method with scanning in the negative direction is applied to obtain the voltammetric signal. Such a method is of great value in determination of Mo(VI) in natural water samples, which is necessary for environmental monitoring.

2. Experimental

2.1. Apparatus

Experiments were conducted using an μAutolab analyzer (Utrecht, The Netherlands) and a controlled growth static mercury drop electrode in the HMDE (MTM-ANKO Cracow, Poland). A conventional three-electrode system consisted of an Hg drop working electrode, with a surface area of 1.4 mm^2, a platinum wire counter electrode and an Ag/AgCl reference electrode (in saturated NaCl) was used in all experiments. The solutions were deoxygenated with high-purity nitrogen for 5 min prior to each experiment and kept under nitrogen atmosphere during the measurements.

2.2. Reagents

All chemicals used were of analytical reagent grade or Suprapur. A stock solution of 1 g L^{-1} Mo(VI) in 0.5 mol L^{-1} NH_3 (ICP standard) and cupferron (benzenamine, N-hydroxy-N-nitroso-ammonium salt) were obtained from Merck (Darmstadt, Germany). The solutions of Mo(VI) of lower concentrations were prepared by dilution of the stock solution as required. A solution of 1×10^{-2} mol L^{-1} of cupferron was prepared every day by dissolving 0.0155 g of the reagent in water in a 10 mL volumetric flask. A solution of 1×10^{-2} mol L^{-1} of chloranilic acid (Fluka-Buchs, Switzerland) was made fresh every week by dissolving 0.0209 g of the reagent in water in a 10 mL volumetric flask. An acetate buffer was prepared from Suprapur CH_3COOH and NaOH obtained from Merck. Triton X-100, sodium dodecyl sulfate (SDS), cetyltrimethylammonium bromide (CTAB) were purchased from Fluka (Buchs, Switzerland). Humic acid sodium salt (HA) was obtained from Aldrich. Amberlite XAD-7 was obtained from Sigma (St. Louis, MO, USA) and it was washed four times with triply distilled water and dried up at temperature of 50 °C. Certified reference material, seawater NAAS-5, was obtained from the National Research Council, Canada. Other reagents were obtained from POCh, Poland. All solutions were prepared using triply distilled water.

2.3. Procedures

2.3.1. Differential pulse method for determination of Mo(VI) using cupferron as a complexing agent

A natural water sample or synthetic sample, 2 mL of 1 mol L^{-1} acetate buffer pH 3 and an adequate volume of triply distilled water, so that the final volume of the solution was 20 mL, were added to a glass vial of 25 mL volume 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. Next, after sedimentation of resin, 10 mL of the solution was pipetted into the electrochemical cell and then 10 μL of 1×10^{-2} mol L^{-1} cupferron was added and deaeration for 5 min was performed. A mercury drop was formed, and the accumulation of the Mo(VI)–cupferron complex was carried out at 0.15 V for 30 s from the stirred solution. After the equilibration time of 5 s, the differential pulse voltammogram was recorded, while the potential was scanned from 0.15 V to −0.4 V, with the intensity of the obtained peak directly proportional to the concentration of Mo(VI) in the sample. The scan rate and pulse height were 20 mV s^{-1} and −50 mV, respectively. The molybdenum peak appeared at ∼−0.26 V.

2.3.2. Differential pulse method for determination of Mo(VI) using chloranilic acid as a complexing agent

A natural water sample or synthetic sample, 2 mL of 1 mol L^{-1} acetate buffer pH 2.5 and adequate volume of triply distilled water so that the final volume of the solution was 20 mL were added to a glass vial of 25 mL volume 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. Next, after sedimentation of resin, 10 mL of the solution was pipetted into the electrochemical cell and 100 μL of 1×10^{-2} mol L^{-1} chloranilic acid was added and deaeration for 5 min was performed. A mercury drop was formed, and the accumulation of Mo(VI)–chloranilic acid complex was carried out at −0.25 V for 30 s from the stirred solution. After the equilibration time of 5 s, the differential pulse voltammogram was recorded, while the potential was scanned from −0.25 V to −0.8 V, with the intensity of the obtained peak directly proportional to the concentration of Mo(VI) in the sample. The scan rate and pulse height were 20 mV s^{-1} and −50 mV, respectively. The molybdenum peak appeared at ∼−0.64 V.

Concerning the small current values of the peaks it is recommended for both procedures to measure the peak heights following the subtraction of the background voltammogram (background voltammogram – all the supporting electrolyte ingredients apart from Mo(VI)).

2.4. River water sample preparation

Natural river water samples Bystrzyca and Czerniejowka were collected with polypropylene bottles and then filtered through 0.45 μm Millipore membrane filters. The samples were kept at the temperature of 6 °C.

3. Results

3.1. Selection of the complexing agent and its influence on the Mo(VI) voltammetric signal in the presence of Amberlite XAD-7 resin

It is possible to carry out the adsorptive accumulation of Mo(VI) onto a mercury surface electrode using its complexes with different complexing agents. In this work two of them were employed, cupferron and chloranilic acid, as being the most frequently used and described in details in literature, producing stable complexes with Mo(VI) and making it possible to achieve low detection limits [13–17]. Preliminary experiments show that both the Mo(VI)–cupferron and the Mo(VI)–chloranilic acid complexes undergo adsorption on Amberlite XAD-7 resin and, as a consequence, the voltammetric signal of molybdenum decreases in time if the resin is present in the voltammetric cell. Considering this, the proposed procedure had to be carried out in two steps. In the first step the resin was added to the analysed sample and at the same time the organic matrix of the sample was removed through its adsorption onto the resin. It was tested that in the absence of a complexing agent such as cupferron or chloranilic acid the molybdenum ions did not adsorb onto the resin. In the second step the sample was pipetted into the voltammetric cell, a complexing agent was added and the voltammetric measurement was performed.

3.2. *Effect of pH and concentration of supporting electrolyte*

The formation of the complexes, their stability, and the potentials of reduction are strongly dependent upon the pH value of the solution [16]. Thus, the influence of the pH of the supporting electrolyte on the molybdenum voltammetric signal in the proposed procedure was examined. Experiments were performed in the range of pH from 2.0 to 4.5. CH_3COOH/CH_3COONa (pH 3.0) and CH_3COOH or NaOH were used to obtain the required medium. In both cases, for cupferron and chloranilic acid alike, a variation of the pH in the whole examined range did not cause a significant change of the molybdenum voltammetric signal. For further measurements, a pH equal to 3 and 2.5 for cupferron and chloranilic acid, respectively, was chosen with respect to the most convenient peak shape and considering the literature data, where it was stated that Mo(VI) produced stable complexes with cupferron at pH 3.0 and this kind of medium was recommended [13,14], and in the case of chloranilic acid the optimal pH in the range of 2–2.8 was suggested [14,15].

It is well known that non-ionic sorbents such as Amberlite XAD require low pH values for effective adsorption of organic compounds [38–40]. The influence of pH on the efficiency of surface active substances removal by XAD-7 in our procedures was also examined. The experiments were performed under standard conditions using 0.5 g of resin and 50 mg L^{-1} of Triton X-100, 1×10^{-9} mol L^{-1} of Mo(VI) for cupferron and 5 mg L^{-1} of Triton X-100, 1×10^{-8} mol L^{-1} of Mo(VI) for chloranilic acid. Measurements were performed for the following values of pH of solutions: 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5. The results show that in the whole studied range of pH the molybdenum voltammetric signal did not undergo a change. Thus it can be assumed that in the tested range of pH efficiency of surface active substances removal by XAD-7 is similar.

The effect of the concentration of the supporting electrolyte, i.e. an acetate buffer on the molybdenum peak current was also studied. The experiments were carried out using standard conditions, but the concentration of the acetic buffer was being changed from 0.01 to 0.5 mol L^{-1}. The results show that a change of the acetic buffer concentration does not significantly influence the peak current but for a concentration lower than 0.05 mol L^{-1} reproducibility of the signal was not satisfactory for both complexing agents, so for further studies a 0.1 mol L^{-1} concentration of the acetic buffer was chosen.

3.3. *Effect of accumulation potential and time*

In the view of fact that the accumulation potential and time have a significant influence on the sensitivity of the method, these parameters were examined precisely in the proposed work. Fig. 1 shows the influence of the variation of accumulation potential on the peak current of molybdenum, examined over the range of −0.4 to 0.15 V and −0.25 to 0.2 V for chloranilic acid and cupferron as the complexing agents, respectively. The experiments were performed in the presence and absence of Amberlite XAD-7 resin. In both cases the dependence of the accumulation potential on the peak current of molybdenum was the same. Because the main purpose of the presented procedures was the elimination of interferences caused by the presence of surface active substances, the effect of Triton X-100 on the molybdenum voltammetric signal for different accumulation potentials was examined. The obtained results are presented in Figs. 2 and 3 for cupferron and chloranilic acid, respectively. As can be seen for both complexing agents, with the employment of a more positive accumulation potential the negative influence of the surface active substances on the molybdenum voltammetric signal becomes more and more insignificant. It is a result of the adsorptive nature of the surface active substances, which can interfere as a result of competitive adsorption at the surface of the mercury electrode and, as is stated in the literature data [41], with the increase of the potential towards positive values, the adsorption becomes increasingly weaker. In the case of Mo(VI)–cupferron complexes the highest signal was obtained at the accumulation potential of 0.15 V (Fig. 1, curve b) and at this potential the interferences from the surface active

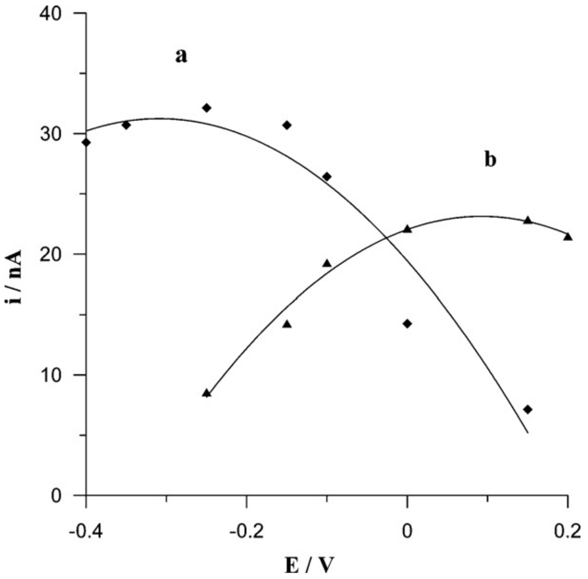

Fig. 1. The influence of accumulation potential on the peak current of 2×10^{-8} and 1×10^{-9} mol L^{-1} Mo(VI) for chloranilic acid (a) and cupferron (b), respectively. Presented data are normalized to the geometric area of the electrode surface equal to 1 mm^2.

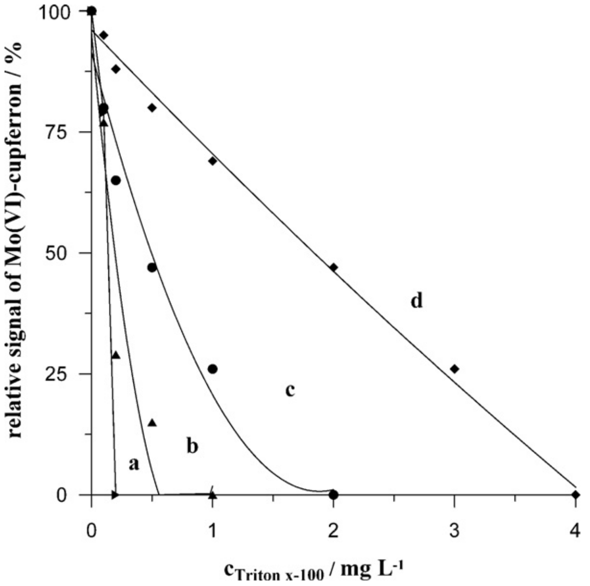

Fig. 2. The influence of Triton X-100 concentration on the peak current of 1×10^{-9} mol L^{-1} Mo(VI) for different potential accumulation: −0.15 V (a); 0 V (b); 0.1 V (c); 0.15 V (d). Accumulation time of Mo(VI)–cupferron complex 30 s.

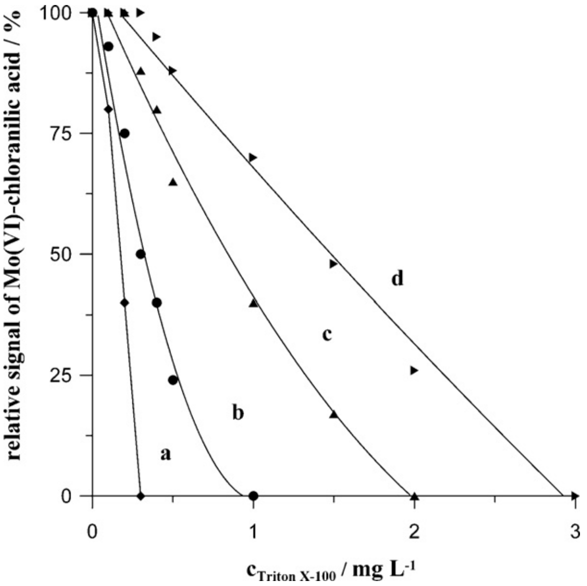

Fig. 3. The influence of Triton X-100 concentration on the peak current of 2×10^{-8} mol L^{-1} Mo(VI) for different potential accumulation: −0.25 V (a); −0.15 V (b); 0 V (c); 0.15 V (d). Accumulation time of Mo(VI)–chloranilic acid complex 30 s.

substances were the lowest (Fig. 2, curve d), so this accumulation potential value was chosen as the most suitable. In the case of adsorptive accumulation of Mo(VI)–chloranilic acid complexes the potential of −0.25 V was chosen for further work although at this potential the interferences from surface active substances are highest. This choice is a consequence of the fact that with the applying of more positive accumulation potential the peak current of molybdenum decreases significantly (Fig. 1, curve a), and additionally the reproducibility and shape of the peak are not satisfactory.

The effect of adsorptive accumulation time on the peak current was examined over the range from 0 to 180 s using standard measuring conditions. The peak current was found to increase linearly with accumulation time up to 60 s for both complexing agents. The peak continues to increase for longer accumulation times but not linearly in the case of Mo(VI)–chloranilic acid complex. In the case of Mo(VI)–cupferron complex the peak current at accumulation time longer than 120 s decreases slightly.

3.4. *Effect of complexing agents concentration*

To choose the optimal concentration of cupferron and chloranilic acid used as complexing agents for Mo(VI), the effect of their concentration on the peak current was studied. The results showed that the peak current increased upon increasing the cupferron concentration to 1×10^{-5} mol L^{-1} and after that it was constant. In the case of chloranilic acid the peak current increased upon increasing its concentration to 1×10^{-4} mol L^{-1} and after that a slight decrease in the peak current was observed. On the basis of these results, cupferron and chloranilic acid concentrations of 1×10^{-5} mol L^{-1} and 1×10^{-4} mol L^{-1}, respectively, were chosen.

3.5. *Elimination of interferences connected with the presence of surfactants*

In procedures that are supposed to be put into practice for elements determination in environmental samples the matrix effect has to be taken into account. Voltammetric methods such as adsorptive stripping voltammetry are especially susceptible to the organic matter inevitably present in natural samples. Among those substances the surface active compounds are one of the most important groups. In the face of more than probable presence of different kinds of surfactants, the quality control procedure should be performed by testing the influence of nonionic, cationic and anionic surfactants. Taking this into account, Triton X-100, cetyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS) were chosen for the examination of the influence of nonionic, cationic and anionic surface active compounds, respectively. The choice of these substances derives from the fact that they are widely used in numerous commercial and industrial products and in consequence they are released into the environment in fair amounts [42].

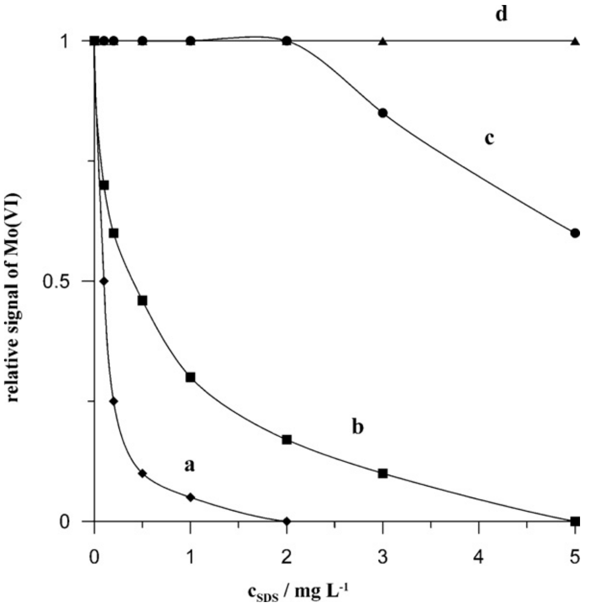

Fig. 4. The influence of SDS concentration on the relative signal of 1×10^{-9} and 2×10^{-8} mol L^{-1} Mo(VI) for cupferron (a and c) and chloranilic acid (b and d), respectively. Determination in the absence (a and b) and presence (c and d) of 0.5 g Amberlite XAD-7 resin.

The effect of Triton X-100 was examined for solutions containing 1×10^{-8} mol L^{-1} Mo(VI) and employing the standard procedures was described in Sections 2.3.1 and 2.3.2. As can be seen (Figs. 2 and 3), the voltammetric signal of molybdenum is very sensitive to the presence of even small amounts of the nonionic surfactant. The addition of resin drastically eliminates the unwanted negative influence of the nonionic surfactant on molybdenum peak heights. In the presence of Amberlite XAD-7 resin the inherency of even 50 mg L^{-1} of Triton X-100 does not affect at all the voltammetric signal of molybdenum owing to its adsorptive accumulation in the form of complexes with cupferron. In the case of accumulation of molybdenum in the form of complexes with chloranilic acid 5 mg L^{-1} of Triton X-100 does not affect the voltammetric signal of molybdenum. Maximum tolerable concentration of Triton X-100 which does not interfere with the molybdenum signal can be enlarged to 20 mg L^{-1} if the accumulation potential of the Mo(VI)–chloranilic acid complexes is changed from −0.25 V to 0 V but in this case the sensitivity of Mo(VI) determination decreases.

The influence of concentration of anionic synthetic surfactant (Fig. 4) and cationic synthetic surfactant (Fig. 5) on the molybdenum signal was examined both in the presence and absence of Amberlite XAD-7 resin. As can be seen, in the case of the cationic surfactant, the voltammetric signal of molybdenum is more suppressed than in the presence of the anionic surfactant. But the addition of resin effectively diminishes interferences caused by anionic and cationic surfactants both in the case of accumulation of Mo(VI) as chloranilic acid and cupferron complexes.

Table 1
Relative signal of Mo(VI) [%] in the presence of HA and FA to the signal obtained in the absence of these substances. Experiments were performed in the presence and absence of Amberlite XAD-7 resin. Concentration of Mo(VI) 1×10^{-9} and 1×10^{-8} for accumulation with cupferron and chloranilic acid, respectively.

Humic substances added		Relative signal of Mo(VI) [%]			
Type of substances	Concentration [mg L^{-1}]	Accumulation in the form Mo(VI)–cupferron		Accumulation in the form Mo(VI)–chloranilic acid	
		In the absence of resin	In the presence of resin	In the absence of resin	In the presence of resin
HA	0.1	85	101	95	98
	0.5	41	98	78	102
	1	0	97	62	103
	2	0	57	33	97
FA	1	48	97	95	101
	2	12	99	53	98
	5	0	96	8	96

3.6. *Examination of humic substances influence on molybdenum signal*

When using adsorptive stripping voltammetry for natural water analysis, the other possible interferents are the humic substances. Humic substances belong to the most widely distributed on earth heterogeneous organic substances with high molecular weight [43,44]. These substances are generally strongly adsorbed on the surface of a mercury electrode fouling it and, as a consequence, they influence the voltammetric signal obtained in speciation studies of metals in natural samples [43,45]. Humic substances are composed of three operationally defined fractions, water soluble under all pH – fulvic acids (FA), acid-precipitated (pH <2) but soluble in water at higher pH values – humic acids (HA) and water insoluble – humins [46]. Thus the effect of the presence of FA and HA on the molybdenum peak current was studied and the obtained results are presented in Table 1. The experiments were performed for samples containing Mo(VI) and different concentrations of HA and FA in the absence or presence of 0.5 g Amberlite XAD-7 resin. As can be seen, HA interfere with the molybdenum signal to a higher degree than FA during the accumulation of molybdenum complexes both with cupferron and chloranilic acid. In both procedures those interferences can be diminished by means of addition of Amberlite XAD-7 resin to the analysed sample prior to the voltammetric measurement. Comparing the effectiveness of removing the negative influences of surfactants and humic substances on the molybdenum signal by Amberlite XAD-7 resin it can be stated that in the case of humic substances the elimination of their interferences is less effective.

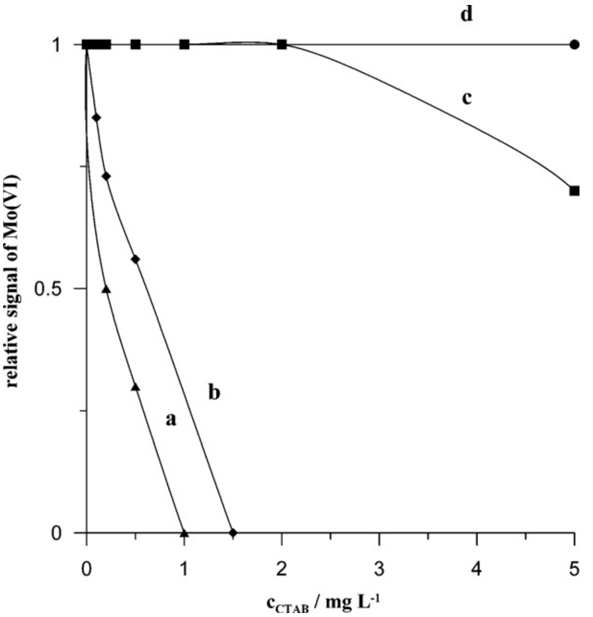

Fig. 5. The influence of CTAB concentration on the relative signal of 1×10^{-9} and 2×10^{-8} mol L^{-1} Mo(VI) for cupferron (b and d) and chloranilic acid (a and c), respectively. Determination in the absence (a and b) and presence (c and d) of 0. 5 g Amberlite XAD-7 resin.

3.7. *Effect of foreign ions and EDTA on the molybdenum signal*

In the adsorptive voltammetric determination of molybdenum, interferences may be caused also by the competitive adsorption of ions and their complexes on the electrode surface. The effects of co-existing ions were tested using a fixed concentration of Mo(VI) and different amounts of foreign ions. A tolerable limit was defined as the amount of foreign ions that produced an error not exceeding 5% in the determination of Mo(VI). The experiments were performed for 1×10^{-9} mol L^{-1} and 1×10^{-8} mol L^{-1} of molybdenum for cupferron and chloranilic acid, respectively, and the results are summarized in Table 2. As can be concluded the majority of ions does not interfere in at least 1000-fold excess. In the presence of a major concentration of Sn(IV), W(VI), U(VI) and Sb(III) it is advisable to apply the accumulation of Mo(VI) in the form of its complexes with chloranilic acid and in the presence of a major concentration of Se(IV) – with cupferron.

Considering that the determination of molybdenum is based on the adsorptive accumulation of its complexes in the case of environmental sample analysis an interference caused by the complexing agent occurring in such samples must be taken into account. In this work EDTA was chosen to study the influence of complexing agents on the Mo(VI) signal. EDTA was selected for this work as a commonly used artificial chelating agent, e.g. in industrial cleaning, household detergents, pharmacy, textile and paper manufacturing and as a consequence EDTA occurs widely as a water pollutant. This compound is not considered as biodegradable and it is susceptible to accumulation in receiving waters [47,48]. Addition of EDTA to a sample solution at a concentration of 2.5×10^{-5} mol L^{-1} does not affect at all the molybdenum signal and 1×10^{-4} mol L^{-1} causes a decrease of molybdenum signal to 40% of its original value when cupferron as a complexing agent is used. In the case of exploiting chloranilic acid the addition of EDTA to a sample solution at a concentration of 1×10^{-4} mol L^{-1} does not affect the molybdenum signal at all and 5×10^{-4} mol L^{-1} causes a decrease of the molybdenum signal to 60% of its original value. According to World Health Organization (WHO) data it has been estimated that generally maximal EDTA concentrations of 2×10^{-7} mol L^{-1} are present in wastewaters. It could be concluded that the complexing agent present in natural samples should not interfere in the proposed procedures of Mo(VI) determination.

3.8. *Characteristics of the analytical procedures*

The analytical characteristic of the proposed procedure using cupferron as a complexing agent is as follows: the calibra-

Table 2
Tolerance levels of foreign ions in the determination of 1×10^{-9} mol L^{-1} and 1×10^{-8} mol L^{-1} of molybdenum for cupferron and chloranilic acid, respectively. Experiments were performed at the recommended conditions.

Ion	Tolerance level of ion [nmol L^{-1}] for accumulation Mo(VI)–cupferron complex	Tolerance level of ion [nmol L^{-1}] for accumulation Mo(VI)–chloranilic acid complex
Al(III)	10^4	10^4
As(III)	10^4	10^4
As(V)	10^4	10^4
Bi(III)	10^3	10^4
Cd(II)	10^4	10^4
Co(II)	5×10^3	5×10^3
Cr(III)	5×10^3	10^4
Cr(VI)	10^4	10^4
Cu^{2+}	5×10^3	5×10^3
Fe(III)	5×10^3	5×10^3
Mg(II)	10^4	10^4
Mn(II)	10^4	10^4
Ni(II)	10^4	10^4
Pb(II)	5×10^2	10^2
Sb(III)	10^2	2×10^3
Se(IV)	5×10^3	10^2
Se(VI)	10^4	10^4
Sn(IV)	10	2×10^2
Ti(IV)	10^2	10^2
U(VI)	10^2	10^4
V(V)	10^3	10^3
W(VI)	5	10^4
Zn(II)	5×10^3	5×10^3
Zr(IV)	10^3	5×10^3

tion graph for an accumulation time of 15 s was linear in the range from 1×10^{-10} to 2×10^{-9} mol L^{-1} and obeyed the equation $y = 31.21x + 1.07$ (y and x are the peak current (nA) and Mo(VI) concentration (nmol L^{-1}), respectively), with a correlation coefficient of $r = 0.9992$; the detection limit estimated from 3 times the standard deviation for a low Mo(VI) concentration and accumulation time of 15 s was about 5×10^{-11} mol L^{-1}; the relative standard deviation for a Mo(VI) concentration of 1×10^{-9} mol L^{-1} was 4.7% ($n = 5$).

The analytical characteristic of the proposed procedure using chloranilic acid as a complexing agent is as follows: the calibration graph for an accumulation time of 30 s was linear in the range from 1×10^{-9} to 1×10^{-7} mol L^{-1} and obeyed the equation $y = 2.20x - 0.15$ (y and x are the peak current (nA) and Mo(VI) concentration (nmol L^{-1}), respectively), with a correlation coefficient of $r = 0.9998$; the detection limit estimated from 3 times the standard deviation for a low Mo(VI) concentration and accumulation time of 30 s was about 3×10^{-10} mol L^{-1}; the relative standard deviation for a Mo(VI) concentration of 1×10^{-8} mol L^{-1} was 3.1% ($n = 5$).

The comparison of parameters of proposed procedures with other adsorptive stripping voltammetric procedures for molybdenum trace determination is presented in Table 3.

3.9. *Application of the proposed procedures*

To validate the method of Mo(VI) determination, the certified reference material – seawater NASS-5 was applied. This material did not undergo any pretreatment and was analysed directly in the form in which it had been purchased. The obtained results of Mo(VI) determination were in good agreement with the certified reference value and they are presented in Table 4. In order to test the possibility of using the proposed methods in samples with more complicated matrices, the NASS-5 was additionally spiked with surface active substances and humic acid. The results received are shown in Table 4. Fig. 6 shows typical voltammograms presenting Mo(VI) quantification in certified reference material NASS-5.

Using the optimal conditions, the proposed procedures were also tested for Mo(VI) determination in the Bystrzyca and Czerniejówka river water samples. The collected samples were submitted to analysis without any pretreatment using the standard addition method. The voltammograms recorded for both river water samples with the use of both cupferron and chloranilic acid did not exhibit any signal of Mo(VI), so the samples were spiked with 2×10^{-9} and 2×10^{-8} mol L^{-1} of Mo(VI) and analysed using cupferron and chloranilic acid as complexing agent, respectively. Samples were analysed with the standard addition method based

Table 3
The comparison of parameters of adsorptive stripping voltammetric procedures for trace molybdenum determination. The procedures are arranged according to the growing detection limit.

Working electrode	Complexing reagent	Linear range [nmol L^{-1}]	Detection limit [nmol L^{-1}]	RSD [%]	Reference
HMDE	Oxine	0.01–5	0.0017 for 60 s	1.9	[22]
HMDE	Methyl tymol blue	0.1–1500	0.02 for 60 s	1.0	[26]
HMDE	Cupferron	0.1–2	0.05 for 15 s	4.7	Proposed method
HMDE	Tiron	0.1–200	0.06 for 60 s	0.9	[30]
Hg(Ag) film electrode	Chloranilic acid	2–200	0.08 for 60 s	1.3	[15]
HMDE	α-Benzoinoxime	25–100	0.1 for 300 s	3.5	[24]
HMDE	Chloranilic acid	1–100	0.3 for 30 s	3.1	Proposed method
HMDE	Cupferron	1–200	0.6 for 60 s	–	[13]
Lead film electrode	Alizarin-S	2–50	0.9 for 60 s	3.9	[18]
Bismuth film electrode	Chloranilic acid	50–500	2 for 60 s	2.6	[17]
Modified carbon paste electrode	α-Benzoinoxime	100–80,000	20 for 60 s	6.4	[25]

Table 4
Results of Mo(VI) determination in certified reference material NASS-5 with certified value of Mo(VI) 9.6 ± 1.0 μg L^{-1}. Experiments were performed at the recommended conditions. In brackets the relative standard deviation in % is given (n = 5).

Sample	Mo(VI) determined [μg L^{-1}]	
	Procedure using cupferron as complexing agent	Procedure using chloranilic acid as complexing agent
NASS-5	9.2 (4.2)	8.8 (3.8)
NASS-5 + 1 mg L^{-1} HA	8.7 (4.9)	8.6 (5.5)
NASS-5 + 5 mg L^{-1} Triton X-100	10.1 (5.7)	9.8 (4.2)
NASS-5 + 1 mg L^{-1} HA + 5 mg L^{-1} Triton X-100	9.0 (6.2)	8.9 (5.8)

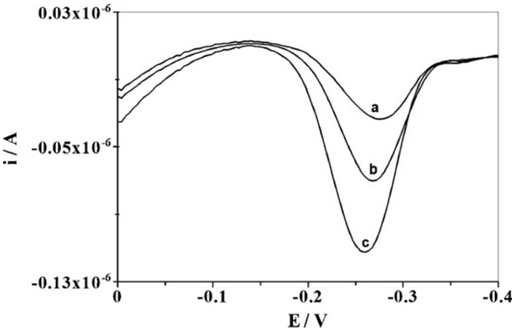

Fig. 6. The adsorptive stripping voltammograms obtained in the course of the determination of Mo(VI) in certified reference material NASS-5 using cupferron as a complexing agent: (a) NASS-5 diluted (1:200); (b) as (a) +5 × 10^{-10}; (c) as (a) +1 × 10^{-9} mol L^{-1} Mo(VI).

on three repetitions of analysis. In the cases of both the Bystrzyca and Czerniejówka river water samples the obtained recoveries were between 94.2 and 98.8%, with relative standard deviation between 7.1 and 5.3%.

On the basis of these results of analysis of certified reference material and natural river water samples it can be concluded that the proposed method can be used for Mo(VI) determination in natural water samples without any pretreatment.

4. Conclusion

Due to the application of Amberlite XAD-7 resin to the elimination of interferences from organic substances it was possible to determine Mo(VI) in natural water samples without the necessity of their preliminary pretreatment. So far the problem with the interferences from organic substances has been omitted in many papers in literature data, while in the others mineralization by UV irradiation or acid digestion coupled with heating before determination was recommended. In this paper two voltammetric procedures using cupferron or chloranilic acid for adsorptive accumulation of Mo(VI) onto a mercury electrode for direct analyses of natural water samples were proposed. Comparing the capabilities of these two procedures it was concluded that employing cupferron as a complexing agent made it possible to obtain very low detection limits of Mo(VI) in the presence of even 50 mg L^{-1} of surface active substances. However, for samples containing higher concentrations of Mo(VI), especially in the presence of a major concentration of foreign ions such as Sn(IV), W(VI), U(VI), Sb(III), the procedure employing chloranilic acid is suggested. The successful practical application of the proposed procedures to the analysis of seawater certified reference material and natural river water samples appears to be promising for their adoption in environmental measurements.

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