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ABSTRACT

The influence of an adsorbed layer of the natural organic matter (NOM) on voltammetric behaviour of copper on a mercury drop electrode in natural water samples was studied. The adsorption of NOM strongly affects the differential pulse anodic stripping voltammogram (DPASV) of copper, leading to its distortion. Phase sensitive ac voltammetry confirmed that desorption of adsorbed NOM occurs in general at accumulation potentials more negative than −1.4 V. Accordingly, an application of negative potential (−1.6 V) for a very short time at the end of the accumulation time (1% of total accumulation time) to remove the adsorbed NOM was introduced in the measuring procedure. Using this protocol, a well-resolved peak without interferences was obtained. It was shown that stripping chronopotentiogram of copper (SCP) in the depletive mode is influenced by the adsorbed layer in the same manner as DPASV. The influence of the adsorbed NOM on pseudopolarographic measurements of copper and on determination of copper complexing capacity (CuCC) was demonstrated. A shift of the peak potential and the change of the half-peak width on the accumulation potential (for pseudopolarography) and on copper concentration in solution (for CuCC) were observed. By applying a desorption step these effects vanished, yielding different final results.

1. Introduction

The bioavailability and toxicity of metal ions to aquatic organisms is mainly related to concentrations of their free (hydrated) form [1–3]. The distribution of inorganic metal species in natural waters with known composition of major anions is predictable. However, for many metals the speciation is predominantly controlled by interactions with ligands/active sites of natural organic matter (NOM) [1–3]. In most cases, complexation of trace metals with organic matter decreases their bioavailability and toxicity. Among several methods for determination of chemical speciation [3], anodic

stripping voltammetry (ASV) is an attractive method which satisfies the requirements concerning sensitivity and selectivity, while offering the benefit of low contamination risk and alteration of original sample composition during analysis. Speciation of trace metals by ASV is usually performed by determination of metal complexing capacity (MCC) [3–5]. As a final result, concentration of ligands forming stable inert complexes with a metal of interest and the corresponding conditional stability constants (K') are determined. It was recently shown that voltammetric titration data (interactions of trace metals with active sites of NOM) are mainly fitted to model encompassing two discrete classes of ligands [4]. To ensure the reliability of the obtained information, application of a wider detection window (using logarithmic additions) is proposed [5].

According to some studies, the limitation of ASV for metal speciation is that it is a kinetically dependent technique [6], i.e. some inert complexes may dissociate during the accumulation period, which could lead to underestimation of complexing parameters. However, this could be a good point because such processes might occur on the biological cell membranes as well [6].

The well-known pseudopolarographic approach in trace metal speciation [7–20] has recently attracted new attention due to the possibility to automate the process of recording of pseudopolarograms. The benefit of using pseudopolarography and a recently developed analogous technique, scanned (deposition potential) stripping chronopotentiometry (SSCP), is that obtained information about metal complexation are similar to classical polarography, but achieved at significantly lower metal concentrations [11,22–24]. As it is theoretically described and experimentally verified, the complexation of a metal by a ligand will cause a (slight) shift of reduction wave of labile complexes towards more negative potentials, while the inert complexes are separately reduced at more negative potentials comparing to labile complexes [7–24]. The magnitude of these shifts (for both labile and inert complexes) is related to the stability constant of the formed complex and to the concentration of the free complexing ligand in the case of labile complexes.

The interferences in voltammetry [3,23–31] are well known, and one important problem is adsorption of surface active substances (SAS) on the electrode surface. As a significant part of NOM usually exhibit the properties of SAS [32], this process is likely to occur when dealing with real sample in ASV. In the literature it has been reported how the adsorption of SAS influences the electrochemical reactions of copper [25–27] and also that the desorption of adsorbed SAS occurs at more negative potentials, producing well-resolved copper peak [25,31].

Each interference affecting measurement is in some extent converted into final speciation data and contributes to more or less erroneous data. Thus, the intention is to exclude interferences as much as possible during measurements.

The main objective of this paper is to explore the impact of an adsorbed layer of SAS on a mercury electrode in measurements of copper complexing properties. The benefit of removing the adsorbed layer by applying desorption step in the procedure of complexing capacity determination and pseudopolarographic measurement in seawater samples is demonstrated.

2.   Experimental

All voltammetric measurements were carried out using an Autolab potentiostat (EcoChemie, Utrecht, The Netherlands) (μAutolab or PGSTAT12) equipped with a Metrohm 663 VA stand (Metrohm, Herisau, Switzerland). The instrument was computer-controlled using GPES 4.9 control software. The working electrode was a static mercury drop electrode (size 1, 0.25 mm^2), the counter electrode was a platinum wire or a glassy carbon rod, and the reference electrode was Ag|AgCl (sat. NaCl). Stirring of the solution was performed by built-in Teflon stirrer rotating at 3000 rpm. All measurements were performed at room temperature ($22 \pm 1\,^\circ$C). pH was controlled by a Metrohm pH meter (Model 713) with a glass pH electrode.

Differential pulse anodic stripping voltammetry (DPASV), phase sensitive ac voltammetry and stripping chronopotentiometry (SCP) were used as measuring techniques under the following conditions (if not otherwise noted in figure captions): pulse amplitude, $A = 20$ mV; potential step increment, $E_{st\,inc} = 2$ mV; time between pulses, $t_{int} = 0.1$ s; pulse duration, $t_{mod} = 0.04$ s; phase angle, $\theta = 90^\circ$. Other procedure parameters are given in figure captions. For pseudopolarographic measurements, accumulation of metal ions was performed during the deposition time (t_{acc}) consecutively, at a selected range of deposition potentials (E_{acc}) in defined steps.

Pseudopolarographic measurements were carried out automatically using the measuring procedure integrated in the PROJECT mode offered by the GPES 4.9 software. A home-written program capable to change either conditioning or deposition potential was integrated in the measurement protocol to simplify the measurement protocol/project. Analysis of voltammetric peaks and construction of pseudopolarograms was performed using home-written software [10] (the two home-written programs are available on request free of charge).

All solutions were prepared in deionised water from a Millipore Milli-Q system (Bedford, USA). Stock metal solutions (Cu, Zn) were prepared by diluting a commercial standard solution (1.0 g L^{-1}, Fluka, Buchs) in MQ-water. Concentrated nitric acid was of *supra pur* grade (Merck, Darmstadt). Samples in the cell (except for a.c voltammetric measurements) were purged with oxygen-free nitrogen for at least 5 min prior the measurement, followed by maintaining a nitrogen blanket above the electrolyte surface during the measurement.

Natural water samples were taken in estuary of the Gapeau river (Hyères, France) (sample 1, salinity = 35‰), in a small port on island Prvić (Šepurine, Croatia) (sample 2, salinity = 38‰) and in estuary of the Krka river (Šibenik, Croatia) (sample 3, salinity = 24‰). Surface water samples (0.2 m) were sampled and stored in pre-cleaned 1 L high-density polyethylene bottles (HDPE) or in 1 L FEP (fluorinated ethylene propylene) bottles (both from Nalgene Labware). Samples were filtered through 0.45 μm cellulose–nitrate filters and stored at 4 °C until analysed.
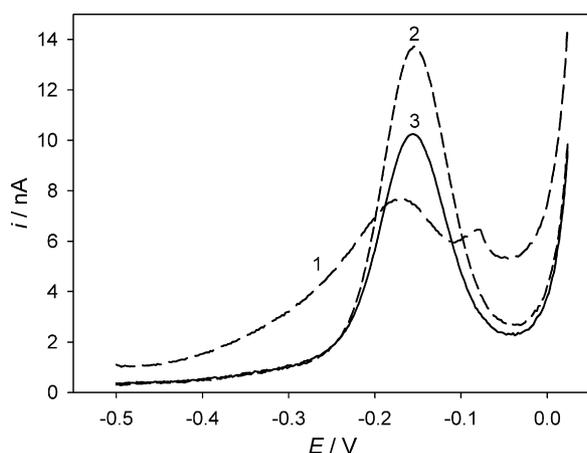
3. Results and discussions

The influence of SAS on the voltammetric behaviour of copper was studied by anodic stripping voltammetry (ASV), phase sensitive ac voltammetry, stripping chronopotentiometry (SCP) and pseudopolarography.

3.1. Influence of SAS on ASV of copper

Voltammograms of copper (1.4×10^{-7} mol L^{-1}, determined after acidification and UV digestion) in seawater using DPASV and different parameters during the accumulation period are shown in Fig. 1. An appropriate accumulation potential to reduce the labile part only was selected on the basis of corresponding pseudopolarograms [10]. Electrochemical reaction of copper in chloride media occurs *via* a monovalent copper (Cu(I)) intermediate [27,33], which causes a shift in the copper peak position toward a more negative potential, a half-peak width which corresponds to a one-electron charge transfer reaction, and a peak height about half the value of that recorded in the absence of chloride (oxidation from monovalent copper to divalent copper also occurs but overlaps with the mercury oxidation and is therefore not observed). The anodic peak observed at −0.17 V in curve 1 (Fig. 1) was obtained with an accumulation potential of −0.45 V. The measured half-peak width is 115 mV, which is wider than expected. The relatively high and slowly rising background current and the poorly defined peak made it difficult to determine exactly the copper peak height. Furthermore, an additional small peak was observed on the anodic side of the main peak, indicating occurrence of non-faradaic surface reactions from the adsorbed state [25,26].
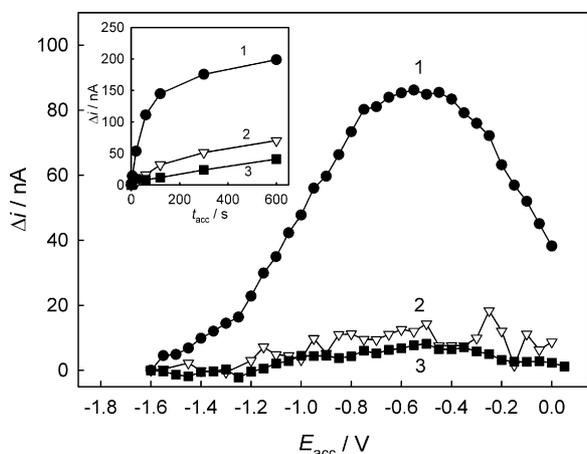
Curve 2 (Fig. 1) was obtained using an accumulation potential of −1.6 V. Compared to curve 1, a more pronounced oxidation peak of copper was observed, together with a significant decrease in the background current. The peak current was increased by a factor of three, and the half-peak width was reduced to 85 mV (corresponding to a reversible one-electron

charge transfer). Taking into account that more stable metal complexes also should be reduced at very negative potentials [12–17], the results obtained in curves 1 and 2 indicate that only approximately 30% of the total dissolved copper exists in labile metal complexes in the actual sample. However, on the basis of curve 3 (Fig. 1), a completely different conclusion is drawn. In this experiment, the same accumulation potential as in curve 1 (−0.45 V) was used for 297 s, and then for the last 3 s the applied potential was set to −1.6 V. The peak height decreased only by about 30% compared to curve 2, and the half-peak width remained surprisingly the same (87 mV). It is obvious that, by applying a very negative potential for only 1% of the total accumulation time, significant changes regarding the electrochemical processes at the mercury surface occur. This phenomenon is described in the literature for model solutions using extracted hydrophobic organic matter from seawater added to perchlorate supporting electrolyte [25]. It is supposed that the adsorbed SAS hinders the electrochemical reaction of copper during the stripping mode (curve 1) although, by applying a very negative potential, desorption of SAS takes place and produces a stripping peak without interferences (curve 3). The small difference between peak heights in curves 2 and 3 could be attributed to the actual difference between the fraction of labile and stronger metal complexes. If experiments are performed in such a way that initial potential is in the range of SAS adsorption (more positive that −1.1 V), some small portion of SAS will be adsorbed on the electrode surface during the equilibrium time and stripping time. However, as during this time the mass transfer is controlled mainly by the diffusion, the extent of adsorbed SAS could be considered as minor. To explore this phenomenon of SAS adsorption, experiments utilizing phase sensitive ac voltammetry were performed.

It is well known that adsorption of surface active substances (SAS) on a mercury electrode surface occurs usually in a potential range from 0.1 to −1.3 V [34–36]. Adsorption of SAS is usually the strongest in the range of an electrocapillary maximum of the mercury electrode (around −0.6 V) and depends both on the type of SAS and on the sample composition (major ions). The content of SAS in a natural sample could be easily quantified and characterized using phase sensitive ac voltammetry (phase angle = 90°) [34–36]. The procedure is based on the measurement of the capacitive current (or capacitance) at a potential of maximum adsorption (around −0.6 V) after applying an accumulation step (usually at accumulation potential of −0.6 V) during the chosen accumulation time. The resulting decrease in capacitive current corresponds to the concentration of SAS, while the capacitive current at zero accumulation time was taken as the reference value without adsorbed SAS. To explore these phenomena observed in Fig. 1, measurements of capacitive current at different accumulation potentials were performed (sample 1). Fig. 2 shows the differences in capacitive currents (related to the current at the most negative accumulation potential, −1.6 V) in relation to the accumulation potential. The procedure for curve 1 was the following: accumulation at desired potentials (during 60 s) followed by measurement of the capacitive current at −0.60 V, while for curve 2 at the end of accumulation time the potential of −1.6 V was applied for 1 s. It is evident that by applying the negative potential, almost a complete layer of

Fig. 1 – DPAS voltammograms of copper in seawater sample (sample 1) obtained using different experimental parameters: (1) t_{acc} = 300 s at E_{acc} = −0.45 V; (2) t_{acc} = 300 s at E_{acc} = −1.6 V; (3) t_{acc} = 297 s at E_{acc} = −0.45 V and t_{acc} = 3 s at E_{acc} = −1.6 V.
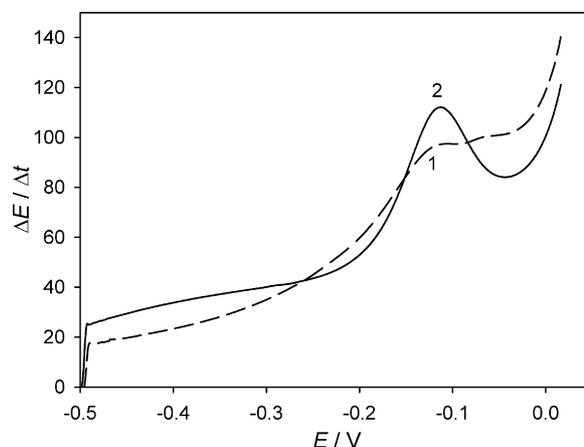
Fig. 2 – Difference of capacitive current (measured at −0.6 V) vs. accumulation potential obtained in seawater sample (sample 1) using accumulation time of 60 s and without (1) and with (2) 1 s at −1.6 V at the end of accumulation time (−1.6 V used as reference potential). Curve 3 corresponds to UV irradiated sample without desorption step. Inset: dependence of the difference of capacitive current on the accumulation time: (1) E_{acc} = −0.6 V; (2) E_{acc} = −0.6 V and E_{acc} = −1.6 V for 1 s; (3) E_{acc} = −1.6 V. Parameters: f = 75.12 Hz, t_{mod} = 0.21 s, t_{int} = 0.61 s, phase angle = 90°.

Fig. 3 – Stripping chronopotentiograms of copper in seawater sample (sample 1) obtained using different experimental parameters: (1) t_{acc} = 300 s at E_{acc} = −0.45 V; (2) t_{acc} = 297 s at E_{acc} = −0.45 V and t_{acc} = 3 s at E_{acc} = −1.6 V. I_{stripp} = 2 × 10^{-9} A. For both curves, an equilibrium potential of −0.5 V for 10 s was used.

adsorbed SAS is removed from the mercury surface. From the inset to Fig. 2, it can be evaluated that a degree of surface coverage attained during 30 s at −0.6 V without the desorption step (curve 1) corresponds to the degree attained during 600 s of accumulation time for curve with the potential jump (curve 2). However, compared to the dependence obtained for the accumulation at only the most negative potential (−1.6 V, curve 3), some SAS still remained on the mercury surface. For comparison, measurements in a UV irradiated sample without using the desorption step was performed (curve 3). As the NOM was destroyed by the prolonged exposure of the sample to UV light (14 h), the observed effect of adsorbed layer decreased to less than 10% of that obtained in the UV untreated sample (curve 1).

From the results given in Figs. 1 and 2, it is obvious that the ASV of copper (curve 1, Fig. 1) is strongly influenced by the adsorbed SAS layer. The simple experiments presented above show that such undesired effects can easily be eliminated or reduced, giving more correct information about speciation.

3.2. Stripping chronopotentiometric (SCP) measurements

Usually, substances adsorbed on an electrode surface have more effect on voltammetric shape obtained using pulse techniques than using direct mode techniques. It was demonstrated in model electrolyte solutions that stripping chronopotentiometry (SCP) in depletive mode has an advantage over ASV in pulsed mode if adsorption processes take place at the electrode surface [21–24]. Because of NOM heterogeneity, such situations are likely to occur in analysis of natural water samples, and SCP should be taken into account
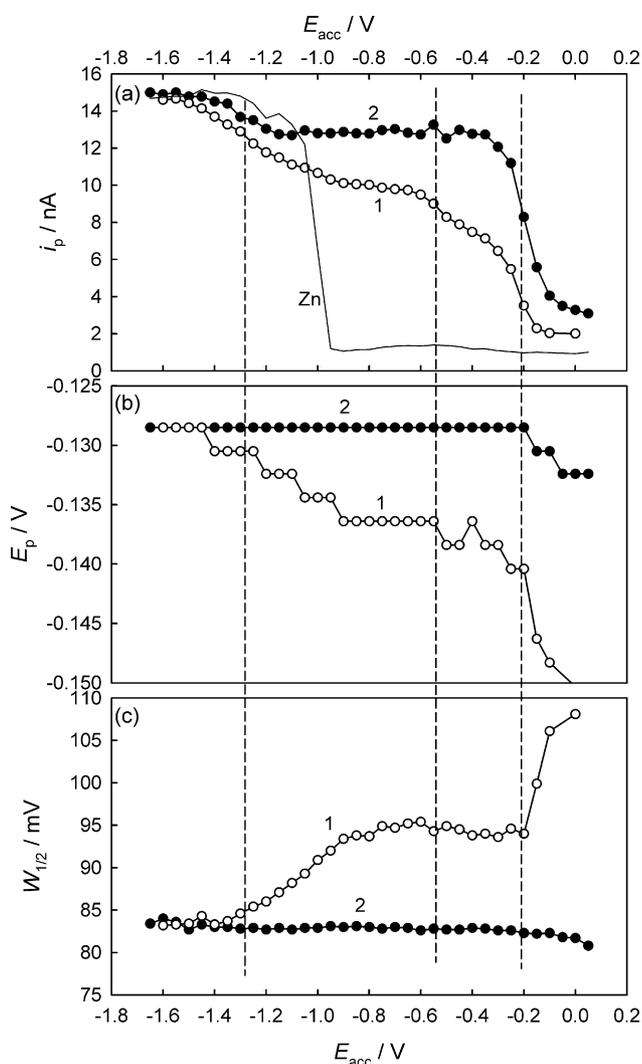
in the measurement protocols as a comparative technique. In general, SCP offers better resolution/separation of adjacent peaks than ASV, but its detection limit is in most cases poorer than that of ASV.

Fig. 3 shows the stripping chronopotentiograms of copper in sample 1. According to the literature, SCP in depletive mode is recommended because all the accumulated metal is stripped out from the mercury, while at the same time slow oxidation produces less interferences on the mercury surface [23]. Thus, the stripping current of 2 × 10^{-9} A was applied in the stripping stage. Curve 1 is acquired by accumulation at −0.45 V during 300 s. Comparing to curve 1 in Fig. 1 a similar shape is obtained, but taking into account the background current, the copper peak is poorly defined, which supports the thesis of lower sensitivity of SCP compared to ASV in pulse mode. Small shoulder on the anodic side of the peak is also noticeable, indicating some surface reaction, probably nonfaradic. Similarly to ASV, keeping the electrode for only three (3) seconds at the end of the accumulation time at a very negative potential (−1.6 V), resulted in a more pronounced peak (curve 2, Fig. 3). This experiment shows that, although the SCP in some cases is superior to ASV, in our sample of seawater the improvement of the signal resolution/evolution was not registered, and all the subsequent experiments were carried out employing only ASV.

3.3. Pseudopolarographic measurements

The influence of SAS adsorption on a mercury electrode on the shape of copper pseudopolarograms in the seawater sample (sample 2) was investigated. Copper pseudopolarograms were recorded without added copper, because relatively high concentration of copper was found in the sample (1.8 × 10^{-7} mol L^{-1}).

Fig. 4a shows two pseudopolarograms of copper obtained with different voltammetric parameters during the accumulation period. To exclude a possible change in the sample

Fig. 4 – Pseudopolarograms of copper in seawater sample (sample 2) obtained without (curve 1) and with (curve 2) desorption step constructed using peak height (a), anodic peak potential (b) and half-peak width (c). Total accumulation time was $t_{acc} = 300$ s. Solid line in (a) corresponds to pseudopolarogram of zinc performed separately in a new sample (peak currents of zinc are scaled by factor of 0.75 to correspond to peak currents of copper).

registered, which indicates that no reduction process of any additional copper species took place. At more negative potentials (<−1.15 V) the copper peak current increased, producing a wave that extended over the potential range of 300 mV. Several speculations could be drawn for this wave: (1) the reduction of a group of inert copper complexes with very high stability constants [9,12–15], (2) an intermetallic compound of Cu and Zn, which is formed in this range of potentials, usually increases the copper peak height [20,23], and (3) a decrease in SAS adsorption on the mercury surface with an increase in the accumulation potential to more negative values (see Fig. 2). The detailed analysis of the pseudopolarograms and additional measurements performed on separate samples showed that the first (1) scenario is the most probable one, i.e. the reduction of inert metal complexes. Assumption 2 was discarded by additional insight in the zinc pseudopolarogram (Fig. 4a), which shows that the rising part of the copper peak height started at potentials where the main portion of the limiting current of zinc pseudopolarogram has already been reached. In the case of formation of an intermetallic compound between Cu and Zn, the starting point of the wave should be more positive than what we observed. Assumption 3 is less probable than assumption 1 since by comparing Fig. 4b and c, it can be noticed that both the peak potential and the half-peak width in this potential range do not change after using the desorption step. As the increase of this wave, compared to the preceding plateau, is about 20%, it is to expect a small change in values of these two parameters (peak potential and half-peak width). This assumption is drawn on the basis of the dependences of peak potential and half-peak width on the accumulation potential without the desorption step, where a considerable change of these two parameters occurred (curves 1).

The three plots in Fig. 4 clearly evidence that the adsorbed layer of SAS has a significant impact on all three parameters of the voltammetric peak (height, potential and half-width). The intensity of this influence is dependent on the accumulation potential, as well as on the concentration of copper inside the mercury drop. The obtained results are in a very good agreement with our results obtained with ac voltammetry. At potentials more negative than −1.4 V the effect is negligible. However, by increasing the accumulation potential, the influence of SAS also increases and remains constant around the potential of maximal adsorption (∼−0.6 V). At accumulation potentials more positive than −0.2 V, the peak height decreased (reduction wave of labile copper) causing a shift in peak potential and broadening of the peak.

A detailed examination of curve 1 in Fig. 4a reveals three separate waves. The height of the first wave at −0.2 V barely reaches 50% of the equivalent wave using the desorption step (curve 2), while the wave at the more negative potential (around −1.3 V) expands from −0.9 to −1.5 V. An additional (third) poorly resolved wave appears at a potential around −0.5 V. Compared to curve 2, a considerable detachment is evident by applying the desorption step. As pointed out in several papers, the position, numbers, and shape of the pseudopolarographic waves is dependent on the metal complexes existing in the sample [10,12–23,37], and stability constants of labile metal complexes can easily be calculated [12–15,38]. The more negative pseudopolarographic wave that we obtained using

properties and experimental conditions during prolonged measurements (several hours), the pseudopolarograms were recorded in a way that both voltammetric procedures (with 3 s of desorption time at −1.6 V and without it) were applied for each accumulation potential one after the other (in a commutation mode). As in previous figures, curve 1 represents the procedure performed without applying the desorption step, while for curve 2, a potential jump to −1.6 V for 3 s at the end of the accumulation time was applied. The difference between the two pseudopolarograms is obvious. Using the desorption step (curve 2), two very well defined waves were obtained. The first wave at a potential of −0.2 V corresponds to the reduction of labile copper complexes. In the potential range between −0.4 and −1.15 V, a wide plateau was

the desorption step corresponds to a thermodynamic stability constant of the formed complex in the order of $\log K \sim 39$ (estimated according to "chelate scale" previously presented by group of Luther III [12–15]). Such a high stability constant of copper complexes has previously been reported by pseudopolarography and ascribed to the complex formed with a ligand produced by cyanobacteria [13]. However, a more detailed study should be performed to confirm such an assumption for our sample.
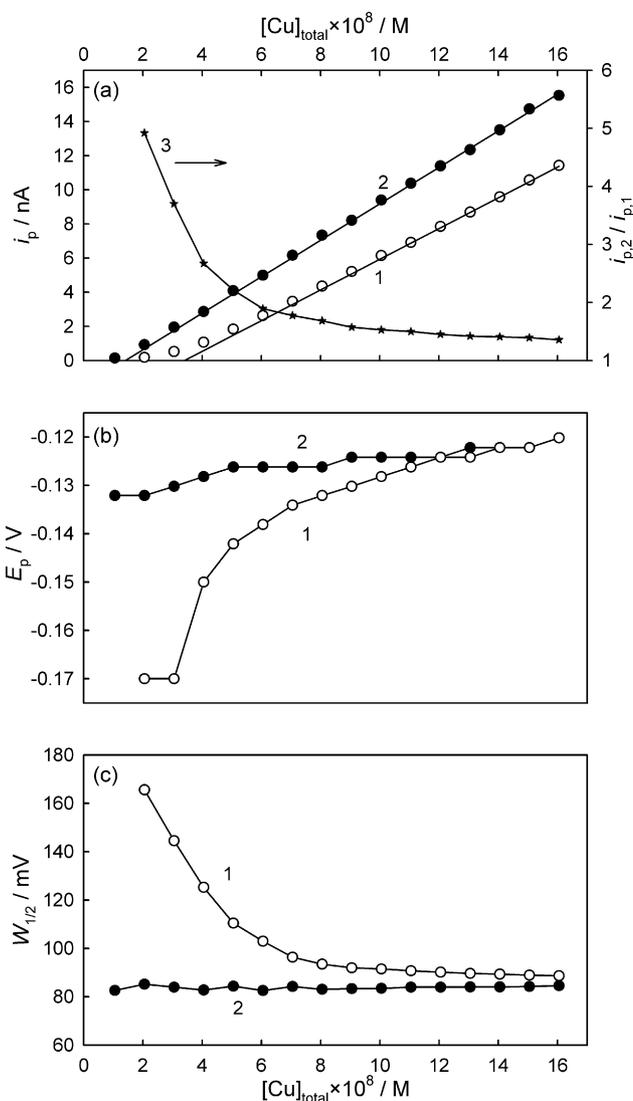
Similarly to the more negative wave, the small (third) wave around −0.5 V observed on curve 1 could be assigned to the reduction of a copper complex. However, as this wave is not registered using the desorption step (curve 2), it is fully clear that its formation is the result of surface reactions on the mercury electrode caused by the adsorbed organic matter, and that metal complex does not exist in the bulk of the sample in sufficient concentration to produce measurable wave.

The curves representing the dependence of the peak position and half-peak width on the accumulation potential (Fig. 4b and c) show strong interaction of copper with ligands from the adsorbed layer during oxidation process and indicate formation of kinetically labile complexes which affect the peak position and half-peak width [26,28]. Although studies of such interactions are important and useful for interpretation of voltammetric data [28,35], the main goal in speciation measurements is characterization of trace metal interactions with ligands within the bulk of the sample [2]. Thus, any interference in the voltammetric measurement occurring at the surface of the electrode is inauspicious and should be avoided. This evident example shows a delicate situation, which could initiate inaccurate conclusion about metal speciation in natural water sample.

3.4. Determination of metal complexing capacity (MCC)

Determination of metal complexing capacity (MCC) is very often used as a method to characterize particular natural water, either as a parameter in metal speciation or the characterization of the natural organic mater (NOM) [1–5]. Copper is usually used as the target metal, because it forms the most stable complexes among metals which are easily determined by ASV. However, the above-mentioned complications regarding the adsorption of NOM in ASV are strongly pronounced in a stripping process of copper [25].

Fig. 5 shows an example of determination of copper complexing capacity (CuCC) in a brackish water sample (sample 3) using the two different protocols mentioned in previous sections. Curve 1 on each plot corresponds to the protocol without using the desorption step, while all curves 2 were obtained by applying a potential jump to −1.65 V for 3 s at the end of the accumulation time (297 s). The initial (ambient) copper concentration in the sample was 1.05×10^{-8} mol L^{-1}. As the reduction of only labile fraction of copper is a prerequisite in CuCC determination, a proper accumulation potential of −0.5 V is selected on the basis of the copper pseudopolarogram shown in Fig. 4a, curve 2. The difference between the complexing curves recorded using the two protocols is evident (Fig. 5a). Although the shape is not strongly influenced, the relatively large difference in peak currents is obvious. The ratio of

Fig. 5 – Copper ion titration curve for the determination of CuCC in brackish water sample (sample 3) without (curve 1) and with (curve 2) applied desorption step. Procedure parameters: total $t_{acc} = 300$ s, $E_{acc} = -0.5$ V, desorption potential, $E_{acc} = -1.65$ V. Curve 3 corresponds to peak height ratio of curve 2 and 1.

Table 1 – Ligand concentration, [L] and apparent stability constant, K' obtained in brackish water sample using two different protocols

	[L] (mol L^{-1})	K' (mol^{-1} L)
Without desorption step	3.40×10^{-8}	4.14×10^{8} ($\log K' = 8.62$)
With desorption step	1.41×10^{-8}	2.70×10^{8} ($\log K' = 8.43$)

peak currents (curve 3) decreases by addition of copper, which indicates a relatively diminishing influence of the adsorbed SAS on copper electrochemical reactions occurring during the stripping step. Complexing capacity parameters (ligand concentration and stability constant) were obtained using the Ružić–van den Berg linearization method [39,40] assuming the 1:1 metal–ligand interaction (Table 1). Without the desorption

step, almost a 2.5 times higher concentration of complexing ligand was obtained, while the apparent stability constant increased only slightly. It is obvious that the increased ligand concentration obtained without the desorption step is the result of the adsorbed SAS. Although the absolute difference in ligand concentration is not large, it is evident that without the desorption step, the ligand concentration is overestimated. As a consequence, different speciation results concerning copper distribution in a particular sample are inevitable.

Very important parameter in the protocol of MCC determination is the sensitivity, which is used for transformation of peak heights into the concentration of metal found in the sample (this step is a prerequisite for all calculations in metal speciation studies using voltammetric methods) [5]. Usually, authors use the sensitivity obtained either in the range where, according to the titration curve, all sites are almost saturated (linear part of the plot) [39,41] or from the separately determined sensitivity in a UV digested sample (where all organic matter is destroyed) [31]. According to the theoretical calculations for metal complexes with known stability constants, the slope which corresponds to the titration curve without the ligands is never reached in real samples (only asymptotically approaching) [5]. The intensity of convergence depends on the stability constant of formed metal complexes. As the apparent stability constant is lower, higher concentrations of added metal are needed in order to be closer to the real slope, and the logarithmic model of metal addition is advisable [5]. If the slope/sensitivity obtained in the UV sample is used for data transformation, more erroneous results could be obtained, if the protocol without the desorption step is used (in the UV sample, SAS are destroyed and the effect of adsorbed SAS on the peak height vanishes, see curve 3 in Fig. 2). However, for the transformation of data obtained using the desorption step, the sensitivity obtained in the UV sample is recommended, but critical examination of both slopes should be done before the final data treatment/conversion.

4.   Conclusion

As shown in many papers, the adsorption of natural organic matter (NOM) on the surface of working electrodes produces effects which interfere with electrochemical reactions of metal ions. Such interferences are amplified in ASV of copper in natural water samples. In this work, we used a protocol which utilizes desorption of the NOM to obtain reliable copper voltammograms, free of interferences. According to phase sensitive ac voltammetric measurements, most of the NOM is desorbed at potentials <-1.4 V. Application of a very negative potential in ASV at the end of the accumulation time for a short period of time (3 s) produced anodic peaks of copper free of artefacts. Although it is shown in the literature that stripping chronopotentiometry in the depletive mode is less sensitive to adsorption processes than ASV in the pulse mode, no benefit is obtained using this technique in measurements in natural samples without the desorption step. The application of desorption step could be very beneficial in ASV measurements using solid electrodes.

Recently, it was shown that pseudopolarography (and an analogue method, scanned stripping chronopotentiometry) is a powerful technique in the speciation of trace metals in natural waters. Various theories, describing probable conditions which could arise in such measurements, were developed and tested in model solutions. However, as the natural water is a mixture of many different compounds, it is very important to resolve/recognize processes which occur during the measurements. We showed that the adsorbed layer of NOM strongly influences a pseudopolarogram of copper, producing changes in its shape and intensity. It also influences the peak potential and half-peak width of single copper anodic voltammograms. Analysis of such pseudopolarograms according to theoretical postulates could lead to incorrect conclusions. Application of the desorption step produces very well resolved pseudopolarograms of copper, without any of the above mentioned drawbacks, which is a benefit in copper speciation consideration.

Similar benefits of the desorption step were registered in the determination of copper complexing capacity (CuCC). The adsorbed layer of NOM caused an apparent 2.5-fold increase in ligand concentration compared to the protocol which utilizes the desorption of NOM, while the conditional stability constant slightly increased. It is important to note that the amount of reduced copper from inert copper complexes during short desorption step at -1.6 V is negligible comparing to amount of labile copper reduced at more positive potentials (~-0.5 V), which is prerequisite in determination of CuCC (desorption step usually contributes to only 1% of the total accumulation).

These experiments show the importance of distinguishing processes which occur as the consequence of metal complexation with ligands from the bulk of the solution, and processes arising as the product of a surface reaction with adsorbed ligands.

To eliminate the artefacts of the adsorption of NOM upon the copper speciation results using ASV, the application of described desorption step is recommended.

Acknowledgments

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