Polish J. Chem., **78**, 1703–1717 (2004)

Anodic Stripping Voltammetry in the Presence of Fumed Silica and Nonionic Surfactants*

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(Received March 22nd, 2004; revised manuscript May 13th, 2004)

In this paper we describe the stripping voltammetric method for the determination of metals in the presence of surfactants at the ppm level. The method employs fumed silica for selective adsorption of surfactants directly in the voltammetric cell. In the present work the suppressing effect of the surfactant is studied. The latter depends mainly on the kind of metal and on the parameters of the deposition stage. The fumed silica usually allows for the full restoration of the suppressed signal. In addition, it is possible to enhance the depolarizer signal in solution with silica suspension if high stirring rates are used during the deposition step. The method is validated by analyzing certified reference material and then tested with the natural sample.

Key words: anodic stripping voltammetry, nonionic surfactants, fumed silica, determination of metals

The voltammetric methods give reliable results as long as the measured current is explicitly defined (as diffusion current, kinetic current, catalytic current *etc.*) and interpreted according to its nature. The current must not be significantly disturbed by processes and factors such as the migration, the electrical double layer charging, unstable or too high background currents, the polarization of the reference electrode and the interfering electrode processes (*e.g.* oxygen reduction, reduction of the supporting electrolyte or oxidation of the electrode material). Thus, for a valid measurement an ideal and reproducible preparation of the electrode surface is essential. The phrase – “ideal and reproducible electrode surface” means that the electrode surface is free of any mechanical imperfections (scratches, craters *etc.*) and surface contaminations (oxide formations, adsorbed layers *etc.*). This point is especially important for the solid electrodes. The surface of a mercury electrode is always mechanically ideal, but susceptible to contamination by adsorption of the surface active substances such as surfactants.

The surfactants may be defined as the substances which tend to accumulate at the phase boundary (liquid-gas, liquid-solid, liquid-liquid *etc.*) decreasing surface tension [1]. This is a particular consequence of surfactants’ structure. The molecules of the latter consists of two parts: the hydrophilic group and the hydrophobic chain. In certain conditions they form aggregates such as micelles, bilayers *etc.* [2,3].

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

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The ability of surfactants to reduce surface tension makes them common and arduous contaminants because they are frequently used as detergents.

The influence of surfactants on the polarographic current transients was studied by several authors [4–8]. Surfactants may shift the halfwave of the peak potential, they can cause current suppression or the splitting of the polarographic wave and other phenomena. These effects arise from the adsorption of the surfactant molecules on the electrode surface. The latter causes the decrease of the electrode surface area accessible to the depolarizer. Still, the depolarizer may be reduced or oxidized on electrode surface covered completely by the surfactant [9,10]. This is the case when either the depolarizer ion penetrates the adsorbed surfactant layer or when the electrons are transferred through the surfactant layer *via* the tunneling effect.

Excluding the cases when the surfactants are introduced to the analyzed solution purposely (for the suppression of polarographic maxima or for the selective suppression of peaks) and quantitively, their presence disturbs or even makes the measurements impossible. Thus, the removal of surfactants from the solution prior to the analysis is necessary. It may be done by adsorption on charcoal [11,12], microfiltration [13] or destruction by UV irradiation in the presence of an oxidizing agent [14]. Because of its simplicity and commercial availability the latter method is widely used. The effective method utilizing fumed silica has been proposed by Kowalski *et al.* [15]. The adsorption of surfactants on the fumed silica is fast and effective. Moreover, fumed silica present in the polarographic cell does not disturb electrode process, thus it may be added directly to the cell prior to the measurement. Fumed silica is the microform of silicon dioxide [16] with very large specific surface area 50–1000 m^2/g. A stable suspension of the latter in aqueous electrolyte solutions is made of 0.3–1.2 μm particles [17]. For the analytical purposes fumed silica has been used in the polarographic and voltammetric measurements in flowing solutions [17–18], in anodic [19] and adsorptive stripping voltammetry [20] as well as in tensammetric measurements [21]. Beside its analytical applications fumed silica may be used for the adsorption of proteins [22] and metal ions [23].

The intention of the present work is to investigate problems associated with the application of fumed silica in the anodic stripping voltammetric trace analysis. These problems were only mentioned in the previous publications [19,21]. The first aspect which deserves particular attention is the possibility to recover voltammetric signals of several metals when they are suppressed by the nonionic surfactants. The second problem is the possibility of sample contamination by silica introduced to the cell. Thirdly, one could also tackle the influence of the fumed silica suspension on measured currents especially when the convection is involved. We also discuss potential removal of highly concentrated surfactants. Our method has been confirmed by the analysis of certified reference material and illustrated by several applications to natural samples.

EXPERIMENTAL

Apparatus. The electrochemical analyzer EA9 with EAGRAPH software (MTM-Anko, Kraków) interfaced with PC computer was used for the voltammetric measurements. The electrode system consisted of the working controlled growth mercury drop electrode (CGMDE, MTM-Anko, Kraków), the silver/silver chloride 3 M NaCl reference and platinum auxiliary electrodes. The same electrode system was used for the differential capacity measurements using the electrical double layer capacity meter and CGMDE controller M153C (both MTM-Anko, Kraków). For the separation of large amounts of fumed silica the laboratory centrifuge WE-2 (Mechanika Precyzyjna, Warszawa) operating at 4000 r.p.m. was used. For mineralization of the natural samples a microwave system UniClever II (Plazmotronika, Warszawa) and UV mineralization system Mineral-6 (Mineral, Warszawa) were used.

Reagents. The standard 0.1 M solutions of Cd, Cu, In, Pb, and Zn have been prepared by the dissolution of 5N metal shots in HNO_3 (Merck, suprapure). 0.1 M Tl standards have been prepared with $TlNO_3$ (Merck), whereas $MnSO_4 \cdot 4H_2O$ (POCh, Gliwice) was used for the preparation of 0.1 M Mn standard. Tritons (polyoxyethylene(n) isooctylphenylether) were obtained from Winsdor Laboratories (UK) (Triton X-100, n = 10), and Aldrich (Triton X-114, n = 8 and Triton X-405, n = 40). Poly(ethylene) glycol M 1500 was obtained from Aldrich and polyethylene oxide M 5000000 from BDH Chemicals Ltd. Washing-up liquids Ludwik (Inco-Veritas, Poland) and Sunlight (Unilever) were purchased in supermarket. Fumed silica of specific surface area 255 and 390 m^2/g were obtained from Sigma. The certified reference material (oriental tobacco leaves CTA-OTL-1) was obtained from ICHTJ, Warsaw. All solutions were prepared from fourfold distilled water (two last stages from quartz).

Procedure. Before measurements the electrochemical cell was conditioned in 0.1 M nitric acid, rinsed with distilled water and shortly conditioned in the sample solution to be measured. Next 10 mL of the sample was introduced to the cell and the oxygen was removed by a 10 min. long argon bubbling. Next, the successive stripping voltammograms for the gradually increasing concentration of surfactant (up to 5 ppm) were recorded. The last voltammogram was obtained after the addition of 50 mg fumed silica to the solution already containing 5 ppm of the surfactant. In most measurements the accumulation was performed during 40 s in the stirred solution at potential –700 mV (Cd, Cu, In, Pb, Tl), –1300 mV (Zn) or –1800 mV (Mn). During the differential pulse stripping step a voltammogram was recorded with the pulse amplitude –20 mV, the sampling time 20 ms and the waiting time 20 ms.

RESULTS AND DISCUSSION

Suppression of stripping peaks by the nonionic surfactants. Triton X-100 suppresses of the current and shifts the potential of the anodic stripping peak of the depolarizer. The magnitude of these effects varies for different metal ions. Fig. 1A shows the dependence of the stripping peak height on Triton X-100 concentration. To fit the plots in to the same scale, the respective peak currents were recalculated to the values relative to the one measured in the surfactant free solution. For the majority of the depolarizers the addition of 1 ppm of Triton X-100 almost completely suppresses the stripping peak (Fig.1A) and shifts it several milivolts (Fig.1B) in the positive direction. This additional reoxidation overpotential is necessary to remove ions from the electrode surface covered by the surfactant. However, a number of metals exhibit different behavior. For example, even at high Triton X-100 concentration the peak of lead is suppressed to about 30% of its initial value only. Simultaneously, the peak potential value shifts linearly and insignificantly. On the other hand, thallium peak seems to be insensitive to Triton X-100 presence. Copper and manganese peaks

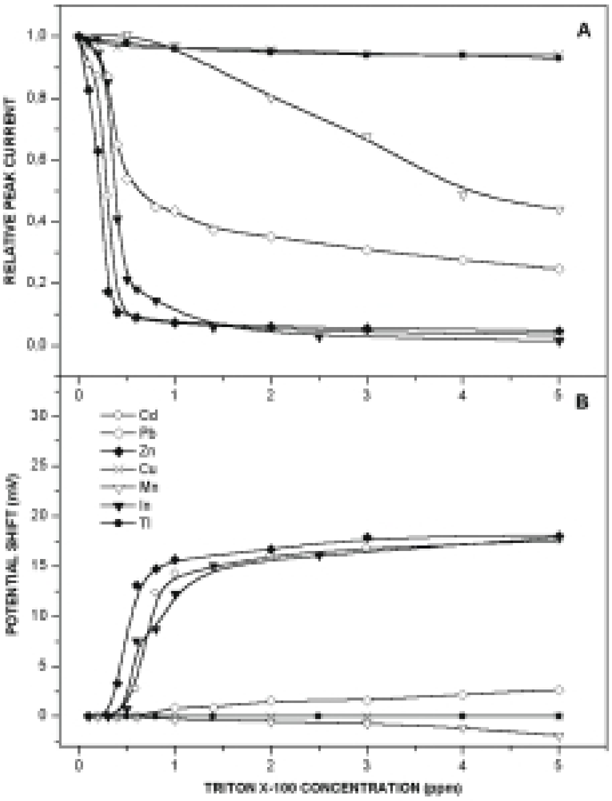

Figure 1. Influence of Triton X-100 on peak current (A) and peak potential (B) for several depolarizers.

exhibit much smaller sensitivity to the presence of the surfactant. In the latter case one should consider the position of the peaks relative to the Triton X-100 adsorption region. The peak of copper is located outside the potential range in which Triton X-100 adsorbs on the electrode surface (Fig. 2). The manganese peak is very close to the Triton X-100 desorption peak and the deposition potential of manganese (–1800 mV) is placed outside Triton X-100 adsorption range. Thus, the suppression of manganese peak is much weaker especially at low Triton X-100 concentrations. The increase of Triton X-100 concentration results in the widening of the potential range in which it adsorbs at the electrode (Fig. 2). The latter is the cause of stronger suppression of manganese stripping peak at higher Triton concentration. At the same time the potential of manganese peak is slightly shifted in the negative direction. That shift is most likely caused by the deformation of manganese peak. Mn peak is partially situated in the Triton X-100 adsorption range, thus apparent shift of the peak in the negative direction is observed. This deformation is more apparent at higher Triton X-100 concentrations because of Triton X-100 adsorption range extension in the negative direction.

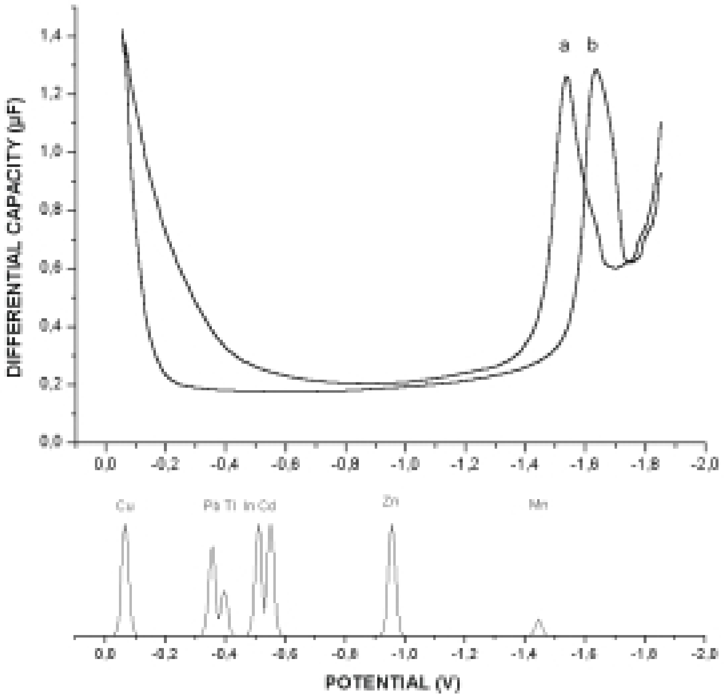

Figure 2. Differential capacity curve for 1 ppm (a) and 5 ppm (b) Triton X-100 solution in 0.2 M KCl and a diagram showing schematically ASV peaks of the depolarizers in the current conditions.

A similar suppression can be caused by other nonionic surfactants such as Triton X-114, Triton X-405, poly(ethylene) glycol M 1500 and poly(ethylene) oxide M 5000000. The suppressing effect of these surfactants is shown in Fig. 3. The characteristic sigmoidal shape of this dependence is common for all surfactants. The difference appears at surfactant concentrations at which significant suppression of the cadmium peak starts. The ultimate suppression degree is usually lower than 10% of the peak recorded in the surfactant free solution. Further increase of surfactant concentration influences the peak insignificantly. For comparison the suppressing effect the two commercial washing-up liquids, *i.e.* Ludwik and Sunlight are shown. The less steep slope is characteristic to the lower contents of surfactant in the studied solutions. A typical suppression characteristics for any surfactant is sigmoidal, *i.e.* the small concentrations do not influence significantly peak height. The extent of this concentration range depends mainly on the kind of the surfactant, the deposition time and stirring rate, the kind of analyzed metal, the concentration and the composition of the supporting electrolyte. The typical limiting concentration under conditions used in this work is 0.1–0.2 ppm. At higher surfactant concentrations the voltammetric peak is significantly suppressed. In a narrow (usually 1 ppm) surfactant concentration range, the peak current is initially suppressed and then peak height becomes unaltered

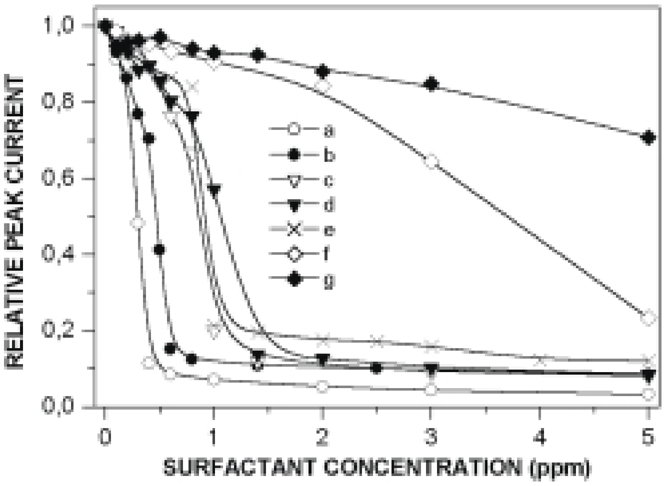

Figure 3. Influence of several nonionic surfactants on cadmium stripping peak: a – Triton X-100; b – Triton X-114; c – Triton X-405; d – poly(ethylene) glycol M 1500; e – poly(ethylene) oxide M 5000000; f – washing-up liquid Ludwik; g – washing-up liquid Sunlight.

by any further increase of surfactant concentration. The peak usually shrinks to 5–20% of the initial height and depends on the same parameters as the limiting concentration. Such suppressed peaks generally do not change when the standard additions are performed. Thus, it is impossible to carry out a quantitative analysis. For several depolarizers a shift of the peak potential (15–20 mV) in the positive direction is observed concurrently with the peak suppression (Fig. 1B). At much higher surfactant concentrations an increase of the peak height may be observed. The latter probably results from the formation of the micelles. This phenomenon is usually observed at concentrations lower than the critical concentration of micelle formation.

One of the most important factors in the stripping analysis is the deposition time. Longer deposition periods cause the enhancement of the stripping peak in the solution without surfactant. Also, the longer deposition times decrease the concentration of surfactants which cause peak suppression. This effect is shown in Fig. 4. At 0.2 ppm Triton X-100 concentration and only 60 second long deposition time the determination with no significant decrease of sensitivity is possible. At 0.5 ppm just 20 s deposition allows determination, whereas at 1 ppm the longest deposition time is 7 second. At Triton X-100 concentrations 2 ppm and higher, the current is suppressed even without the deposition period.

The composition of the supporting electrolyte influences the magnitude of the stripping peak suppression. In order to effectively use the fumed silica, the principles described previously [21] should be followed. These conditions are: the ionic strength higher than 0.5 M and the pH lower than 8. Under such conditions the

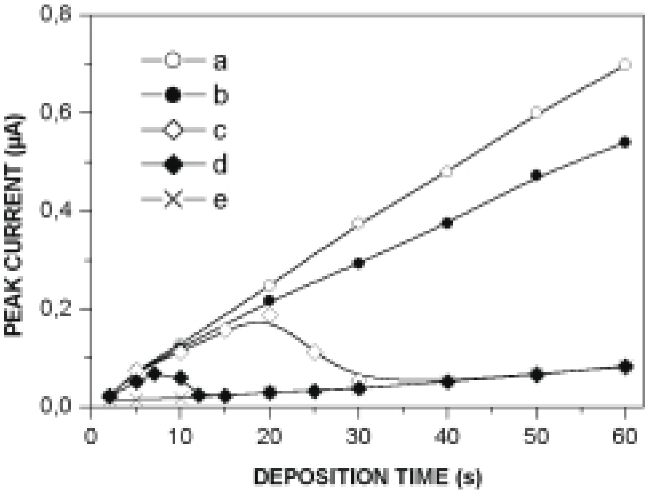

Figure 4. Influence of the deposition time on cadmium stripping peak current at several Triton X-100 concentrations: a – 0; b – 0.2; c – 0.5; d – 1.0; e – 2.0 ppm.

nonionic surfactants strongly adsorb on electrode causing current suppression. For instance the ionic strength (Fig. 5) higher than 0.1 M does not influence either the suppressed or the unsuppressed peaks. Thus, the conditions for effective fumed silica application coincide with the conditions in which nonionic surfactants adsorb on the electrode causing voltammetric peak suppression.

The suppression of stripping peak is not dependent on the number of different metal ions in the solution. The suppression characteristics for numerous metal ions in the mixture and for a single metal ion are identical. Fig. 6 presents the stripping voltammograms for a solution containing zinc, cadmium, lead, copper and a gradually increased concentration of Triton X-100. The comparison of this data with the relation presented in Fig. 1 shows that the suppression and the peak shift are the same for a single metal and for a metal mixture.

The relative suppression effect is nearly independent from the depolarizer concentration (Fig. 7). Only at concentrations as low as 10 nM the ultimate suppression is 35% of the initial peak height, whereas at higher concentrations of the depolarizer the peak is suppressed to the less than 20%. Thus, the our findings for higher concentrations are also valid for lower concentrations. Most of the measurements of the stripping peak suppression were performed in the 10 μM solution. This restriction was caused by the fact that, in the potential region involved (–1.4 ÷ –1.5 V) and under experimental conditions applied (0.1 M KCl, pH 4.5) it was impossible to obtain an apparent peak for the manganese metal ion at concentrations lower than 10 μM. Thus to keep the same conditions for all studied metals, the concentration 10 μM was applied.

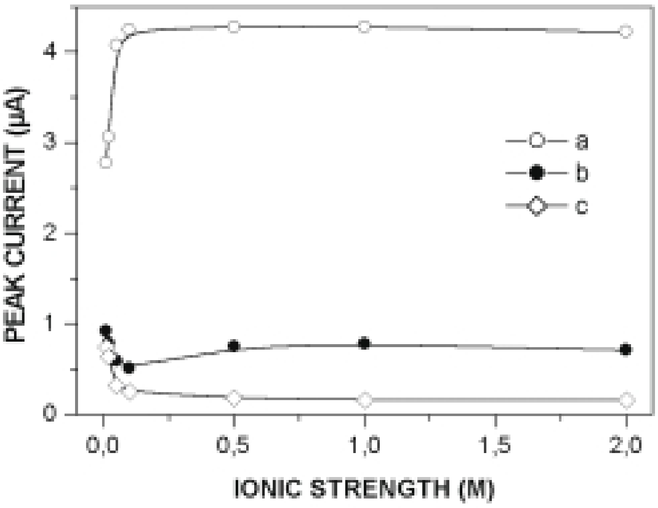

Figure 5. Influence of the ionic strength of supporting electrolyte on cadmium stripping peak current in solutions of different Triton X-100 concentrations: a – 0; b – 0.6; c – 5 ppm.

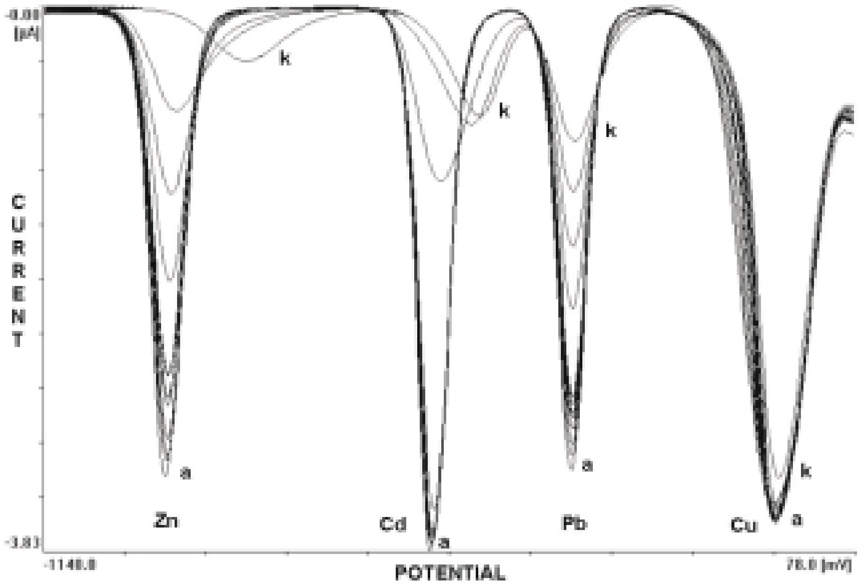

Figure 6. Stripping voltammograms of zinc, cadmium, lead and copper in the presence of Triton X-100 in the following concentrations: a – 0; b – 0.2; c – 0.4; d – 0.6; e – 0.8; f – 1.0; g – 1.2; h – 1.6; i – 2.0; j – 2.5; k – 3.5 ppm. Only the letters a and k are presented.

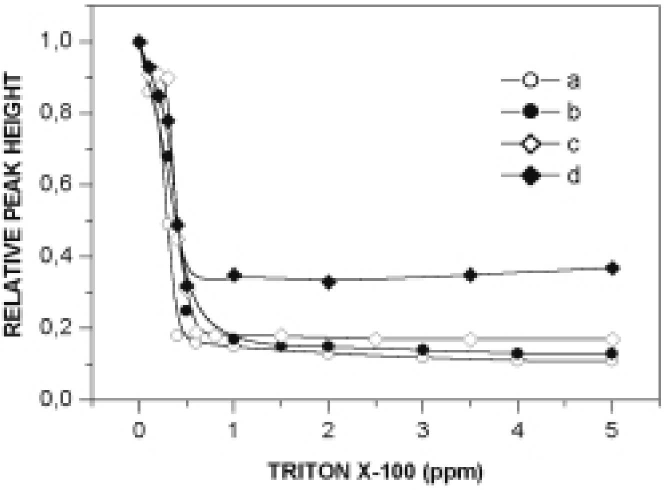

Figure 7. Dependence of the relative stripping peak height on Triton X-100 concentration for several concentrations of cadmium: a – 10^{-5}; b – 10^{-6}; c – 10^{-7}; d – 10^{-8} M.

Stripping peak height in solution with fumed silica. We have shown that the depolarizer stripping peak is in most cases suppressed after the addition of Triton X-100. The introduction of a proper amount of the fumed silica to voltammetric cell causes peak recovery. In the standard procedure 50 mg of fumed silica is added to 10 mL of solution in the voltammetric cell and after 2–3 min argon bubbling the voltammogram is recorded. The effect of gradual addition of the fumed silica was reported previously [18,21]. In this work we study the highest possible amount of silica, *i.e.* 50 mg/10 mL that can be used directly in a voltammetric cell. This amount defines the maximal removable surfactant concentration under the procedure applied. The final effect depends on the kind of fumed silica and on the method of its activation [21]. In this work two kinds of fumed silica were used (fumed silica with the specific surface areas: 255 and 390 m^2/g activated by roasting 30 min. in 950°C). Table 1 lists the stripping peak recoveries upon addition of fumed silica to the solution containing 5 ppm of Triton X-100 and several metal ions. Column II of Table 1 shows the recoveries (calculated as a ratio of peak heights before and after the addition of fumed silica) obtained during deposition step for fumed silica 255 m^2/g in the stirred solution at 250 r.p.m. Under such conditions the stripping peaks of Cd, Pb and Zn are recovered in 60–80%, Mn and In above 90%. Thallium is neither affected by the surfactant nor by the silica, while copper is not influenced by the surfactant but in the presence of fumed silica its stripping peak drops to about 80%. In contrast to the peaks suppressed by the surfactant, the peaks recovered in the presence of silica increase upon the standard addition, which makes the quantitative analysis possible.

Table 1. Stripping peak recovery after the addition of 50 mg of the fumed silica to 10 mL solution containing 5 ppm of Triton X-100.

Depolarizer	Recovery by silica 255 m^2/g at stirring 250 r.p.m. [%]	Recovery by silica 390 m^2/g at stirring 600 r.p.m. [%]
Cu	78	132
Pb	62	133
Tl	100	113
In	93	107
Cd	77	142
Zn	80	135
Mn	109	124

In the third column of Table 1 lists the recoveries obtained for fumed silica of 390 m^2/g during the deposition step in the solution stirred at 600 r.p.m. Our data shows that the recovery is better than 100% for all depolarizers examined. However, if the 255 m^2/g type silica in the same stirring conditions is used, the recoveries are few percent lower but still exceed 100%. Table 2 shows the suppression and recovery effects obtained for several surfactants and two depolarizers – cadmium and lead. It can be seen that, for several Tritons the suppression is sufficiently strong, *i.e.* the peaks drop to less than 10% of the initial height for cadmium and to about 20% for lead. The recovery is above 60% and increases with the number of ethylene oxide units in the surfactant molecule. In the case of polyethylene glycol and polyethylene oxide the cadmium peak is suppressed to about 10%, while the peak of lead is close to 30% of the initial peak. Here, the recovery of the cadmium peak is worse than in the solution containing Tritons, but the recovery of lead is better. The commercial washing-up liquids are efficiently removed by silica (recoveries close to 100% are obtained).

Table 2. Normalized peak heights after addition of 5 ppm of surfactant (suppression) and subsequent addition of 50 mg of fumed silica 255 m^2/g to 10 mL of solution (recovery), stirring at 250 r.p.m. The values were normalized with respect to the peak height in solution without the surfactant and the silica.

Surfactant	Cadmium		Lead	
	suppression	recovery	suppression	recovery
Triton X-114	7.6	60	14	58
Triton X-100	3.0	77	19	62
Triton X-405	5.8	96	24	91
Poly(ethylene) glycol M 1500	8.6	72	37	81
Poly(ethylene) oxide M 5000000	12	71	34	95
Ludwik	23	99	33	120
Sunlight	71	95	40	110

The increase of the peak after the addition of silica was observed previously [19]. In order to explain this phenomenon the two possibilities were considered. Firstly, the impurity of silica was taken into account. The latter hypothesis was verified by the addition of the fumed silica to the pure electrolyte. In the outcome no peaks were observed. Thus, the increase of the peak height is not due to the contamination by the fumed silica. The second hypothesis assumed that even the standard solution can be contaminated by a minute amount of the surfactant which may result in the slight suppression of the peaks. This possibility was rejected because the suppression effect was still observed in the solutions and glassware from which the surfactants were very carefully removed. The explanation of the discussed phenomenon is supplied by Fig. 8, which shows the silica influence efficiency of deposition step in the stirred solutions. At low stirring rates, *i.e.* below 350 r.p.m. (with typical magnetic stirring bar), the peaks recorded in the solutions with silica are smaller than in the silica free medium. But at the higher (exceeding 350 r.p.m.) stirring rates the presence of silica increases the deposition efficiency giving substantial increase of the peak height. This effect is shown in Fig. 8 for two deposition times: 40 and 120 seconds.

The advantages of the direct use of fumed silica in a voltammetric cell are evident, nevertheless the maximal silica loading is restricted to 50–70 mg for 10 mL of the sample solution. Higher amounts of suspended silica make the solution too thick to perform measurements. A 50–70 mg amount of the fumed silica is sufficient to remove approximately 10 ppm of surfactant from 10 mL of solution. If the concentration of surfactant is higher than recommended it is possible to eliminate its excess from the sample prior to its introduction to the voltammetric cell. In such case the silica should be removed from solution. Because the colloidal solution of fumed silica is very difficult for filtering, the only effective way is to use centrifugation. To explore that possibility a standard solution containing 0.5 μM of Cd and Pb and 50 ppm Triton X-100 was prepared. The subsequent addition of 50 mg of fumed silica allowed for partial signal recovery. The concentrations determined by the standard

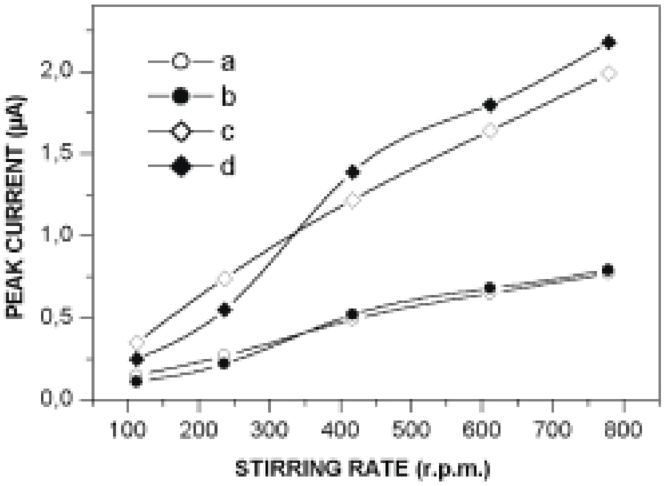

Figure 8. Dependence of the stripping peak height on the stirring rate during the deposition step for solutions without added silica (a, c) and with 50 mg of silica (b, d) and for deposition time 40 s (a, b) and 120 s (c, d).

addition method were 0.35 μM for lead and 0.23 μM for cadmium and appeared to be significantly lower than the real values. In the second procedure fumed silica in an amount of 200 mg was added to the solution. Later, after 5 minutes of suspension the silica was separated by centrifugation at 4000 r.p.m. A clear solution was then pipetted to the voltammetric cell and after oxygen removal the stripping voltammograms were recorded. In the outcome the signal was recovered completely. The concentrations determined by the standard addition were 0.50 μM for lead and 0.51 μM for cadmium. The latter were in good agreement with the real values. When a sufficiently large amount (exceeding 400 mg/10 mL of solution) of fumed silica is used the effect of chemically bounded water should be take into consideration, as it may increase the concentration of metal ions in the solution.

Analytical applications. Anodic stripping voltammetry with fumed silica has been carefully tested using standard solutions. It has been found that there is no significant difference in the determination of several depolarizers no matter if the analysis is performed with or without fumed silica in the analyzed solutions. If the surfactant is present in the sample in concentrations below 10 ppm, the determination is possible only when the silica is added to the solution. The accuracy and the precision of measurements are similar as in the solution without surfactant and silica. Such conclusions were published previously [17–21]. To test method performance for natural samples the best approach is to analyze the certified reference material (CRM). Unfortunately no CRM of sample containing surfactants in the ready-for-use form is available. Thus, the CRM of plant tissue, *i.e.* oriental tobacco leaves (CTA-OTL-1, ICHTJ, Warsaw), was chosen. The standard microwave assisted wet mineralization with nitric acid (Merck, Suprapur) was applied. Next, the sample was diluted. Then, 50 mg of fumed silica (390 m^2/g) was added to 10 mL of diluted sample. After subsequent removal of oxygen the standard addition method determinations were performed. In the prevailing conditions it was possible to determine lead and copper. Unfortunately, cadmium was below detection limit and zinc was masked by the reduction of supporting electrolyte (very low pH). Lead was found 5.3 ± 0.6 ppm (certified value 4.91 ± 0.80 ppm) and copper 14.7 ± 1.1 ppm (certified value 14.1 ± 0.5 ppm). The measured concentrations were in good agreement with the certified values.

Fumed silica may be useful for samples containing surfactants at ppm level. Such concentrations are observed in several natural waters like the rivers, streams, lakes and wells. For example in an untreated water from the Vistula river (only nitric acid to set the pH value to 3 and KNO_3 to obtain 0.1 M supporting electrolyte were added), the copper was impossible to determine, whereas 0.78 ± 0.03 ppb of lead and 2.2 ± 0.4 ppb of zinc were found. When 50 mg of fumed silica (390 m^2/g) was added to 10 ml of the analogously treated sample the determination of copper (1.49 ± 0.12 ppb), lead (1.11 ± 0.04 ppb) and zinc (5.6 ± 0.8 ppb) was possible. These results show that the presence of fumed silica allows the determination of copper and improves the determination of lead and zinc. However, if the water sample contains higher amounts of surfactants, the silica is unable to remove them completely. In such case UV mineralization may help. Still, even after UV mineralization the organic matter residues may interfere with the measurements. Namely, in the sample from Vistula river (with the nitric acid to prevent adsorption of heavy metals) after UV mineralization it was possible to determine copper (0.65 ± 0.09 ppb) and zinc (1.5 ± 0.4 ppb) and impossible to determine lead. The addition of 50 mg of fumed silica to 10 ml sample after UV mineralization enabled the determination of lead (1.3 ± 0.2 ppb) and improved the determination of copper (1.8 ± 0.2 ppb) and zinc (4.8 ± 0.5 ppb).

In the case of organic and bioorganic matter such as the plant tissue, the determination of heavy metals must be preceeded by mineralization. Fig. 9I shows the voltammograms for the lettuce leave sample after its microwave mineralization. Curves A were measured in 0.1 M KNO_3 supporting electrolyte (pH = 3). Figure 9I collects the curves for the sample and the three standard additions. It can be seen that the peaks for copper do not change upon the standard addition making copper determination impossible. When fumed silica is added to the solution (curves B) the determination of copper and lead becomes possible. The voltammograms of sample mineralized traditionally (at the hot plate) are shown in Fig. 9II (curve a). After the standard addition of lead and cadmium (curve b) to the latter solution the peaks did not appear. However, when fumed silica was added to the same sample (Fig. 9II curve c) evident peaks of Cd and Pb were observed after the standard addition (curve d).

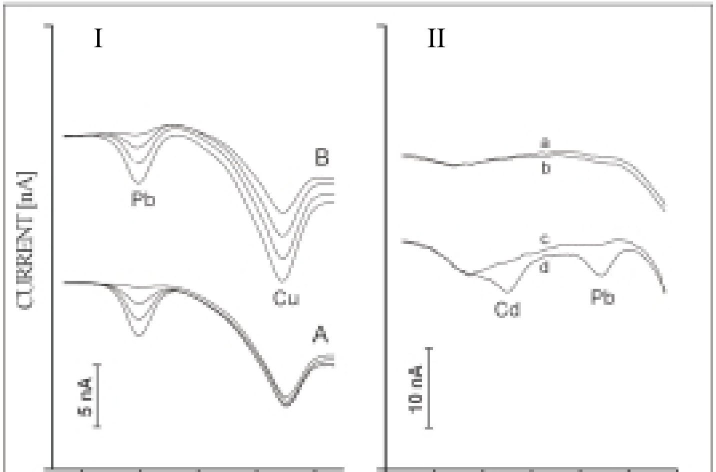

Figure 9. Stripping voltammograms of lettuce leaves mineralized in microwave oven (I) and at heating plate (II). I: A – sample and the three standard additions of Cu and Pb; B – the same as "A" but in solution containing 50 mg of fumed silica. II: a – sample; b – sample with addition of 2.5 nM of Cd and Pb; c – sample containing 50 mg of fumed silica; d – the same as "c" but with the addition of 2.5 nM of Cd and Pb.

If the sample contains surfactant in amounts low enough to allow direct determination, the addition of fumed silica may improve the precision of the measurement. For example during zinc determination in homeopathic preparation the relative standard deviation was 4.1%. After fumed silica addition the precision was enhanced, *i.e.* the relative standard deviation droped to 0.27%.

CONCLUSIONS

Nonionic surfactants suppress stripping peaks making the voltammetric determination of several metals impossible. The suppression effect depends on the kind of metal, the kind of surfactant, ionic strength of the supporting electrolyte and the conditions of the deposition step. The direct addition of the fumed silica to the electrochemical cell restores the stripping voltammetric peaks and allows for the determination of heavy metals, as long as the concentration of surfactants is on the ppm level. The application of larger amounts of silica followed by the separation of suspension together with the adsorbed surfactants prior to the analysis allows to remove surfactants at several dozen ppm level. If the fumed silica suspension is present in the voltammetric cell the deposition step may be enhanced when the stirring rate is high enough. The novel method of surfactant removal by its adsorption on fumed silica is useful for natural samples containing surfactants at ppm level. Our method may as well be used for the removal of the organic matter residues from the samples after their UV or wet mineralization. The method was validated using certified reference material.

Acknowledgments

This work was supported by the Polish State Committee for Scientific Research (grant No. 7 T09A 134 20).

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