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Determination of Trace Heavy Metals by Flow Injection Analysis with Adsorptive Stripping Voltammetric Detection

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The adsorption of heavy metal complexes with 8-hydroxyquinoline at a hanging mercury drop electrode was used for determination of lead and cadmium traces in the flow injection system. The best results were obtained in 0.01 mol l^{-1} ammonia buffer of pH 9.5. The optimal concentration of oxine differs for lead and cadmium. Selection of the proper time for starting deposition and stripping allowed to obtain the signal practically independent of flow rate. For 200 µl samples the response was linear over the entire examined concentration range. The detection limits were 1 nmol l^{-1} for Cd and 5 nmol l^{-1} for Pb. Possible interferences as well as conditioning of the system are also discussed. Examples of determinations in river water are presented.

Adsorpcję kompleksów metali ciężkich z 8-hydroksychinoliną na wiszącej elektrodzie rtęciowej wykorzystano do oznaczania śladów ołowiu i kadmu metodą wstrzykowej analizy przepływowej. Najlepsze rezultaty otrzymano w buforze amonowym o stężeniu 0.01 mol l^{-1} i pH 9.5. Optymalne stężenia oksyny są różne dla kadmu i ołowiu. Dobór odpowiedniego momentu rozpoczęcia zatężania i strippingu pozwala uzyskać sygnał praktycznie niezależny od szybkości przepływu. Dla próbki o objętości 200 ml proste kalibracji Cd i Pb są liniowe w całym badanym zakresie stężeń przy granicy oznaczalności równej 1 nmol l^{-1} dla Cd i 5 nmol l^{-1} dla Pb. Zbadano interferencje pochodzące od innych, spodziewanych składników próbki oraz opisano sposoby kondycjonowania układu w celu zapewnienia wysokiej czułości i powtarzalności wyników. Zastosowanie metody zilustrowano przykładami oznaczenia w próbkach wody rzecznej.

The increasing environmental pollution by lead and other toxic heavy metals has increased the demand for fast and precise quantitative analysis of heavy metals in various samples. Anodic stripping voltammetry (ASV) is well known as an efficient

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method for the determination of trace metals, especially in environmental samples [1]. Detection limits in the subnanomolar range are possible in some cases as a result of the preconcentration procedure, during which the metal ions are reduced and dissolved in a mercury electrode. Thus the analytical usefulness of ASV is limited to the metals that form amalgams. In addition, analysis of very dilute samples (*e.g.* natural waters, blood *etc.*) may require relatively long preconcentration periods. Serious problems may be also caused by the formation of intermetallic compounds and the back-diffusion effects.

Therefore alternative nonelectrolytic procedures [2] were also intensively studied in recent years. The spontaneous adsorptive properties of some reactants are utilized in adsorptive stripping voltammetry (AdSV) to preconcentrate effectively organic compounds and complexes of metals at a stationary electrode. The method has been proved to be extremely useful for analysis of species that cannot be accumulated by electrolysis. Nevertheless even in heavy metals trace analysis, where ASV has been commonly recognized as the best electroanalytical technique, adsorptive stripping voltammetry may be at least a method of choice. In some cases the use of adsorptive type accumulation may allow measurements at the concentration level that is not accessible for conventional stripping voltammetry.

Several chelating agents forming surface-active complexes with metal ions have been used successfully in AdSV [3]. Among others 8-hydroxyquinoline (oxine) forms strong complexes with majority of toxic heavy metals and is relatively stable and easy to prepare. Van den Berg has studied the use of 8-hydroxyquinoline for the determination of various trace metals in seawater. The highly sensitive procedures have been reported by van den Berg for analysis of molybdenum [4], uranium [5], and copper, lead and cadmium [6].

Adsorptive methods have been used in flow injection analysis (FIA) for determination of organic compounds [7–9] and recently for analysis of metals in brine as complexes with diethylenetriaminepentaacetic acid, dimethylglyoxime, mandelic acid and Solochrome Violet RS [10].

In the present paper, we report on the possibility of the use of flow injection analysis for determination of heavy metal traces by adsorptive stripping voltammetry with 8-hydroxyquinoline. Flow injection analysis ensures high sample throughoutput, small sample volumes and reproducible treatment of each analyzed sample. Determination of heavy metal traces by ASV/FIA has been demonstrated by several workers [11,12]. However, in flow injection systems, the preconcentration period is limited by the residence time of the sample plug in the detector. Therefore, under typical flow injection conditions (20–200 μl sample volume and flow rate of 0.3–1.0 ml min^{-1}), the inferior sensitivity is observed. As a result the fast and precise analysis of heavy metal traces in many natural samples of small volume may be difficult or even impossible. Higher sensitivity in the FIA determinations can be realized by using rather adsorptive accumulation of heavy metals complexes with oxine than electrolytic deposition. To demonstrate the utility of this approach the determinations of lead in river water samples were presented in the present work.

EXPERIMENTAL

Reagents

Double-distilled water from quartz was used to prepare all solutions. Metal ion stock solutions, 10^{-1} mol l^{-1}, were obtained by dissolving the appropriate metal or its nitrate in nitric acid and diluting as required. The stock solution of 10^{-2} mol l^{-1} oxine (BDH) in 0.02 mol l^{-1} HCl (Merck) was stable for several weeks. The carrier electrolyte was 0.01 mol l^{-1} ammonia buffer of pH=9.5, which was prepared by mixing 0.01 mol l^{-1} ammonium chloride (analytical grade, POCh Gliwice) with ammonia solution (25 %, analytical grade, POCh Gliwice).

Apparatus

The flow system consisted of a 0.25 l solution reservoir, an ABU-12 autoburette Radiometer pump with a 25 ml syringe, and a Rheodyne Model 7010 sample injection valve with sample loop of 200 µl and a flow detector. All interconnections were made with 0.5 mm i.d. Tygon tubing. The length of tubing between the valve and the detector was 0.5 m. The home-made detector (based on the same principle as a PAR Model 310 Polarographic Detector) was used with hanging mercury drop electrode (HMDE) of surface area 1.75 mm^2 (Fig. 1). A saturated calomel electrode (SCE) and platinum auxiliary electrodes were immersed in the supporting electrolyte together with the detector. Pulse polarograph PP-04 (ZUT Telpod) with X–Y recorder (BAS) were used to obtain stripping voltammograms. UV irradiation equipment consisted of a type Q-125 quartz lamp (MEDICOR, Hungary) and a quartz beaker. Irradiation was performed for 30 min with the distance of 15 cm.

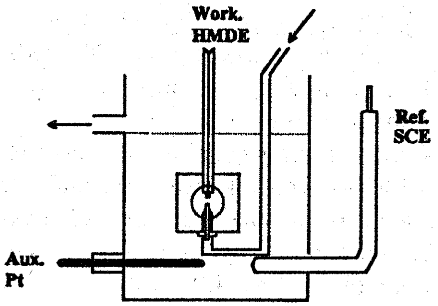

Figure 1. Flow-through detector with a hanging mercury drop electrode

Procedure

The sample solutions were based on the ammonia buffer. Oxine of the appropriate concentration (usually 8×10^{-5} mol l^{-1}) was added to the sample solution. To remove oxygen the sample and carrier solutions were purged with argon.

0.01 mol l^{-1} ammonia buffer carrier solution (pH 9.5) was used to transport samples to the detector. Each sample was injected into the flowing stream and after a delay time necessary for the sample to reach the cell, preconcentration was initiated by polarizing the electrodes to -300 mV for a selected time. Both delay and preconcentration times depend on flow rate and the sample volume; *e.g.* for a 200 µl sample volume and 0.71 ml min^{-1} flow rate the delay time was 5 s and the accumulation time 20 s. After accumulation time the negative-going differential pulse potential scan was initiated (scan rate 40 mV s^{-1}, pulse amplitude 50 mV) without stopping the flow. All measurements were performed at a fresh mercury drop.

RESULTS AND DISCUSSION

Stationary conditions

Preliminary studies have been carried out under stationary conditions in order to optimize the measurements conditions for the determination of trace amounts of Cd and Pb.

From the results of the measurements performed in various supporting electrolytes (potassium nitrate, ammonia buffer, borate buffer, phosphate buffer, acetate buffer) it can be concluded that the best conditions for this analysis are in neutral or slightly alkaline solutions. Since HCl based solutions of oxine are applied, supporting electrolytes of buffering properties should be used. For further studies ammonia buffer has been selected because of the best sensitivity and resolution of voltammetric measurements.

Preliminary measurements have shown that the metal concentrations of 10^{-8} mol l^{-1} (at oxine concentration of *ca.* 10^{-5} mol l^{-1} and the deposition time of 30 s) give well-defined peaks in cathodic stripping voltammograms. They are significantly shifted towards negative potentials with respect to the theoretical values of the ammonia-complexes halfwave potentials. Thus potentials of Cu, Pb and Cd peaks (*vs.* SCE) were equal to -450 mV, -550 mV and -700 mV, respectively. The biggest shift of the peak potential in the case of Cu results from the highest stability constant of copper oxinates [13]. Partial overlapping of Pb and Cu peaks may lead to difficulties in the interpretation of voltammograms. The half widths and the differences between the cathodic and anodic peaks potentials agree with theoretical values for a two-electron reversible electrode reaction.

The influence of pH on the peak heights for the metals studied is shown in Fig. 2. For further studies pH=9.5 has been selected since under these conditions the best results for Pb and Cd have been obtained (for Cu, maximum current has been observed at slightly lower pH). Van den Berg recommends buffer HEPES (pH=8) for simultaneous determination of Cu, Pb and Cd [6].

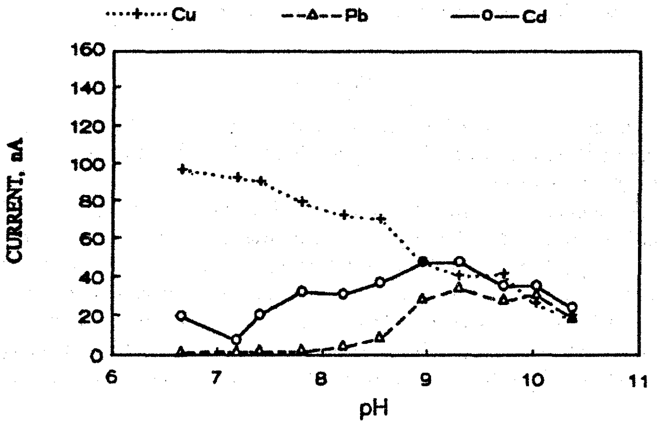

Figure 2. Effect of pH on the peak current in the presence of 4×10^{-5} mol l^{-1} oxine. Metal concentrations 40 nmol l^{-1}; accumulation potential -200 mV; accumulation time 30 s

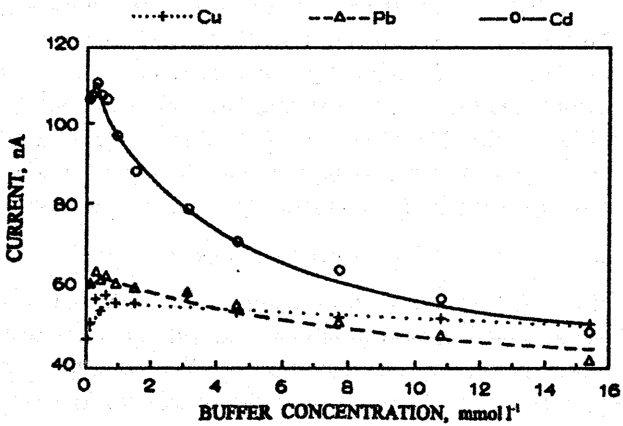

Figure 3. Effect of the ionic strength on the AdSV peak current; 40 nmol l^{-1} Cu, Pb and Cd in ammonia buffer in the presence of 4×10^{-5} mol l^{-1} oxine; accumulation potential -250 mV; accumulation time 30 s

Figure 3 illustrates the influence of ionic strength of the supporting electrolyte on the peak heights of the determined metals. The diagrams show a type of dependence characteristic for many adsorptive systems. An increase of the peak current at lower concentrations of the electrolyte is observed; the highest currents are at buffer concentration of *ca.* 3×10^{-4} mol l^{-1}. Below this concentration the voltammograms become less legible because of significant increase of the background. The ionic strength has a biggest impact on the peak heights in the case of Cd, and the smallest in the case of Cu. Therefore it can be concluded that copper oxinates are strongly adsorbed on the HMDE and they are not so sensitive to the ions of electrolyte present in the layer of the solution next to the electrode surface. A decrease of the current with increase of the ionic strength that is clearly observed in the case of Pb and Cd can be explained by weaker adsorption of these metals oxinates. The possibility of using the supporting electrolyte of low concentration is an AdSV advantage; quite often, however, higher concentrations are required to ensure the appropriate buffer capacity and conductivity of the solution. In the case studied 0.01 mol l^{-1} ammonia buffer seems to be a good compromise between higher sensitivity, lower risk of introducing impurities present in the reagents, and the desired buffer capacity and conductivity of supporting electrolyte.

The proper choice of oxine concentration in the solution influences to a great extent the sensitivity and selectivity of the determination by the AdSV method. It has been found that even at very small oxine concentrations (of the order of 10^{-8} mol l^{-1}) a small peak of Cu appears in the voltammograms; to obtain Cd and especially Pb peaks, higher concentrations of oxine are required. For small oxine concentrations the peaks are clearly asymmetric and of increased half width. As the ligand concentration increases – apart from the increase of the peak height – the peak potentials shift towards more negative values. At the same time the half width decreases and the difference between peak potentials corresponding to various metals slightly grows. Starting from oxine concentration of 8×10^{-6} mol l^{-1} the peaks are symmetric and of the half width *ca.* 50 mV. Even though the optimum concentration ranges of oxine differ for various metals, the oxine concentration of *ca.* 4×10^{-5} mol l^{-1} seems to be appropriate for simultaneous determination of Pb and Cd (at the concentration levels studied).

For short accumulation times (20 s) the calibration curves of Pb and Cd show good linearity and high sensitivity. The detection limits obtained (10^{-9} mol l^{-1} or 0.2 µg l^{-1} in the case of lead) make it possible to apply the method in flow injection systems for analysis of small volume samples (short times of the sample presence in the detector).

Flow injection analysis

Reproducibility of the determination results in the FIA system is influenced by the adsorption of oxine and metal oxinates on the tubing walls and on the detector elements. This causes two basic consequences for FIA measuring procedure. First, the analysis to be done in a fresh system (*i.e.* the system which was not operated with oxine) requires saturation the elements being in contact with the solution with oxine. For a mixing coil of 1 m/0.5 mm, a sequence of 7–8 measuring cycles is usually sufficient to reach the adsorption–desorption equilibrium at the tubing surface. Thus such operational parameters as: frequency of sample injection, flow rate, *etc.* have greater influence on the reproducibility than in other FIA measurements. The second effect is a dispersion caused by adsorption of the metal oxinates on the tube walls. This phenomenon decreases the effect of the radial diffusion process – the main factor limiting dispersion of the sample. However, when using SV techniques in the FIA, the sample dispersion does not influence the obtained results if the proper moments for the beginning of the preconcentration and for stripping step has been selected. In these methods stripping is usually carried out in the pure supporting electrolyte after the whole sample has passed through the detector. Thus an increase in the dispersion will cause a slight increase in the analysis time of individual samples.

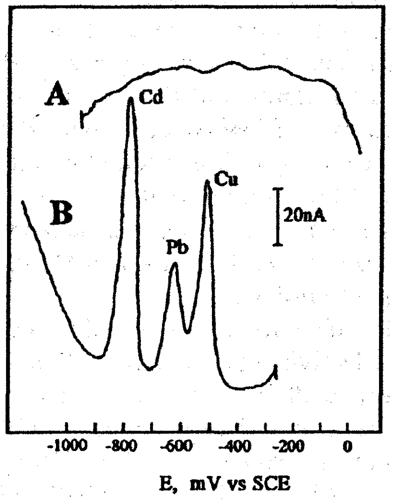

Figure 4. Comparison of anodic stripping and adsorptive stripping FIA voltammograms for accumulation time of 20 s: A) ASV; accumulation potential -900 mV, B) AdSV; accumulation potential 300 mV; 8×10^{-5} mol l^{-1} oxine. Other conditions: Cu, Pb and Cd concentrations 60 nmol l^{-1}; carrier electrolyte 0.01 mol l^{-1} ammonia buffer (pH 9.5); oxine concentration 8×10^{-5} mol l^{-1}; mixing coil 0.5 m/0.5 mm; flow rate 0.71 ml min^{-1}; sample volume 200 µl

Figure 4 illustrates a comparison of adsorptive and anodic stripping voltammograms recorded in the FIA system at the same current range of polarograph. The studies have been carried out under the same experimental conditions, *i.e.* Cu, Pb and Cd concentration of 60 nmol l^{-1} in 0.01 mol l^{-1} ammonia buffer of pH = 9.5, flow rate of 0.71 ml min^{-1} and sample volume of 200 μl. In AdSV 8×10^{-5} mol l^{-1} oxine was added to the sample solution. Under such conditions adsorptive stripping voltammetry exhibits higher sensitivity (curve B, Fig. 4), ensuring the determination of heavy metals at typical for FIA sample volumes and analysis times. The peak currents of the metals determined by ASV (curve A, Fig. 4) are close to the background level. It is possible to increase the sensitivity of the ASV detection using a bigger sample volume, lower flow rate, and the reversal flow accumulation [14].

The impact of the preconcentration time on the FIA/AdSV current

In the flow injection analysis the effective preconcentration time is limited to the period during which the sample passes through the detector. Therefore an increase of the preconcentration time can be achieved either by an increase of the injected sample volume or by a decrease of the flow rate.

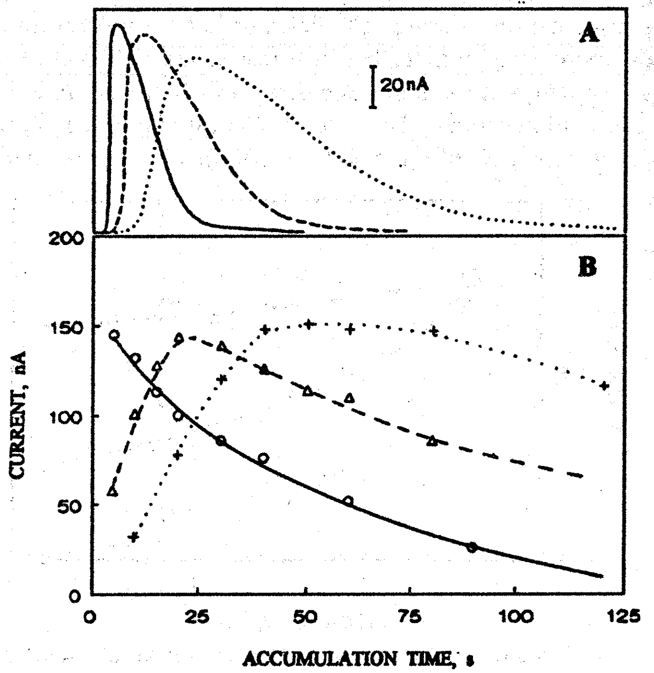

Figure 5. FIA sample profiles (A) and dependence of cadmium peak current on the accumulation time (B) for different flow rates: dotted line – 0.36 ml min^{-1}; dashed line – 0.71 ml min^{-1}; solid line – 1.41 ml min^{-1}. Other conditions: carrier electrolyte 0.01 mol l^{-1} ammonia buffer (pH 9.5); Cd concentration 80 nmol l^{-1}; oxine concentration 8×10^{-5} mol l^{-1}; accumulation potential -300 mV; mixing coil 0.5 m/0.5 mm; sample volume 200 μl

In Figure 5 the dependences of Cd peak current on the accumulation time for various flow rates are compared. In the diagram the relevant concentration profiles of the samples injected at the same time scale are also shown. The AdSV peak height increases when the accumulation time increases, then it reaches a maximum; further enhancement of the accumulation time leads to a decrease of the signal which depends on the flow rate. The highest currents are obtained for the preconcentration times shorter than the residence time of the sample in the detector. This means that the elution of the adsorbed oxinates from the HMDE surface during flow of the pure supporting electrolyte takes place. Therefore the stripping should be started when the sample is still in the detector. Such effects are most strongly pronounced for high flow rates.

Dependence of the peak current on the flow rate

In the to-date applications of SV in the flow injection analysis it is usually underlined that the analytical signal magnitude obtained significantly depends on the sample flow rate through the detector. As the flow rate increases a clear decrease of the effectiveness of the analyte preconcentration can be observed which in turn leads to a poorer sensitivity of the method. For example Wise, Heineman and Kissinger [11] have found that in the case of ASV, at the flow rate of 1–2 ml min^{-1}, only *ca.* 10 % of the sample passing through the detector is accumulated in the form of an amalgam on the mercury electrode. The best results are obtained for the small flow rates which ensure long sample residence time in the detector and higher effectiveness of the accumulation process. However, in the case studied a clear impact of the flow rate on the peak heights of the metals determined has not been observed. It has been established that the effectiveness of the accumulation of oxine on the HMDE is practically independent of the flow rate, provided the measurement conditions have been accurately optimized (delay time, preconcentration time). Dependence of the

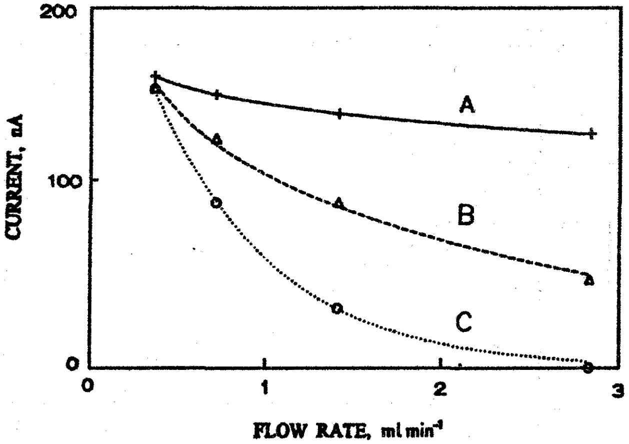

Figure 6. Dependence of cadmium peak current on the flow rate for: A) optimal delay and accumulation times (55, 23, 7, 0 s for successive flow rates); B) accumulation time corresponding to time of sample passage through the detector (85, 42, 20, 10 s); C) accumulation time constant (85 s). Other conditions as in Fig. 5

signal magnitude on the flow rate for various ways of the accumulation time selection is presented in Fig. 6. For curve A the delay and preconcentration times have been selected in such a way that they corresponded to the maximum current for a given flow rate in Fig. 5. Curve B reflects the accumulation times equal to the time during which the whole sample passes through the detector for a given flow rate; in the case of curve C a constant accumulation time has been applied independently of the flow rate (corresponding to the residence time of the sample for the lowest flow rate). A significant decrease of the peak heights as the flow rate increases, for the preconcentration times equal to or longer than the residence time of the sample in the detector, is observed. Optimization of the FIA procedure leads to practically identical current responses of the electrode for various flow rates.

The absence of a clear dependence of the peak current on the flow rate indicates that two effects are competing: first, a decrease of the effective preconcentration time as the flow rate increases, and the second, a faster transport increases adsorption [15] (if the adsorption process is fast enough).

The most important advantage of the system studied is a possibility to use – without a significant sensitivity loss – higher flow rates and hence shorter analysis times. For the sample volume of 200 μl the throughoutput of 60 samples per hour (at the flow rate of 0.71 ml min^{-1}) can be achieved. The application of larger sample volumes (for the determination of smaller metal contents) should not result in a decrease of the analysis speed when higher flow rates are applied.

Interferences

As it is for each AdSV measurement, the proposed method is sensitive to the presence of surfactants in samples. Also the interferences of other metals forming complexes with oxine are possible. The presence of surfactants in the samples may be responsible for a significant lowering of the sensitivity of the method because of competing adsorption on the HMDE surface. Therefore appropriate methods of removing these substances from the solutions before the analysis are usually necessary. However, such methods are often time-consuming and the most important advantages of the FIA method, *i.e.* simplicity and speed of analysis, are lost. Direct measurements without significant sensitivity loss are possible only in the analysis of water containing small amounts of surfactants.

Among metal ions which can be present in samples of natural water magnesium can be an important interfering element in the analysis of Pb. The influence of the magnesium ion concentration on the determination of Pb and Cd is shown in Fig. 7. For cadmium the AdSV peak heights are practically independent of Mg concentration. However, in the case of lead a negative influence of Mg starting from the concentration of Mg as low as *ca.* 5×10^{-5} mol l^{-1}, is evident. Thus determination of Pb in many natural-water samples may be troublesome. Unfortunately, the intensity of interferences increases when higher oxine concentrations are used. Under these conditions both Pb and Cd peak heights are lower.

The high sensitivity of the method causes problems with the blank. In case of lead and cadmium, it is possible to obtain a blank close to the background line, using the procedure for the standard trace analysis methods (low concentrations and selected reagents of high purity, water double distilled from quartz, flushing system with diluted nitric acid, and conditioning by injecting samples containing oxine only). However, it was impossible to obtain a blank without copper peak. The source of copper contamination was probably oxine itself. When oxine made by several producers was used (different serial numbers from POCh, Merck) the blank changed only insignificantly. Thus copper was treated as an interference.

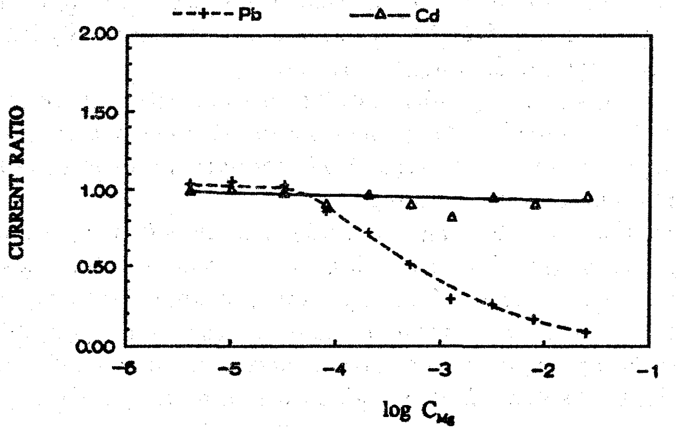

Figure 7. Effect of magnesium concentration, in mol l^{-1} on Cd and Pb peak height. Values of "current ratio" axis are referred to the peak height in the absence of Mg. Cd and Pb concentration 10^{-7} mol l^{-1}; accumulation time 20 s; flow rate 0.71 ml min^{-1}. Other conditions as in Fig. 5

The presence of copper in many samples and reagents may create some difficulties, especially in the lead determination, because Cu and Pb peaks partially overlap. It has been found that the decrease of Cd and Pb peaks at the same concentration of copper (30 nmol l^{-1}) was negligible (5 % for Cd and 10 % for Pb). At the copper concentration ten times higher Cd and Pb peaks were reduced by 15 and 40 %, respectively. However, such concentrations of copper in natural waters are very rare.

Analytical applications

The calibration curve of Cd (for flow rate of 0.71 ml min^{-1}, 0.2 ml sample volume, accumulation time of 20 s, and oxine concentration in the sample of 8×10^{-5} mol l^{-1}) is linear in the concentration range from 2 to 50 nmol l^{-1} (slope – 1.837 nA l $nmol^{-1}$; correlation coefficient – 0.9998; detection limit – 1.0 nmol l^{-1} = 0.1 μg l^{-1}). The determination of lead under the same conditions gave slightly worse results. A better sensitivity of the lead analysis under FIA conditions is obtained with the higher oxine concentrations in the sample. In this case the following results for Pb have been obtained (for oxine concentration in the sample of 5×10^{-4} mol l^{-1} and other conditions similar to Cd determination): concentration range – 20–250 nmol l^{-1}, slope – 0.597 nA l $nmol^{-1}$; correlation coefficient 0.9993; detection limit – 4.9 nmol l^{-1} = 1 μg l^{-1}.

The reproducibility of the results in the AdSV/FIA approach is good. A series of 8 successive injections of a 0.1 ml sample of metals present at the concentration of 80 nmol l^{-1} yields the mean peak currents of 79.8 and 27 nA, the current ranges of 77–82 and 26–29 nA, and the relative standard deviations of 2.7 and 4.1 %, for cadmium and lead, respectively.

The method was used for the determination of lead in river water samples. Adsorptive stripping voltammograms for various methods of sample pretreatment are shown in Fig. 8A. An analytical interpretation of the curve "a" (obtained without any pretreatment of the sample) is not possible. A slight improvement is achieved after an addition of fumed silica in order to remove surfactants from the solution (curve "b"). After destroying surfactants by UV irradiation (curve "c") the method may be successfully used for the determination of lead and cadmium. This procedure is not necessary for the water samples taken from the river near the sources. Because of significantly smaller concentrations of surface active substances a direct measurement is possible in this case. However, the inferior sensitivity as compared with the model studies is observed. Some voltammograms of river water samples obtained after successive addition of lead are shown in Fig. 8B. The concentration of lead in the river water was determined by standard addition method repeated five times as equal to 11.3±0.5 nmol l^{-1}.

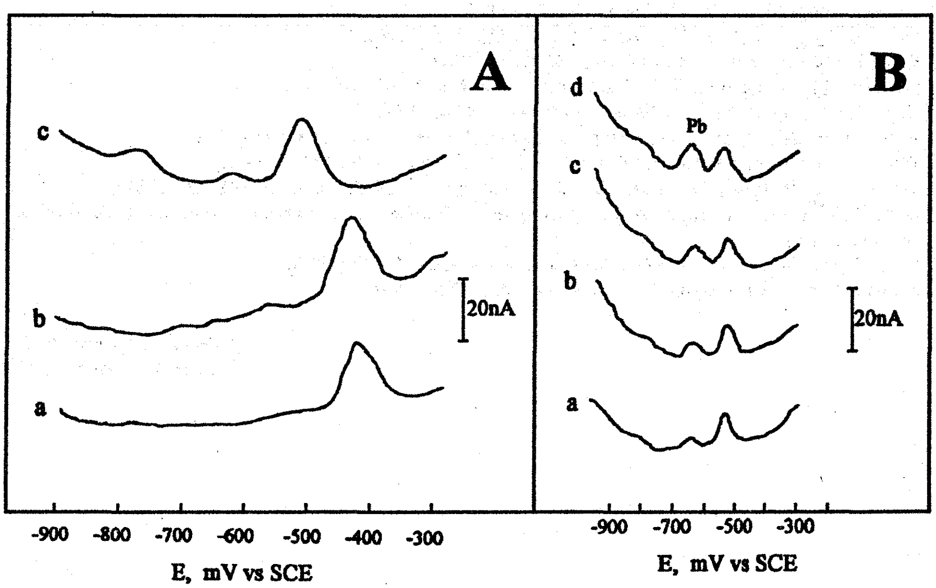

Figure 8. Adsorptive FIA voltammograms of natural-water samples. A) The Sztola River (near Bukowno): a) water sample, b) water sample with 5 g l^{-1} of fumed silica, c) water sample after UV irradiation; B) The Sztola River (near sources): a) water sample only, b, c, d) after successive addition of lead (20, 47 and 87 nmol l^{-1}, respectively). Conditions: accumulation time 20 s; accumulation potential -300 mV; carrier electrolyte 0.01 mol l^{-1} ammonia buffer (pH 9.5); oxine concentration 5×10^{-4} mol l^{-1} (A) or 8×10^{-5} mol l^{-1} (B); mixing coil 0.5 m /0.5 mm; flow rate 0.71 ml min^{-1}; sample volume 200 μl

In conclusion, it has been found that adsorptive stripping voltammetry may be successfully used for the determination of trace amounts of cadmium and lead by flow injection analysis in spite of some difficulties corresponding to the sensitivity of the method to the presence of surfactants and magnesium ions in the solutions. The adsorptive method offers significant sensitivity enhancement as compared with anodic stripping voltammetry. Owing to high sensitivity of AdSV and effectiveness of accumulation process in FIA, system it makes possible the determination of the samples of 0.2 ml volume, of the metal concentration in the order of 10^{-9} mol l^{-1}, and with the sample throughoutput of 60 samples per hour. The careful optimization of the measuring procedure allows to obtain the analytical signal independent of the flow rate.

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