Mercury Determination in Fish Samples by Flow Injection Using Gold Electrodes Made from CD-R's

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A new flow injection set up was developed for mercury determination by stripping chronopotentiometry. The FIA system was based on using solenoid valves controlled by a computer. A flow cell was manufactured with the gold working electrode made from a recordable compact disk (CD-R). The following operational parameters were studied and optimized: sample flow rate, time of mercury deposition by electrolysis on the electrode surface and current imposed for mercury dissolution off the working electrode. Mercury could be measured within 5 - 100 ng/mL domain at a deposition time of 180 s. Detection limit was 0.1 ng/mL at 600 s deposition time. RSD for a concentration of 40 ng/mL mercury was 1.04% (n=6) under optimal working conditions. . A concentration of 0.157±0.031µg mercury/g sample was found in a cod sample with this method. Recovery degree of a known amount of mercury introduced in the analyzed sample was 96.2%.

Keywords: mercury analysis, gold electrodes, stripping chronopotentiometry, flow injection analysis, fish analysis

Mercury in different samples is mainly determined by means of cold vapor atomic absorption spectrometry (CVAAS) [1,2] and cold vapor atomic fluorescence spectrometry (CVAFS) [3]. The detection limit is placed around a 0.2 ng/g value in the case of CVAAS [4] and respectively, 2 ng/L in the case of CVAFS [5] if a stage for preconcentration of mercury on gold is provided.

Some electrochemical techniques have also applications in mercury determination. These are based on different types of chemically modified electrodes [6-9] (for mercury preconcentration followed by its redissolution), ion selective electrodes [10-14], anodic stripping with gold electrodes [15-19], etc.

Stripping chronopotentiometry is also interesting for mercury determination [20-22]. This method can be applied directly to liquid samples with a minimal pre-treatment of the latter and does not need a solution deoxygenating prior to analysis. Detection limit is 8 ng/L with a fairly good selectivity [23]. Due to its, both high sensitivity and selectivity, stripping chronopotentiometry can be alternative for CVAAS and CVAFS in mercury determination from a large variety of samples. The technique has important advantages such as: apparatus and also the running cost are much cheaper than in the case of CVAAS or CVAFS, has smaller size and there are commercially available portable devices for field analyses at a much lower cost price.

It is worth mentioning the fact that gold electrodes (commercially available) were also used for flow analysis of mercury based on its preconcentration by electrolysis followed by either an anodic stripping step for mercury redissolution [24], or by chronopotentiometric stripping [25]. The main advantages of such system were consisted in simplify of operation, short time needed for analysis and a low price of apparatus. As an important disadvantage of the method, we mention the fact that expensive gold working electrodes were required.

A new source for gold electrodes was represented by recordable compact disks (CD-R's), which have a gold film as a reflecting layer. Several studies were reported in literature regarding the gold electrode manufacturing starting from CD-R's [23, 26-29] and their use in mercury determinations by chronopotentiometric stripping analysis. This type of electrodes were used also for amperometric determination of ascorbic acid [30] and dipyrone [31] in pharmaceutical formulations, for on-line amperometric determination of Ce(IV) [32] during polymerization reactions, for amperometric detection [33] in capillary electrophoresis, for determination of Cu(II) and Pb(II) [34] in lubricating oils by using square-wave anodic stripping voltammetry, for determination of Cu(II) [35] in sugar cane spirits and tap waters by chronopotentiometric stripping analysis and for developing small flow cells for voltammetry and flow injection analysis [28, 30, 31, 36, 37].

In a previous paper [29] we presented a study regarding the determination of mercury by chronopotentiometric stripping analysis using gold electrodes prepared from recordable CDs by working in batch mode. In this study we adapted the developed method to flow injection analysis technique [39-42] and a more completed study of interference in mercury determination has been also done.

A flow cell was manufactured with the working electrode made from a recordable compact disk (CD-R) at a very low cost price, accessible to any analytical laboratory. FIA system was based on using solenoid valves controlled by a computer. After an optimization of the analytical parameters, the proposed method was applied to mercury determination from fish samples. Determination of mercury in fish samples is very important owing to its toxicity [38, 43] and the electrochemical methods can be applied with good results for detection of this metal [15-19, 27, 28, 44].

Experimental part

Reagents

Fuming nitric acid 100%, sulfuric acid 98% and hydrochloric acid 37% were purchased from Merck. 1000 mg/L mercury standard solution for AAS was obtained from $Hg(NO_3)_2$ in 2 mol/L HNO_3 (Fluka). An intermediary standard of 10 mg/L was prepared from this solution by diluting it with 0.05 M HCl solution containing 0.3 M Na_2SO_4.

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Standard solutions were prepared on a weekly basis and subsequently used for preparing daily standard solutions of 0.1 mg/L by dilution with a 0.05 M HCl solution containing 0.3 M Na_2SO_4. Anhydrous sodium sulfate was obtained from Romania and selenium dioxide from Poland. Crystallized copper sulfate, crystallized zinc acetate, lead nitrate, crystallized manganese acetate and iron and ammonium double sulfate were purchased from Romania. 0.2 M sulfuric acid and 0.05 M hydrochloric acid solutions were prepared by diluting the corresponding volumes of concentrated acids with bidistilled water. Standards of different concentrations of mercury were prepared by diluting the corresponding volumes of 0.1 mg/L Hg with 0.05 M HCl containing 0.3 M Na_2SO_4. Solutions of Cu(II), Zn(II), Pb(II), Fe(II), Mn(II), and SeO_3^{2-} with concentrations of 1000 mg/L metallic ion were prepared by dissolving salts of the respective ions, and respectively SeO_2 in bidistilled water. All electroanalytical measurements were carried out in 0.05 M HCl containing 0.3 M Na_2SO_4. The latter was introduced in all analysed samples and standard solutions in order to increase their electrical conductivity. In the absence of 0.3 M Na_2SO_4 in the analysed samples, it was found out that reproducibility decreased drastically and, in some cases, measurements could not be done at all, because a too low electrical conductivity of solutions. All vessels used were cleaned as following: kept in water with detergent for 16 h and then washed with tap water. Subsequently, they were kept in 6 M nitric acid for another 8 h and then cleansed with tap, distilled and finally bidistilled water.

Apparatus

Manufacture of the working electrode

Kodak Gold Preservation CD-R's [45] were used for making the gold electrodes. Such a CD-R is constituted from a polycarbonate support on which the following layers are deposited: phtalocyanine, reflective gold (24 karats, with thicknesses between 50-100 nm and an area of about 100 cm^2) and three protective polymeric layers.

Phtalocyanine is a photosensitive colorant which can melt on the spots where is touched by the laser beam used for registering the information on CD. The zones where the colorant was melted are called "burnt" zones and have optical properties that are entirely different from those where the colorant is not affected. The information is stoked on CD as successive "burned" and "not-burnt" zones.

The gold layer on CD constitutes the active surface of the working electrode studied in the following.

In order to manufacture a gold electrode from a CD, the three protective polymer layers were removed by treating the CD with concentrated nitric acid for several minutes. This acid dissolves polymeric layers but has no effect on either polycarbonate support or gold film. The CD was washed with tap and bidistilled water and then cut into pieces which were subsequently used for making the flow cell electrode.

The flow cell for mercury determinations is shown schematically in figure 1. It was made of two Plexiglas blocks separated by 1 mm thick rubber band from which a elipse-shaped fragment was cut off so as the resulting free space to be 9 mm long, 3.5 mm wide and has an area of approximately 25 mm^2 and a volume of about 6 µL.

The gold electrode was placed underneath the rubber band. A new working surface of the gold electrode can be obtained when the plate is shifted.

A laboratory made Ag/AgCl/Cl^- (1M) electrode [46] was employed as reference.

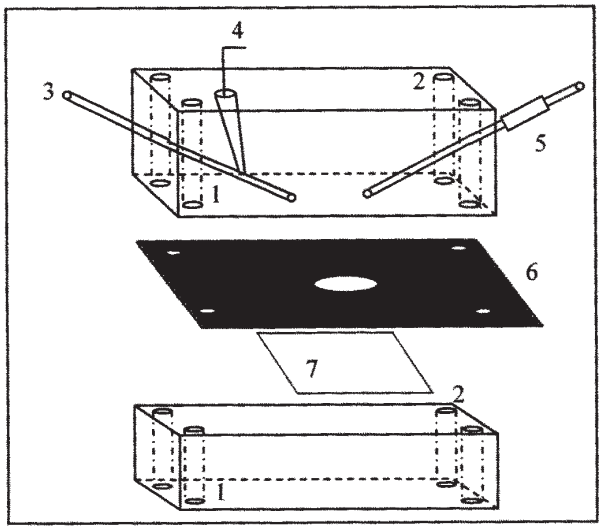

Fig. 1. Scheme of the flow cell: 1) Plexiglas blocks; 2) screw hobs; 3) Teflon tube (liquid flow intake); 4) hole for miniaturized (Ag/AgCl/Cl^- (1M)) reference electrode; 5) counter electrode (liquid flow outlet); 6) rubber band with an elipse-shaped orifice constituting the flow cell; 7) gold electrode (fragment of a CD-R)

The counter electrode was a stainless steel tube with an inner diameter of 1.4 mm, length 30 mm and surface 132 mm^2.

The reference electrode was positioned on the intake track, while counter one on the cell outlet. The three electrodes were connected to a potentiostat (Netherland) by means of "crocodile"-type clips. The potentiostat was coupled to a Pentium IV PC for acquisition and processing of data.

Experimental set up for flow analysis

The employed set up for flow analysis is depicted in Figure 2. It was made of two solenoid valves (USA), V1 and V2, the above described flow cell and a peristaltic pump (Gilson). Connecting tubes are made of Teflon and have inner diameter of 0.8 mm.

Working procedure

The solenoid valves, V1 and V2, were programmed as following: V1 was coupled first to aspirate the 0.05 M HCl containing 0.3 M Na_2SO_4 solution for 50 s. For the last 10 s a potential of 0.85 V (*vs.* Ag/AgCl/Cl^- (1M)) was applied in order to clean the working electrode surface. After 50 s V1 was shut off and V2 coupled to aspirate a mercury standard solution or a sample for 205 s. The first 25 s were necessary

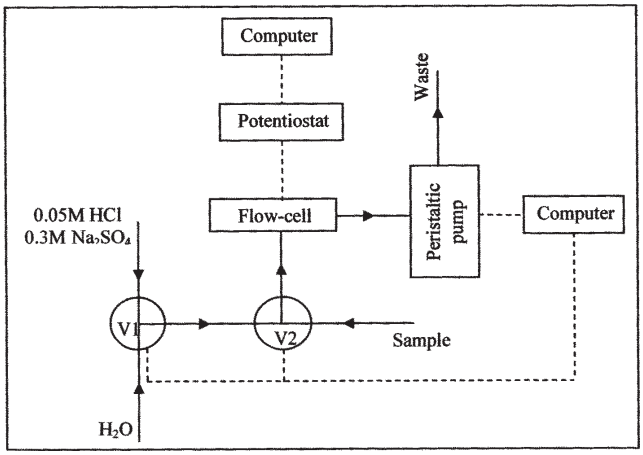

Fig. 2. Scheme of flow injection analytical set up for mercury determination. V1 and V2, solenoid valves controlled by the computer.

for washing the flow cell and the counter electrode. For the next 180 s, a potential of 0.3 V (*vs.* Ag/AgCl/Cl^- (1M)) was applied to the working electrode. Mercury deposition takes place under these conditions. After that, it follows an equilibration step of 15 s. The electrode potential variation between 0.3 V ÷ 0.7 V was then measured when a constant current of +0.75μA was applied to the working electrode. The peristaltic pump was switched off during the step for equilibration and switched on during redissolution of mercury.

The valves and peristaltic pump start and stop automatically after a cycle of 280 s is completed. Changing of standard solutions and samples was done manually. The flow rate was in all cases 1 mL/min.

The signal for a blank (0.05 M HCl containing 0.3 M Na_2SO_4 solution) was registered at first. The latter is to be subtracted from the signal for the analyzed samples. On the registered differential chronopotentiometric curve dE/dt – f(E), the measured parameter was the area of the peak corresponding to mercury redissolution.

Results and discussions

Study of the electrochemical behaviour of the electrode surface

A cyclic voltammogram was registered in order to study the working electrode behaviour. The potential was scanned between -0.25 and 1.5 V (*vs.* Ag/AgCl/Cl^- (1M)) while a continuous flow of 0.2 M H_2SO_4 flew through the cell. Scanning rate was 0.02 V/s. An anodic peak was noticed around a value of 1.32 V corresponding to gold oxidation and a cathodic one at approximately 0.87 V attributed to gold reduction. This voltammogram was quite similar with the one reported in literature [35] as registered when a disk gold electrode was used. We can draw the conclusion that our electrode has the same properties as those of a commercially available disk gold electrode.

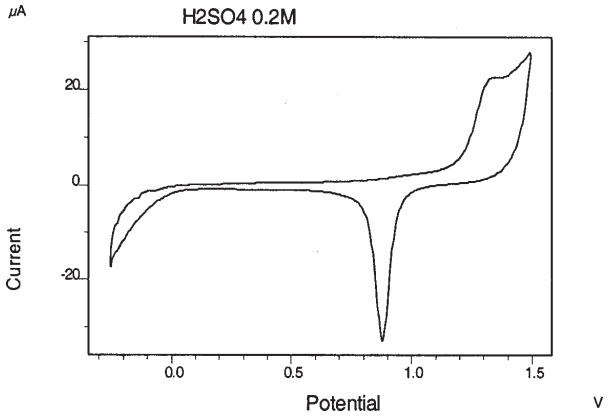

Fig. 3. Cyclic voltamogram registered at scanning the working electrode surface in 0.2 M H_2SO_4 solution. Scanning rate was 0.02 V/s in a range between -0.25 and 1.5 V. The cell in Figure 1 with a Ag/AgCl/Cl^- (1M) reference electrode was used.

Influence of the potential applied to the working electrode for mercury deposition from solution

Literature data [21] indicate that mercury reduces within a wide potential range (from negative values up to approximately +0.3 V (*vs.* Ag/AgCl/Cl^- (1M)), but its reduction can be accompanied by reduction of some other species from the analyzed sample such as: Cu(II), Pb(II) or Cd(II)). We consider +0.3 V as the most appropriate value for mercury deposition because the deposition of many other species at the electrode surface is decreased at this positive potential value. Therefore, the selectivity of determinations was enhanced.

Influence on the analytical signal of sample flow rate during mercury deposition stage

The determinations were made by using a standard solution of 40 ng/mL mercury prepared in a solution of 0.05 M HCl containing 0.3 M Na_2SO_4. For all studied flow rates, the deposition time for mercury was of 1 min. The analytical signals obtained at different values of sample flow rates were shown in figure 4A and peak areas as function of flow rate in figure 4B. A linear dependence was obtained for peak areas as a function of sample flow rate within 0.25 – 4 mL/min domain. A value of 1 mL/min was chosen for the next measurements, high enough to get well defined signals in a reasonably time and a low consumption of analysed sample.

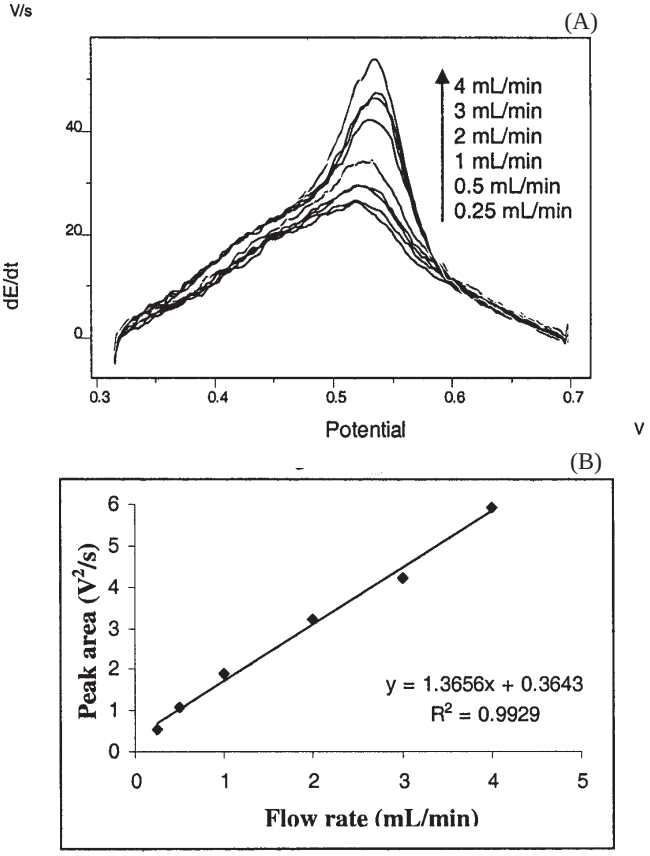

Fig. 4. A) Signals obtained at a concentration of 40 ng/mL Hg(II) for different values of the sample flow rate (0.25; 0.5; 1; 2; 3, 4 mL/min). The deposition time for mercury was of 1 min. The other working conditions were the same as described at the working procedure. Two recordings are given for each flow rate.
B) Influence of the sample flow rate on analytical signal of mercury for a concentration of 40 ng/mL Hg(II).

Influence of time for electrolytic deposition of mercury on gold electrode surface

Analytical signals registered at different values of the mercury electrolytic deposition time on the gold electrode and at a flow rate of 1 mL/min were shown in figure 5A. As can be seen from figure 5B a linear dependence between the registered signal and time was obtained for 30-600 s range. The deposition of mercury was made at a potential of 0.3 V. The longer the deposition time, the more mercury was deposited on the electrode surface and the signal was stronger. Duration of 180 s was chosen, a time long enough to get reproducible well defined signals and not to increase much the time needed for an analysis.

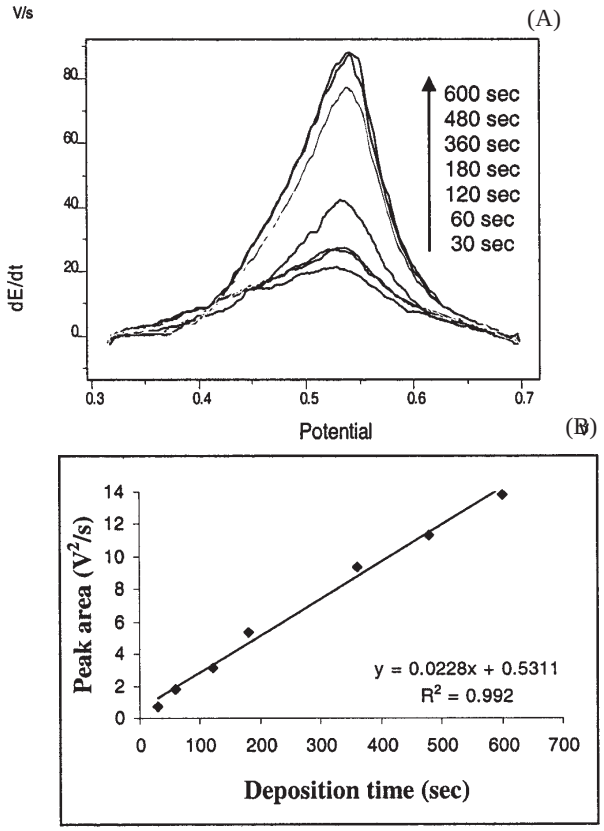

Fig. 5. A) Signal registered for a concentration of 40 ng/mL Hg(II) at different times: 30, 60,120, 180, 360, 480 and respectively 600 s. Flow rate was of 1 mL/min. The other working conditions were the same as described at the working procedure. Two recordings are given for each deposition time. B) Influence on the analytical registered signal of time for electrolytic deposition of mercury. Mercury concentration was 40 ng/mL Hg(II)

Influence on the analytical signal of the imposed current for mercury redissolution

The relationship between registered peak area and the imposed current for mercury redissolution was studied for a 0.75 μA - 10 μA range. An exponential decrease of the peak area was observed when the current increases (fig. 6). The other parameters, flow rate (1 mL/min), deposition potential (0.3 V), deposition time (60 s), were the same.

Drawing of the calibration line

In figure 7A were depicted the registered analytical signals for mercury determination by using the flow injection analysis set up with solenoid valves, and in figure

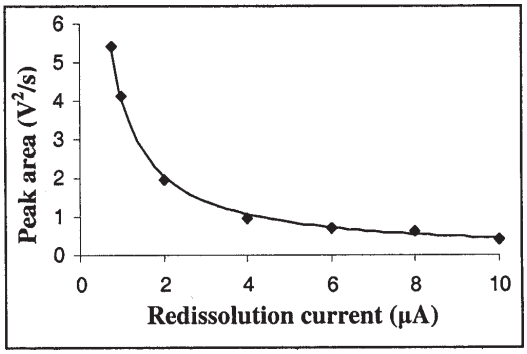

Fig. 6. Influence on the analytical signal of the imposed current for mercury dissolution. Mercury concentration, 40 ng/mL Hg(II); flow rate, 1mL/min; deposition potential, 0.3 V; deposition time, 60 s. The other working conditions were the same as described at the working procedure

7B was depicted the corresponding calibration straight line. The equation of the straight line was: y = 0.1178x + 0.3761 and R^2 = 0.9986 (where y represent the peak area and x represent the mercury concentration). Mercury could be determined in the 5 - 100 ng/mL domain. RSD = 1.04% (n=6; $c_{mercury}$ = 40 ng/mL). The experimental conditions described at the working procedure were employed.

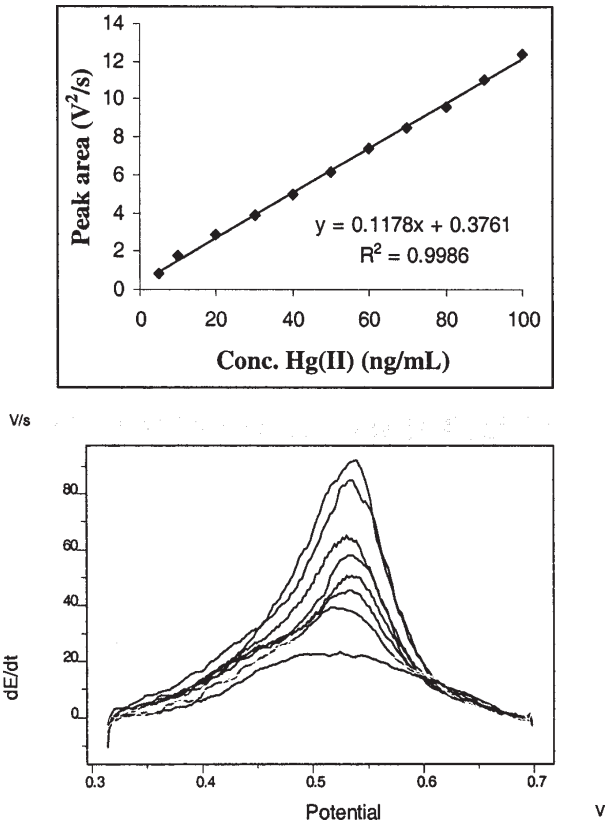

Fig. 7. A) Signals for different Hg(II) concentrations: 0; 5; 10; 20; 30; 40; 50; 60; 70; 80; 90; 100 ng/mL, in the ascending order of the registered curves. B) Calibration straight line obtained for the system with solenoid valves. The working conditions were the same as described at the working procedure

Lower detection limits can be achieved by using longer deposition times of mercury on the electrode surface. A calibration straight line was drawn at a deposition time of 600 sec. Straight line equation was: y = 0.6214x + 0.2645 and R^2 = 0.9895.

The detection limit was estimated to be 0.1 ng/mL (three times the standard deviation of the background noise) at a deposition time of 600 s and the determination limit was 0.3 ng/mL (ten times the standard deviation of the background noise (n = 10).

Interference study

In order to study the influence of some metallic ions on the analytical signal of mercury, ions of different concentrations were added to a 20 ng/mL mercury solution, so that $C_{Me(II)}/C_{Hg(II)}$ ratio had the following values: 1; 2.5; 5; 10; 20; 25; 50, and 100.

The signals registered for a 20 ng/mL mercury solution with zinc ion additions so that $C_{Zn(II)}/C_{Hg(II)}$ ratios were: 0; 1; 2.5; 5; 10; 20; 25 and respectively 50 are presented in Figure 8A.

In the case of Zn(II), Pb(II), Fe(II) and Mn(II) ions, no influence on the analytical signal was noticed up to a value of 25 for $C_{Me(II)}/C_{Hg(II)}$ ratio. When $C_{Me(II)}/C_{Hg(II)}$ ratios are higher than 25 (for Zn(II), Pb(II), Fe(II) and Mn(II) ions), a widening of the mercury peak is noticed together with an increase

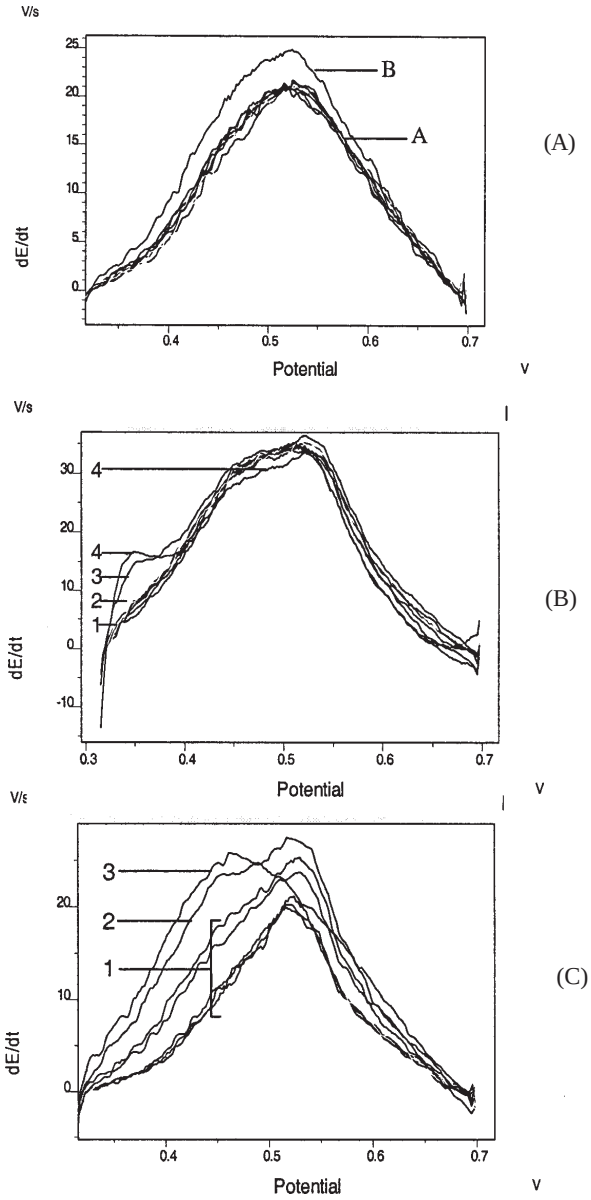

Fig. 8. A) Signal for de 20 ng/mL Hg(II) solutions with additions of Zn(II). $C_{Zn(II)}/C_{Hg(II)}$ ratio were: 0; 1; 2.5; 5; 10; 20; 25 (superposed curves noted with a) and 50 (curve b). B) Signals for 20 ng/mL Hg(II) solutions with different Cu(II) additions. $C_{Cu(II)}/C_{Hg(II)}$ ratios of 0; 1; 2.5; 5; 10 (superposed curves noted with 1), 20 (curbve 2), 25 (curve 3) and respectively 50 (curve 4). C) Signals for a 20 ng/mL Hg(II) solution with additions of SeO_3^{2-} ions together with the signal registered for a sample containing only SeO_3^{2-}ions. $C_{SeO3}^{2-}/C_{Hg(II)}$ ratios were: 0; 1; 2.5; 5; 10; 20; 25 (curves noted with 1) and 50 (curve 2). Curve 3 is for the signal containing only SeO_3^{2-} ions at a concentration of 1000 ng/mL (curve 3). The working conditions were the same as described at the working procedure.

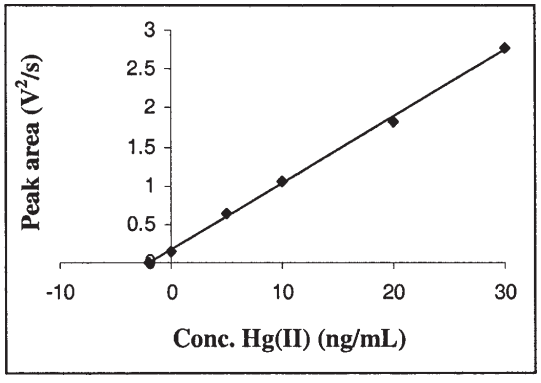

Fig. 9

of the analytical signal, but the second well defined peak to be attributed to the interfering species does not appear, as can bee seen in figure 8A.

In the case of Cu(II) ion interference, a slight change in the peak shape was noticed for a $C_{Cu(II)}/C_{Hg(II)}$ ratio higher or equal to 20 as well as apparition of a supplementary peak around 0.35 V. The signal registered for a 20 ng/mL mercury solution with addition of copper ions in $C_{Cu(II)}/C_{Hg(II)}$ rations between 0 and 50 were given in figure 8B. All the interference studies were made under given working procedure conditions.

The signal for a 20 ng/mL mercury solution with additions of SeO_3^{2-} ions in $C_{SeO3}^{2-}/C_{Hg(II)}$ ratios between 0 – 50 are given in figure 8C .

A slight modification of the peak shape was observed when SeO_3^{2-} ion interference was studied at $C_{SeO3}^{2-}/C_{Hg(II)}$ ratios lower or equal to 5. When $C_{SeO3}^{2-}/C_{Hg(II)}$ is higher than 5, the second peak is not well defined so as to be attributed to the interfering species, but a widening accompanied by an increase of the analytical signal in the zone where mercury peak forms (fig. 8C) was noticed. At $C_{SeO3}^{2-}/C_{Hg(II)}$ ratio equal to 50, another peak, very close to the mercury peak, appears and indicates the fact that SeO_3^{2-} ions are deposited on the electrode surface and then redissolve during the stripping stage.

Analysis of fish samples

Working procedure for sample digestion

The fish (cod) was purchased from a local supermarket and kept in a freezer (-20°C). Samples were kept for one hour at room temperature, cut into pieces and then water excess was removed with filter paper. Approximately 50 fish fillet was homogenized in a mortar and the samples to be analyzed were extracted from thus obtained fish paste. The samples were digested according to a receipt adapted from literature data [47] as follows: in an Erlenmayer flask of 250 mL, 2 g fish were weighed and 5 mL 100% (fumans) nitric acid, 2.5 mL 98% sulfuric acid and 1 mL 37% HCl added. The flask was covered with a watch glass and when reaction stopped (after approximately 20 min) placed on a water bath at 100°C. After one hour, the flask was removed and, after cooling down, brought with bidistilled water to a 50 mL volumetric flask. Samples of 3 mL were extracted from this solution, diluted to 10 mL with 0.05 M HCl solution containing 0.3 M Na_2SO_4 and analyzed.

Results of fish sample analyses

The method using fumans nitric acid for sample digestion proved efficient as the resulting solutions could easily be analysed. No interferences were registered during the analysis.

We consider that this method of fish sample digestion was easier to be used in the laboratory in comparison with other method for fish sample digestion [25] based on the use of "Microwave Sample Preparation System". In the later case were used closed flasks in which a high pressure was developed during digestion that can be dangerous.

Because the acids used for digestion may contain a certain amount of mercury and sample matrix is quite complex, the recovery degree of a known mercury amount introduced as standard solution was determined in order to establish the correctness of results.

A comparison sample (acid mixture as that used for digestion), a fish sample as well as another fish sample to which 0.6 μg mercury (as standard solution) were added, were digested.

Table 1
RESULTS OBTAINED FOR ANALYSIS OF A COD SAMPLE BY MEANS OF THE PROPOSED METHOD AND CVAAS [42]

Sample amount (g)	Proposed method (μg/g)[a]	Recovery (%)[b]	CVAAS (μg/g)[a]	Recovery (%)[b]
Cod (2.1066 g)	0.157±0.031	-	0.149±0.006	-
Cod (2.0583 g + 0.6 μg Hg (standard solution))	0.438±0.019	96.23	0.436±0.008	98.28

a.All values are means of four measurements ± k x relative standard deviation (where k=3). b. Recovery. Mercury recovery was calculated by determining the mercury amount (μg/g) in a cod sample and in another one to which a known amount of mercury was added (μg/g). The difference between these two quantities represents the recovered mercury. Ratio between recovered mercury to the added one

The method of standard additions was applied for mercury determinations in both cases (for fish samples and fish samples with a known mercury amount added prior digestion). For that, standard mercury solutions were added to the digested fish sample so that mercury concentration in the analyzed sample was respectively, 5, 10, 20 and 30 ng/mL (fig. 9). Four replicates for each sample were analysed and their mean value computed. The signal registered for the comparison sample was subtracted from the one for analysed samples.

The recovery degree for a known amount of mercury introduced in a fish sample before digestion was 96.23% (n=4). Mercury recovery was calculated by determining the mercury amount (μg/g) in a cod sample and in another one to which a known amount of mercury was added (μg/g). The difference between these two quantities represents the recovered mercury. Ratio between recovered mercury to the added one gives the recovery degree.

The samples were also analyzed by cold vapor atomic absorption spectrometry (CVAAS) and the obtained results are listed in table 1.

Conclusions

A set up of flow injection analysis was built for mercury determination by stripping chronopotentiometry. It was made of two solenoid valves, a flow cell, a peristaltic pump and an instrument for chronopotentiometric measurements.

The flow cell was laboratory made and contains: a gold electrode made in laboratory from a CD-R as working electrode, a reference electrode of Ag/AgCl/Cl^- (1M) also built in laboratory and a counter electrode made of a stainless steel tube.

The flow injection analysis is monitored by a computer whose software allows for programming the valves and peristaltic pump.

The following operational parameters were studied and optimized: sample flow rate, time of mercury deposition by electrolysis on the electrode surface and current imposed for mercury dissolution off the working electrode.

Mercury could be measured within 5 - 100 ng/mL domain at a deposition time of 180 s. Straight line equation: $y = 0.1178x + 0.3761$ and $R^2 = 0.9986$. In the case of a deposition time of 600 sec, mercury could be determined at lower concentrations, between 0.5 ng/mL – 5 ng/mL, and the obtained straight line was expressed by: $y = 0.6214x + 0.2645$ and $R^2 = 0.9895$. Detection limit was 0.1 ng/mL at 600 s deposition time. The standard relative deviation for a concentration of 40 ng/mL mercury was 1.04% (n=6).

Mercury from fish samples was determined by using a digestion method with concentrated acids: 100% (fumans) nitric acid, 98% sulfuric acid and 37% hydrochloric acid.

A concentration of 0.157±0.031 μg mercury/g sample was found in a cod sample with this method. Recovery degree of a known amount of mercury introduced in the analysed sample was 96.23%. When the same sample was analyzed by CVAAS, the results were 0.149±0.006 μg mercury/g sample.

The manufactured flow system has several advantages: simplicity, robustness and low price. Very important is the fact that either working solution or analysed samples do not need deoxygenation prior measurement and that makes the system easy to be used.

When the gold electrode made from a CD-R is employed as working electrode coupled to a flow system with chronopotentiometric detection, the electrode life time increases very much in comparison with the case when it is used a conventional set up (using the same detection method) [36]. Thus, if in a conventional set up an electrode ca be used for approximately 40 experimental runs, when the flow analysis is used no damage is noticed even after 100 runs.

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