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Centri-voltammetric study with amberlite XAD-7 resin as a carrier system

Ülkü Anik Kirgöz*, Hüseyin Tural, F. Nil Ertaş

Chemistry Department, Faculty of Science, Ege University, 35100 Bornova-Izmir, Turkey

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Abstract

Centri-voltammetry is a novel method, which allows combining the advantages of centrifugation and voltammetry. The method offers a practical way for application of coprecipitation in trace analysis allowing direct voltammetric scan hence prevents the loss of the analyte, which usually is the case for other preconcentration techniques. The performance of the method was successfully tested using trace amounts of Pb^{2+} ions in aqueous solution in a vessel specially designed to be compatible to both centrifugation and voltammetry. XAD-7 resin was used as the carrier material and the parameters related to the carrier material and medium characteristics as well as the centrifugation settings were investigated. The sensitivity of the method was found comparable to that of stripping techniques and the detection limit for lead ions was calculated as 5.2×10^{-9} M with mercury coated gold sphere electrode. The precision of the method depends on the configuration of the working electrode and better reproducibility was obtained with mercury coated plate electrodes (R.S.D. 3.3%, $n = 6$).

Keywords: Centri-voltammetry; Preconcentration; Coprecipitation; Amberlite XAD-7 resin; Lead ion

1. Introduction

In trace analyses, the preconcentration of the analyte plays a vital role in terms of sensitivity, and in some case the selectivity [1–8]. In stripping techniques, this step usually includes an electrochemical deposition process on the electrode surface at a controlled potential under stirred conditions [9]. On the other hand, coprecipitatiton techniques provide a simple and efficient way of preconcentration of trace elements in many matrixes prior to the detection [2–7]. Coprecipitation with a selective carrier precipitate followed by electrochemical detection provides a proper separation and sensitive measurement of trace amounts of metals [3]. The advantages and limitations of combining separation techniques with voltammetry have been reviewed [8]. As stated by Moller and Scholz, the sample preparation procedure that requires much time and labor limits the broader application of coprecipitation methods.

Present study describes a practical method for application of coprecipitation in trace analysis eliminating those time consuming and laborious decantation, filtration and dissolution steps. In this method, the analyte is preconcentrated with an appropriate carrier by means of centrifugation and directly measured on the same electrode. For this purpose, a specially designed cell compatible to both voltammetry and centrifuge was constructed that contains a planar working electrode at the bottom to provide a flat surface for the deposits. In this manner, the procedure is simplified while maintaining the selectivity and sensitivity inherited from the coprecipitation techniques. Authors recommend the name of Centri-voltammetry since it combines the advantages of centrifugation and voltammetry.

Various carrier materials can be used for this purpose. Pioneering study with Centri-voltammetry includes the enrichment process with a commonly used coprecipitant $Al(OH)_3$ [10]. The main idea was to trap the analyte between the alumina layer and the mercury thin film electrode surface (MTFE) by coprecipitation. A thin layer of $Al(OH)_3$ was produced by means of centrifugation at the electrode surface to facilitate for adsorption and then preconcentration trace elements. This layer also provides a conductive coat-

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* Corresponding author. Tel.: +90 232 388 82 64; fax: +90 232 388 82 64.

E-mail address: ulkuanik@yahoo.com (Ü. Anik Kirgöz).

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ing which allows the voltammetric measurement directly in the same cell eliminating lengthy steps. The analyte, i.e. lead ion, trapped in the layer by adsorption allows to direct monitoring of the reduction current. Resulting dp peak current at −0.5 V was used in optimization of the experimental parameters and it was shown that lead ions can be determined at nanomolar levels. The sensitivity of the method is comparable with those stripping techniques such as anodic stripping voltammetry (ASV).

The main difference of this technique from the conventional ASV technique lies on the deposition process. In ASV, only a small part of the analyte is preconcentrated at the electrode surface under controlled conditions to represent the concentration of the bulk solution [9]. However, in Centri-voltammetry, it is possible to accumulate most of the analyte on the electrode surface by maintaining the bulk deposition with an appropriate reagent. This constitutes an advantage for attaining lower detection limits by using higher bulk volumes. However, the method requires freshly prepared $Al(OH)_3$ precipitate for enrichment process and preparation conditions limits the reproducibility of the measurement.

Alternatively, Centri-voltammetry can be applied with a non-conductive layer maintained as a thin film on the electrode surface by means of centrifugation. For the last two decades, chelating resins have widely been used for metal enrichment due to their high selectivity and preconcentration factor as well as their good mechanical stability [11]. Present study describes the use of Amberlite XAD-7 resin in Centri-voltammetry for enrichment of test material, i.e. lead ions, on the electrode surface. This procedure is simpler than the previous study since the dry resin is added into the test solution in precise amounts prior to the centrifugation step. Experimental parameters, which may have profound effect on the analytical characteristics of the method, have been presented.

2. Experimental

2.1. Apparatus

Voltammetric studies were performed with a Metrohm 693 VA Trace Analyzer and 694 VA Stand. Nüve NF 800 was used for centrifugation and the pH measurements were made with Jenway ionmeter.

The cell, made from a polyethylene cubic tube with height of 11.5 cm and internal diameter of 3 cm, was constructed to be compatible to the centrifugation system (Fig. 1). Initial studies were made with square shaped Pt electrode with a surface area of 6 mm^2. For establishing optimum parameters and calibration graphs, lab made gold sphere electrode ($r = 0.6$ mm) that was fixed at the bottom of the cell was utilized. On both working electrodes mercury thin film was deposited from Hg^{2+} ions via electrochemical process. The working electrode was placed at the bottom of the cell and a silver wire made electrical connection. Reference (Ag/AgCl) and counter (Pt rod) electrodes were immersed in the same cell.

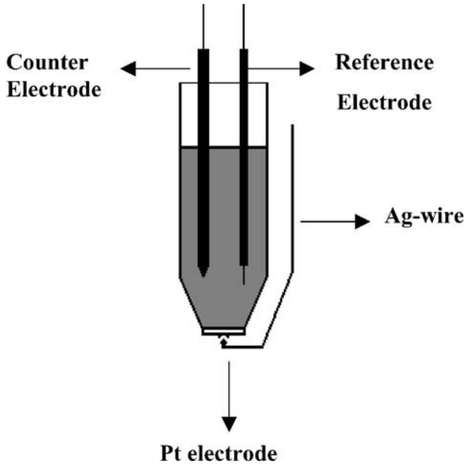

Fig. 1. The working cell used for Centri-voltammetric studies.

2.2. Reagents

All reagents were of analytical grade and the solutions were prepared with the water obtained from Ultra Pure Water System. Amberlite XAD-7 was purchased from Sigma. Mercury plating solution contains 200 μg mL^{-1} Hg^{2+} ions in 1.0 M HCl solution. Ammonium acetate solution was used as the supporting electrolyte and the pH of the solution was adjusted by adding diluted ammonia (25%) solution obtained from BDH.

2.3. Procedure

MTFE was prepared from a 30 mL of mercury plating solution placed in the cell by applying a potential of −0.8 V for 5 min. During this step nitrogen gas was bubbled thorough the solution for stirring. The cell was rinsed and 30 mL of supporting electrolyte containing Pb^{2+} ions was placed into the cell.

Amberlite XAD-7 resin was homogenized in an agate mortar and the resin particles were sieved by using 400 mesh sieve. Upon addition of 3.0 or 6.0 mg of resin, the mixture was deareated for further 6 min allowing the adsorption process to complete. Then the mixture was centrifugated for 5 min at 3000 rpm. The cell was carefully placed in the voltammetric stand and reference and auxiliary electrodes were immersed into the solution. The potential was scanned either in negative or positive direction in the range of −800 to 200 mV with a rate of 10 mV s^{-1}. The waveform used was square-wave mode with a 20 mV of pulse amplitude. Measuring time was 2 ms and current was sampled in every 0.30 s while the frequency was 50 Hz and potential step was 10 mV. Resulting current–potential recordings related to the lead ions that enriched between the electrode surface and the resin layer were used for the analytical purposes.

3. Results and discussion

Initial studies were conducted to see the influence of experimental parameters such as adsorption time, resin amount, pH, centrifugation speed and centrifugation time, resin dimension.

3.1. The effect of adsorption time

The time elapsed during adsorption process is of great importance for an effective preconcentration of lead ions in the resin. This time must be long enough for the adsorption process to be completed; therefore more sensitive results can be obtained. The cell content (1.0×10^{-6} M Pb^{2+} ions in 0.02 M ammonium acetate solution) was subjected to interact with 3.0 mg resin for several time intervals and then the Centri-voltammetric results were recorded. As shown in Fig. 2, the shape of the plot has fitted the adsorption phenomena. The peak currents at −0.5 V gave an increase with the adsorption time as expected. Here, it should be noted that the peak currents were plotted against the adsorption time and this parameter excludes the time passed during centrifugation step. Thus, it is reasonable to have a current value around 3 μA without waiting for adsorption process.

The peak current shows a decline for interaction times longer than 8 min indicating a loss in the analyte between the electrode surface and the resin layer probably due to the diffusion of the analyte to inner sites of the resin. Therefore 6 min. adsorption time was found to be adequate for further studies.

3.2. The effect of resin amount

In terms of sensitivity, the amount of resin that will yield the maximum peak current should be optimized. Since more resin can carry with more analyte to the electrode surface, it is expected to cause an increase in the current values. However, the results obtained by using 6 min of adsorption time has shown a decrease in peak current with resin amount more than 8.0 mg (Fig. 3). It should be emphasized that monolayer of resin which is in contact with the surface is the only source of analyte. Higher amounts were avoided since they cause poly layer formation, which results in lower current values. For this reason further studies were carried out with 6.0 mg resin.

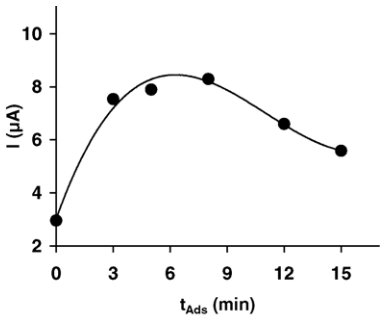

Fig. 2. Influence of adsorption times on the square-wave peak currents of test solution containing 1×10^{-6} M Pb^{2+} in 0.02 M NH_4CH_3COOH (pH 6.8, resin amount: 3.0 mg, V_{cent}: 3000 rpm, t_{cent}: 5 min).

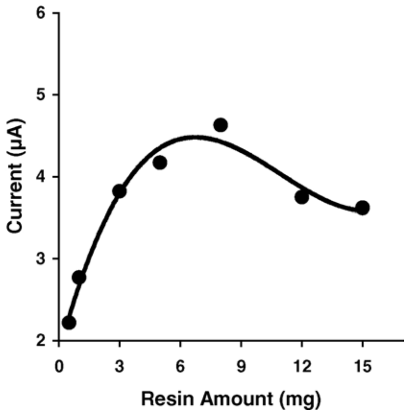

Fig. 3. Dependence of the square-wave peak current on the resin amount for the test solution containing 1×10^{-6} M Pb^{2+} in 0.02 M NH_4CH_3COOH (pH 6.8, t_{ads}: 6 min, V_{cent}: 3000 rpm, t_{cent}: 5 min).

3.3. The effect of pH

The medium pH affects the form of the analyte. As the pH was changed in the range of 2.0–9.0, the peak current gave an increase as shown in Fig. 4. In acidic media Pb^{2+} ions were carried by means of the resin to the electrode surface. At higher pH values, the hydroxide forms are brought about that will act as a carrier precipitate and tend to carry the ions other than Pb^{2+} ion found in the medium. At pH = 8 media, $Pb(OH)O^-$ formation occurs and split peaks are obtained with poor precision. The medium pH was selected as 6.8 for further studies.

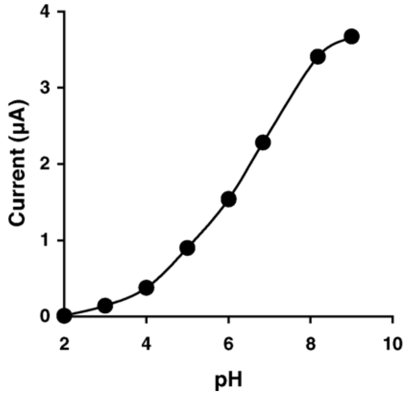

Fig. 4. The influence of pH on the square-wave peak currents of test solution containing 1×10^{-6} M Pb^{2+} in 0.02 M NH_4CH_3COOH (resin amount: 6.0 mg, t_{ads}: 6 min, V_{cent}: 3000 rpm, t_{cent}: 5 min).

Table 1
The effect of centrifugation speed on the peak current for a test solution containing 1 × 10^{-6} M Pb^{2+} in 0.02 M NH_4CH_3COOH (pH 6.8, resin amount: 6.0 mg, t_{ads}: 6 min, t_{cent}: 5 min)

V_{cent} (rpm)	i_p (µA)
0	0.56
1000	2.20
2000	2.62
3000	3.62
3500	4.55

3.4. Centrifugation parameters

In this method, centrifugation plays a vital role, as it is core of the preconcentration step. The resin particles should be deposited on the electrode surface as a thin film since it carries the analyte ions throughout the solution. The thickness of this film is predicted to be inversely proportional of the centrifugation speed. Thinner film formation is preferred to concentrate the analyte amount per unit volume. Therefore, the effect of centrifugation parameters namely speed and duration were examined. Table 1 demonstrates the influence of the speed on Centri-voltammetric results for 1 × 10^{-6} M Pb^{2+} ions. Although the peak currents have increased with centrifugation speed in the range studied, a speed of 3000 rpm was selected for avoiding the distortion of the cell that is usually the case when using homemade cells. However, special effort has been made to use the same cell for optimization of a particular parameter. Higher speeds can also cause removal of most of the electrolyte from the layer that will decrease the conductivity of the film and the peak current as well.

The duration of centrifugation step was also examined and Centri-voltammetric results were given in Table 2. The peak currents gave a sharp increase with the centrifugation time up to 5 min. For longer times, a slight decrease in the peak current is observed indicating the loss of the analyte from the film. This may be attributed to the decrease in the analyte holding capacity of the resin due to the removal of the electrolyte from the layer.

3.5. The physical condition of the resin

So far the studies were carried out with dry resin particles. In order to see the effect of physical condition of the resin, the difference between swollen and dry resin was examined. For this purpose, 6 mg of Amberlite XAD-7 resin was added into 30 mL of 0.02 M NH_4CH_3COOH solution and waited over night. The Centri-voltammetric results for both resin has shown that the peak current obtained with dry resin is 19.11% higher than that of swollen resin (data not shown). This difference may arise from the exchange mechanism of lead ions with NH_4^+ cations adsorbed by swollen resin particles. On the other hand, Pb^{2+} ion concentration per volume decreases with swollen resin which may also cause the polylayer formation over the electrode.

Table 2
The influence of the centrifugation time on the peak current for a test solution containing 1 × 10^{-6} M Pb^{2+} in 0.02 M NH_4CH_3COOH (pH 6.8, resin amount: 6.0 mg, t_{ads}: 6 min, V_{cent}: 3000 rpm)

t_{cent} (min)	i_p (µA)
1	1.13
3	2.94
5	4.51
8	4.45
15	3.42

Table 3
The list of optimal working conditions

Examined parameters	Optimal conditions
Adsorption time	6 min
Resin amount	6 mg
pH	6.8
Centrifugation speed	3000 rpm
Duration of centrifugation	5 min
Physical conditions	Dry<400 mesh resin

The resin dimension was kept under the 400 mesh throughout the study. In comparison to the voltammograms that were recorded with grounded (400 mesh) and ungrounded (20–60 mesh) resin a 90.45% enhancement in the peak current was observed. It can be concluded that smaller particles provide more effective surface for the adsorption of the analyte ions.

3.6. The versatility of the method

The overall parameters of the method were summarized in Table 3. The efficiency of the method developed was tested upon utilizing these parameters for comparison the results obtained with 1 × 10^{-6} M Pb^{2+} ion in the presence and absence of the procedure. The peak current obtained without any pretreatment was in nA levels. This value was enhanced to µA levels for the same concentration by means of Centri-voltammetry as shown in Fig. 5. The enrichment

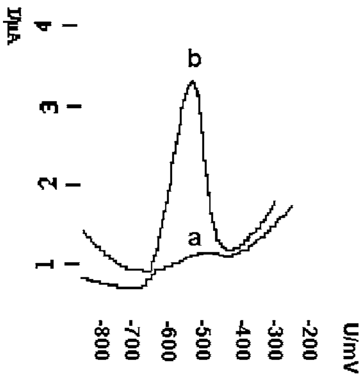

Fig. 5. The comparison of the square-wave peak currents obtained (a) without, (b) with applying Centri-voltammetric procedure for a test solution containing 1 × 10^{-6} M Pb^{2+} in 0.02 M NH_4CH_3COOH (pH 6.8, resin amount: 6.0 mg, t_{ads}: 6 min, V_{cent}: 3000 rpm, t_{cent}: 5 min).

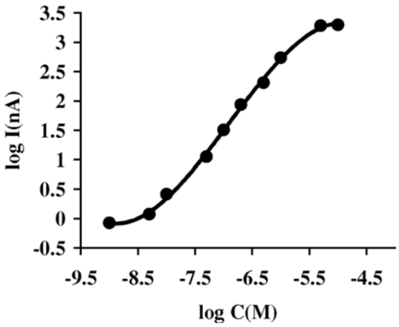

Fig. 6. The calibration graph for lead ions in 0.02 M NH_4CH_3COOH obtained with mercury plated gold sphere electrode (pH 6.8, resin amount: 6.0 mg, t_{ads}: 6 min, V_{cent}: 3000 rpm, t_{cent}: 5 min).

in the analytical signal was calculated as 170 fold. This value clearly indicates the effective aspect of the developed method.

3.7. Analytical characteristics

By employing the optimal conditions in Table 3, the Centri-voltammetric results, obtained with mercury film coated gold sphere electrode, were plotted against the lead ion concentration. The calibration graph shown in Fig. 6 fits the Langmuir isotherm. The curve was found to be linear in the concentration range of 5.0×10^{-9} to 1.0×10^{-6} M and saturation state was reached after the addition 5.0×10^{-6} M Pb^{2+} solution. For the linear range the regression coefficient was calculated as 0.995. A detection limit of 5.20×10^{-9} M can be estimated based on the signal to background characteristic of these data. In fact, as the Centri-voltammetry utilizes the voltammetric signal of the analyte accumulated with bulk deposition, further sensitivity can be attained by using higher bulk volumes.

The precision was tested upon using both electrodes. The R.S.D. was calculated and found as 7.8% for 1×10^{-6} M Pb^{2+} concentration ($n = 6$) from the studies carried out with mercury film coated gold sphere electrode. Better reproducibility (R.S.D. 3.3%) was obtained with Pt-plate electrode. This indicates that the configuration of the electrode is important in terms of precision and the platinum electrode provides a flat surface to collect the lead ions effectively.

Besides, better precision value was obtained with Amberlite XAD-7 compared to the former study carried with freshly prepared $Al(OH)_3$ precipitate [10]. This can be explained by the addition of precise amount of resin instead of freshly prepared precipitate in inconsistent amounts.

3.8. Interference study

The effect of some selected cations (Zn^{2+}, Cd^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, K^+, Na^+) and anions (Cl^-, $SO_4{}^{2-}$, and $NO_3{}^-$) on the Centri-voltammetric results was tested by using mercury coated gold sphere electrode. 1×10^{-4} M solutions of KCl, $Mg(NO_3)_2$, $Ca(NO_3)_2$, Na_2SO_4 had no significant effect on resulting peak current of 1×10^{-6} M Pb^{2+} solution. On the other hand, Cu^{2+} and Cd^{2+} ions increase the peak current of lead ion when presented 10 fold or more than 5×10^{-6} M. This may be attributed to the formation of hydroxide complexes of these ions at this pH which were acted as carrier precipitates for lead ions. Considering the enrichment of these metal ions on the resin, this occurrence may be more predictable. This interference can be a problem in studying with natural samples and can simply be eliminated by changing the pH or by using more selective coprecipitant.

3.9. Conclusion

Centri-voltammetry provides a very sensitive and versatile tool for trace analyses of reducible ions. The analyte was trapped between the electrode surface and thin layer of selective adsorptive material by means of centrifugation and therefore the loss of the analyte is eliminated which usually is the case for other preconcentration techniques. The method was also shown to be simpler than those methods based on coprecipitation since it does not require any decantation, filtration, elution or dissolution steps. All the procedure is applied on a single cell, which allows monitoring the voltammetric scan. In addition, the resin does not require any regeneration process since the procedure involves single use of the collector material.

The sensitivity of the method was found to be comparable to those of stripping techniques. On contrast to the ASV, this method provides the accumulation of most of the analyte on the electrode surface by maintaining the bulk deposition with an appropriate reagent. This constitutes a distinguished improvement for attaining lower detection limits by using higher bulk volumes. Besides, ASV method is limited to the amalgam forming metals whereas Centri-voltammetry allows determining reducible metals even those do not form a soluble amalgam as well as the other electroactive substances. On the other hand, the nature of the method permits for accumulation of the analyte without changing its oxidation state leading speciation studies. These features demonstrate the wide scope of the method.

The choice of carrier system and the signal waveform can provide a further selectivity in the measurement. Future studies will be deal with the cell design and search for various carrier systems for improving the selectivity.

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