

## Voltammetric Determination of Lead at Chemically Modified Electrodes Based on Crown Ethers

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The feasibility of fabricating lead-sensitive chemically modified electrodes (CMEs) for trace analysis in aqueous and 40% (v/v) ethanol-water media was investigated. Carbon paste electrodes modified with crown ethers were constructed by mixing the crown ethers into a graphite powder-paraffin oil matrix. The thus-formed electrodes were able to bind Pb(II) ions chemically, and gave better voltammetric responses than unmodified ones. The crown ethers studied and compared were 18-crown-6 and dibenzo-18-crown-6. With a 5% 18-crown-6 CME, Pb(II) could be quantified at sub-ppm levels by differential pulse voltammetry with a detection limit of 0.02 ppm. It was possible to selectively pick up Pb(II) from a solution of several other ions at an open circuit through complexation. A simultaneous analysis of Cu(II) and Pb(II) was also attempted. By differential pulse anodic stripping voltammetry Pb(II) could be quantified over the range of 1 to 100 ppb. Interference from metal ions like Ni(II), Co(II), Mn(II), Zn(II), Cd(II), Ag(I), Fe(III), Ca(II) and Mg(II) was also studied. The method was successfully applied to artificial as well as commercial samples of alcoholic beverages.

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As a continuation of our work in the fabrication of chemically modified electrodes (CMEs) for the analysis of metal ions in alcoholic beverages,<sup>1</sup> we have now made use of a 18-crown-6 CME for the trace analysis of lead. Modified electrodes capable of preconcentrating an analyte onto an electrode surface have been employed to enhance the analytical sensitivity and selectivity. Complexation prior to the electron-transfer step is particularly attractive, because the species may be trapped in a chemical environment that is conducive to rapid electron transfer; also, the analyte can be protected from interference by other species. A DNA-modified gold electrode<sup>2</sup> has been used for determination of Co(II) with a detection limit of  $4 \times 10^{-8}$  M. Self-assembled monolayers of 3,3'-thiodipropionic acid and *n*-decyl mercaptan formed on gold electrodes<sup>3</sup> were developed for the determination Cu(II) and Ag(I) with detection limits of  $2 \times 10^{-9}$  M and  $6 \times 10^{-8}$  M for copper and silver, respectively. CMEs consisting of a mixture of carbon paste and a modifying reagent have been widely used, since they can be easily prepared and have a stable electrode response.<sup>4</sup> Dimethylglyoxime has been employed for the determination of nickel;<sup>5</sup> dithiocarbamates,<sup>6</sup> diquinolyl-8-disulfide,<sup>7</sup> Alizarin Red S,<sup>8</sup> for copper; 1,11-bis(8-quinoyloxy)-3,6,9-trioxundecane<sup>9</sup> for mercury; *N*-*p*-chlorophenylcinnaohydroxamic acid<sup>10</sup> and 1,10-phenanthroline<sup>11</sup> for cobalt; and Dowex 50W-X8 for cadmium.<sup>12</sup>

Crown ethers have been used as modifiers for the determination of silver<sup>4</sup> and mercury.<sup>13,14</sup> They have been known to form complexes with a host of cations<sup>15</sup> including alkali, alkaline earth metal ions,  $\text{NH}_4^+$ , lanthanides and transition-metal ions. However, complexations with transition-metal ions have been rarely studied. The major thrust has so far been confined to the complexation of alkali metal ions, with

oxygen containing crown ethers and of transition-metal ions with aza/thia crown ethers. However, some authors have reported that oxygen-containing crown ethers do form complexes with transition-metal ions, albeit weak ones.<sup>16</sup> We obtained similar results from conductometric experiments in ethanol-water mixtures.<sup>17,18</sup> We found that 18-crown-6 and dicyclohexano-18-crown-6 formed very strong complexes with lead ( $\log K \sim 6$ ), but weak complexes ( $\log K \sim 2 - 3$ ) with transition-metal ions like copper, cobalt, zinc, nickel and silver.

In this paper, we describe the use of 18-crown-6 and dibenzo-18-crown-6 (because it offers the advantage of having very low solubility) as modifiers in carbon paste electrodes, for the quantification of lead by differential pulse voltammetry (DPV) and differential pulse anodic stripping voltammetry (DPASV). Here, the advantages of strong complexation and a suitably applied reduction potential were used to obtain enhanced voltammetric signals for trace analysis and to prevent interference, respectively. A 40% (v/v) ethanol-water mixture was chosen from an application point of view, because it resembles the composition of some common alcoholic beverages like rum, whiskey, vodka and gin. Lead and other metallic impurities happen to enter into these beverages during the manufacturing and storage processes, or in the case of adulteration. The standard method<sup>19</sup> for quantification at such low levels is by AAS. Here, an attempt has been made to provide an alternative method for analysis that is equally fast and reliable, but at reduced cost. In addition, a simultaneous analysis of lead and copper has also been carried out.

### Experimental

#### Apparatus

The voltammetric system used for the studies was an EG & G Princeton Applied Research 264 A potentiostat with a Model

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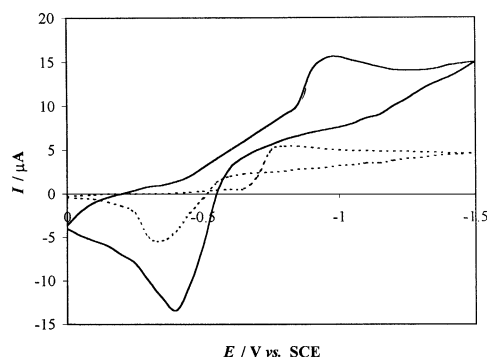


Fig. 1 Cyclic voltammograms obtained by PCPE (dotted curve) and 5% 18-C-6 CME (smooth curve) for  $4.95 \times 10^{-4}$  M Pb(II) in 0.01 M  $\text{NH}_4\text{NO}_3$  + 0.01 M  $\text{CH}_3\text{COONH}_4$  at 50 mV/s in aqueous medium.

303 A electrode assembly and an X-Y chart recorder (RE0089).

The autotitrator used for Karl Fischer titration and for the standardization of metal salt solutions was the Mettler Toledo DL53 Model. The probes used were, a double-pin Pt electrode (DM-142) and a conductometric sensor (Inlab-717), respectively.

A GBC 906AA atomic absorption spectrophotometer with an air-acetylene flame was used to analyze real samples of alcoholic beverages for comparison.

#### Chemicals

Double-distilled, deionized water was used to prepare all solutions. Triple-distilled ethanol (over molecular sieves), containing less than 0.2% water (as determined by Karl Fischer titration), was used to prepare ethanol-water mixtures. Both solvents were stored in sealed containers to prevent atmospheric contamination. Appropriate volumes of ethanol and water were mixed to give a 40% (v/v) solvent mixture.

The crown ethers, 18-crown-6 (18-C-6) Fluka and dibenzo-18-crown-6 (DB-18-C-6) Aldrich, were used as received. Lead nitrate, copper nitrate, cobalt nitrate, nickel nitrate, *etc.*, were of analytical grade.

Stock solutions of the metal salts were prepared and standardized by titration against EDTA on a DL53 autotitrator.

#### Electrodes

Modified carbon pastes were prepared by thorough mixing of coated graphite powder and paraffin oil in a mortar, as described earlier.<sup>1</sup> Plain (unmodified) carbon paste was prepared in a similar fashion, but no crown ether was added. The modified pastes contained 5% and 10% of the crown ether by weight. Fresh electrode surfaces were obtained by squeezing out a small amount of paste from a syringe, scraping off any excess and polishing the tip with zero grade polishing paper until the surface had a shiny appearance.

A platinum electrode served as an auxiliary electrode and a saturated calomel electrode (SCE) as a reference electrode.

#### Procedure

The response of CMEs prepared in the above-mentioned manner was studied in aqueous and 40% (v/v) ethanol-water mixtures as follows.

Initially, cyclic voltammograms of Pb(II) solutions in different electrolytes were recorded with a plain carbon paste electrode (PCPE) at a scan rate of 50 mV/s from +0.5 to -1.5 V vs. SCE. (The reference electrode was taken in a separate compartment with an ammonium nitrate salt bridge to avoid the

Table 1 Effect of modification on the cyclic voltammetric peak currents for  $4.95 \times 10^{-4}$  M  $\text{Pb}(\text{NO}_3)_2$  in 0.01 M  $\text{NH}_4\text{NO}_3$  + 0.01 M  $\text{CH}_3\text{COONH}_4$  at scan rates of 50 and 100 mV/s

Electrode	50 mV/s		100 mV/s	
	$I_{\text{pc}}/\mu\text{A}$	$I_{\text{pa}}/\mu\text{A}$	$I_{\text{pc}}/\mu\text{A}$	$I_{\text{pa}}/\mu\text{A}$
Unmodified	2.4	4.3	3.0	5.2
5% 18-C-6	7.6	14.5	8.9	15.9
5% DB-18-C-6	3.7	7.1	4.3	7.9

precipitation of  $\text{PbCl}_2$ ). Then, cyclic voltammograms of Pb(II) solutions in aqueous and 40% ethanol-water media using 0.01 M  $\text{NH}_4\text{NO}_3$  + 0.01 M  $\text{CH}_3\text{COONH}_4$  as a supporting electrolyte, were recorded with different CMEs under identical conditions. We used 5% 18-C-6 CME to study the effect of the scan rate on the peak currents. Open-circuit accumulation was carried out by stirring the solutions for 1 and 2 min with the CMEs dipping in a solution containing lead nitrate and ammonium nitrate. The CMEs were then transferred to another cell containing only the supporting electrolyte to record the voltammograms. The 5% 18-C-6 CME was also used to quantify lead and copper by DPV and DPASV at a pulse amplitude of 100 mV and a scan rate of 10 mV/s. In DPASV the deposition was carried out at -0.90 V vs. SCE with stirring. Artificial samples were prepared by mixing appropriate volumes of stock solutions, and were analyzed under identical conditions. The method of standard addition was used to quantify the copper and lead in artificial and real alcoholic samples by DPASV and DPV (as above). Here, a small volume of concentrated solution of  $\text{NH}_4\text{NO}_3$  +  $\text{CH}_3\text{COONH}_4$  was directly added to each sample so as to make it 0.01 M with respect to  $\text{NH}_4\text{NO}_3$  and  $\text{CH}_3\text{COONH}_4$ . Even though 18-C-6 has greater solubility in water and ethanol + water, due to the presence of paraffin in the paste, no leaching effects were observed for over a period of 2 h, which was more than sufficient for the analyses.

Real samples of gin, vodka and country liquor were appropriately preconcentrated and analyzed by AAS at 217.0 nm for lead and 324.7 nm for copper to compare the results obtained by the above-mentioned method.

## Results and Discussion

#### Voltammetry in aqueous medium

From the cyclic voltammograms obtained with a plain carbon paste electrode in 0.01 M KCl, 0.01 M  $\text{KNO}_3$  and 0.01 M  $\text{NH}_4\text{NO}_3$  + 0.01 M  $\text{CH}_3\text{COONH}_4$ , it was found that the ammonium nitrate-acetate medium was most suitable. Figure 1 shows cyclic voltammograms for Pb(II) solutions obtained with PCPE and 5% 18-C-6 CME electrodes in 0.01 M  $\text{NH}_4\text{NO}_3$  + 0.01 M  $\text{CH}_3\text{COONH}_4$ , respectively. It is observed that the unmodified paste electrode shows a typical "current cross over", which is a characteristic of an electrolytic deposition-stripping<sup>1,14</sup> mechanism; however, no such behavior was observed in the case of modified electrodes, indicating the effect of complexation by crown ethers. The cyclic voltammograms show that both the cathodic as well as anodic peaks are enhanced compared to the unmodified one. This happens due to the increased uptake of lead ions by the CME through complexation. Table 1 shows the effect of modification on peak currents observed by cyclic voltammetry. The enhancement was greater for the 18-C-6 modified electrodes and also the peaks are sharper. This was expected, since our previous studies<sup>18</sup> had shown strong complexation between 18-C-6 and

Table 2 Cyclic voltammetric peak currents obtained by open-circuit deposition of Pb(II) from  $8.317 \times 10^{-4}$  M Pb(NO<sub>3</sub>)<sub>2</sub> in 0.01 M NH<sub>4</sub>NO<sub>3</sub> for 1 and 2 min

Electrode	1 min		2 min	
	$I_{pc}/\mu A$	$I_{pa}/\mu A$	$I_{pc}/\mu A$	$I_{pa}/\mu A$
PCPE	0.12	0.25	0.22	0.38
5% 18-C-6	0.33	0.78	0.67	1.54
10% 18-C-6	0.69	1.58	1.40	3.22
10%DB-18-C-6	0.50	1.10	1.10	2.10

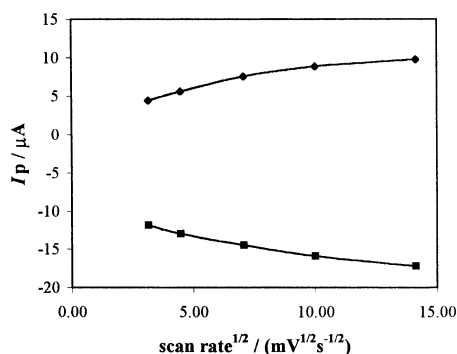


Fig. 2 Plot of  $I_{pc}$  and  $I_{pa}$  vs.  $v^{1/2}$  at 5% 18-C-6 CME for  $4.95 \times 10^{-4}$  M Pb(II) in 0.01 M NH<sub>4</sub>NO<sub>3</sub> + 0.01 M CH<sub>3</sub>COONH<sub>4</sub>.

Pb(II). Though the cavity size of DB-18-C-6 is more or less the same as that of 18-C-6, it shows a lesser uptake of lead ions, which could be due to the hindrance caused by the benzo groups. It was possible to accumulate Pb(II) at the CMEs at an open-circuit. Table 2 gives a comparison of the peak currents obtained by open-circuit deposition. Though 10% 18-C-6 CME showed higher sensitivity, the sensitivity shown by 5% 18-C-6 CME was considered to be sufficiently suitable for trace analysis. So, the 5% 18-C-6 modified electrode was used for further studies.

Voltammograms were recorded for Pb(II) solutions of two different concentrations, at varying scan rates. Figure 2 shows a representative plot of  $I_p$  vs.  $v^{1/2}$  which are not straight lines, but curve at higher scan rates, indicating that the process is not totally diffusion controlled, but some kinetic parameter, *i.e.* complexation, is effective. Also, a shift in the peak potentials is observed with the value of  $I_{pc}/v^{1/2}$  decreasing with an increase in the scan rates (Table 3). This implies that the chemical step precedes electron transfer.

The cathodic peak enhancement was used for determining lead in the range 0.1 to 1.5 ppm (1 ppm = 1  $\mu$ g/mL) by DPV. Well-defined peaks were obtained within the potential range scanned (−0.3 V to −1.3 V vs. SCE) with a current proportional to the concentration of copper ions (coefficient of correlation = 0.9991). A comparison of the peak currents obtained under identical conditions by plain carbon paste and 18-C-6 modified electrodes by DPV showed that the sensitivity of the modified electrode is about 2.5 times higher than that of the unmodified one. A detection limit of 0.02 ppm (RSD = 3.1% for  $n = 5$ ) was obtained under these conditions.

Under these conditions, the effects of interference by Co(II), Ni(II), Mn(II), Cd(II), Mg(II) and Zn(II) were studied. None of them was found to affect the Pb(II) peaks when present in 50-times excess concentration. A 70-fold excess of Cd(II),

Table 3 Effect of scan rate on the behavior of 5% 18-C-6 CME for  $4.95 \times 10^{-4}$  M Pb(II) in 0.01 M NH<sub>4</sub>NO<sub>3</sub> + 0.01 M CH<sub>3</sub>COONH<sub>4</sub>

Scan rate/mV s <sup>−1</sup>	$v^{1/2}$	$E_{pc}/V$	$E_{pa}/V$	$I_{pc}/\mu A$	$I_{pa}/\mu A$	$I_{pc}/v^{1/2}$
10	3.16	−0.92	−0.43	4.4	11.9	1.39
20	4.47	−0.93	−0.42	5.6	13.0	1.25
50	7.07	−0.95	−0.40	7.6	14.5	1.07
100	10.00	−0.97	−0.38	8.9	15.9	0.89
200	14.14	−0.99	−0.36	9.8	17.2	0.69

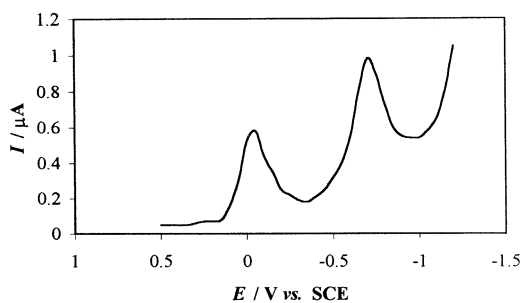


Fig. 3 Differential pulse voltammetric curves obtained for a solution containing 3.2 ppm Cu(II) and 0.2 ppm Pb(II) by 5% 18-C-6 CME at a scan rate of 10 mV/s for 100 mV pulse amplitude in 0.01 M NH<sub>4</sub>NO<sub>3</sub> + 0.01 M CH<sub>3</sub>COONH<sub>4</sub>.

Ca(II) and Mg(II) showed a lowering of peak height (by about 10%), which may be due to blocking of the crown ether sites, whereas 80-times excess Mn(II) caused a lowering of the peak height by about 5%, within the potential range studied. Co(II), Ni(II) and Zn(II) did not seem to interfere even when present in 100-times excess concentration. Three artificial samples containing similar amounts (0.3 ppm each) of Mn(II) + Ni(II) + Cd(II), Mn(II) + Zn(II) + Co(II) and Mn(II) + Mg(II) + Ca(II) along with Pb(II) were prepared and analyzed. The peak currents obtained for the samples were the same as those obtained for a pure Pb(II) solution, which shows that these ions do not interfere even when present together in a sample. However, as Cu(II) gives a reduction peak at around −0.05 V vs. SCE, the method can be used for simultaneous determination of lead and copper. Figure 3 shows a differential pulse voltammogram of 3.2 ppm Cu and 0.2 ppm Pb. It can be seen that the peak due to lead is higher than that of copper, even though its concentration is about one-sixteenth that of copper, which can be attributed to the selective uptake of Pb(II) by the crown ether at the electrode surface. Open-circuit deposition of Pb(II) (0.3 ppm) in presence of 50-times excess of Ag(I), Fe(III), Cu(II), Co(II), Ni(II), Mn(II) and Zn(II) from acidic media (pH = 5, using HNO<sub>3</sub>, to prevent hydrolysis of ferric ions), followed by DPV gave only the peak for lead, which shows the selectivity of the CME. However, ten times excess of Mg(II) or Ca(II) caused a lowering of the peak height of Pb(II). Thus, in samples containing Mg(II) and Ca(II) but no Ag(I) or (Cu), direct DPV is recommended.

As the anodic peak was found to be much more enhanced, this observation was used to quantify lead at ppb levels by DPASV. After some trial experiments, it was found that for a 1-min deposition period, a linear calibration curve (coefficient of correlation = 0.9995) was obtained over the range 10 to 100 ppb (1 ppb = 1 ng/mL) and over the range 1 to 10 ppb (coefficient of

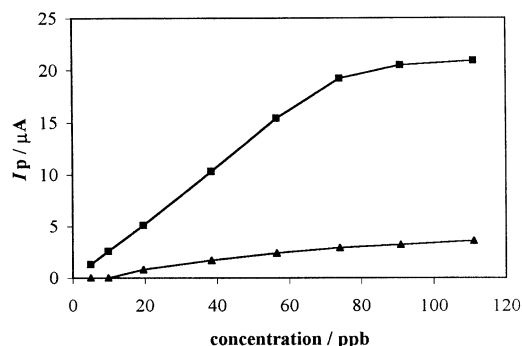


Fig. 4 Plot of the peak currents obtained for Cu (▲) and Pb (■) by 5% 18-C-6 CME for a deposition period of 30 s at  $-0.9$  V vs. SCE in  $0.01$  M  $\text{NH}_4\text{NO}_3$  +  $0.01$  M  $\text{CH}_3\text{COONH}_4$  at a scan rate of  $10$  mV/s and  $100$  mV pulse amplitude.

correlation =  $0.9993$ ) for a 2-min deposition period. On increasing the deposition times to 3 and 4 min, the sensitivity was increased and quantification up to the level of  $0.4$  ppb was possible. However, a further increase in deposition times did not yield better responses to further lower levels of Pb(II) due to the background currents. The deposition potential used was  $-0.9$  V vs. SCE, at which the other ions mentioned before (except copper and silver) do not get deposited, and hence do not interfere. A detection limit of  $0.2$  ppb ( $\text{RSD} = 6.6\%$  for  $n = 5$ ) was obtained for a deposition period of 4 min. A comparison of the peak currents obtained by 5% 18-C-6 CME and PCPE under identical conditions of deposition period, pulse amplitude, concentration, etc., showed that an enhancement by about eight times was obtained. It was also possible to deposit and analyze copper and lead simultaneously at this CME with a recovery of  $98 \pm 2\%$  for both Cu(II) and Pb(II) in artificial samples.

#### Voltammetry in 40%(v/v) ethanol-water mixture

The voltammograms obtained in this medium were almost the same as those in aqueous medium, but with higher peak currents. Here again, "current cross over" was observed in the case of an unmodified electrode, whereas the modified paste electrode showed increased peak currents without any "current cross over". The anodic peak, being sharper and more enhanced, was used for quantitative analysis of lead by DPASV. In this medium, deposition times of 20 s and 40 s were sufficient to obtain well-defined peaks and a linear calibration plot over the range 10 to 100 ppb and 1 to 10 ppb, respectively. This can be attributed to the fact that 18-C-6 forms a more stable complex with Pb(II) in this medium. Linearity was observed (Fig. 4) for both copper (20 to 80 ppb; coefficient of correlation =  $0.9961$ ) and lead (5 to 80 ppb; coefficient of correlation =  $0.9993$ ) in case of simultaneous DPASV (deposition time = 30 s). Again, on increasing the deposition times to 60 s and 80 s, the sensitivity was increased and quantification up to a level of  $0.25$  ppb was possible with a detection limit of  $0.1$  ppb. However, a further increase in the deposition times did not yield better responses due to background currents. In case of artificial samples, the percentage recovery of lead was generally found to be  $98.5 \pm 1.0\%$  and in particular for a 20 ppb sample the RSD was  $5.4\%$  ( $n = 6$ ). Here again, no interference was observed from the ions mentioned above. This method was applied to the determination of lead in commercial samples of gin, vodka and country liquor. The presence of lead could not be detected in the branded samples. The amounts of lead and copper in

Table 4 Comparison of the results obtained by DPV and AAS

Liquor	DPV		AAS	
	Cu, ppm	Pb, ppm	Cu, ppm	Pb, ppm
Sample 1	0.180	0.295	0.186	0.303
Sample 2	0.110	0.408	0.103	0.412
Sample 3	0.209	0.480	0.214	0.486

country liquor were quite high and were determined by DPV. Table 4 gives the results obtained by DPV and AAS for samples of country liquor.

## Conclusion

The strong complexation of 18-C-6 with Pb(II) has been advantageously used to enhance voltammetric signals. Also, interference from other transition-metal ions is prevented by means of potential control and the use of 18-C-6, which does not form strong complexes with transition-metal ions. The studies conducted in aqueous medium may be applied for trace analysis of lead and copper in environmental samples, like seawater, river water etc. The studies conducted in ethanol-water mixture can be directly applied to check for contamination in alcoholic beverages during processing.

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