Voltammetric Determination of Trace Levels of Hg in Ayurvedic Medicine and in Cobalt-Containing Samples Using a Carbon Paste Electrode

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An analytical method has been described for the determination of mercury using a carbon paste electrode. Conditions for the preparation of the carbon paste electrode were optimized for low background current in order to use it for the determination of ultra trace levels of mercury. The carbon paste electrode was found to be a good electrode material for the determination of mercury. The optimized pH for the determination was in the range of 2.5 to 3.5. The three sigma detection limit of mercury was obtained as $0.095 \mu\text{g L}^{-1}$. Method has been modified for determination of mercury in cobalt sulfate samples.

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Introduction

The rapid diffusion of heavy metals as environmental contaminants has called for more attention to their determination at trace and ultra trace levels.^{1,2} Determination of toxic trace metals is an important problem in environmental research, marine and aquatic chemistry, clinical and food chemistry. Mercury contamination is more severe than those of many other toxic heavy metal elements. Inorganic mercury undergoes methylation by microorganisms present in the environment and easily accumulates in the food chain.³ Mercury accumulates in the human body through the food chain, resulting in nausea, vomiting, abdominal pain and ultimately kidney damage³ in the case of an acute mercury exposure. Mercury exhibits very complex behavior in the food chain and in the human body system. The toxicity of mercury varies with its chemical form. Its toxic effect also depends upon the route of entry into the body system, dosage, frequency and the victim's age at the exposure.⁴ Mercury is known to be a potent neurotoxin which affects the central nervous system, resulting in irreversible brain damage. These studies indicated that special attention needs to be given to the possible heavy metal contents in water, soil and in certain special items such as herb medicine and nourishing diet that are becoming popular in recent times. There are many methods available for the determination of mercury at different concentration levels, among these, the electrochemical techniques⁵⁻⁷ and the cold vapor atomic absorption spectrometry^{8,9} are the most popular methods. There are some recent reports of the determination of mercury using nanoparticle modified electrodes¹⁰⁻¹³ where biomolecule-mercury interactions were used for selective preconcentration and a nano-particle modified electrode for signal enhancing.^{12,13} Carbon paste is an excellent electrode material for the determination of heavy metals in trace levels.^{14,15} The use of modified and unmodified carbon paste, glassy carbon and boron doped diamond electrodes and their

comparative behavior for the determination of mercury was reported in some papers.¹⁶⁻¹⁸ The problem due to the memory effect of mercury on glassy carbon or gold electrodes can be reduced in carbon paste electrode by simple regeneration of the surface; this solution has made carbon paste electrodes especially important in such analyses. In the present study a carbon paste electrode was prepared for use in electrochemical applications as the working electrode. The interfacial behavior of the electrode was studied using electrochemical impedance spectroscopy. A method for the determination of mercury at ultra trace level was developed in the present study. This method was used for the determination of mercury in ayurvedic medicines. Determination of mercury in cobalt containing compounds has some difficulty due to the interference of cobalt plated on the electrode surface with the cathodic preconcentration step. The method of determination of mercury in water samples and ayurvedic medicines has been modified for its use for the determination of mercury in trace levels in cobalt sulfate samples. In such high cobalt-containing samples, bare carbon paste electrodes perform better compared to the modified carbon paste or gold electrodes.

Experimental

Instrumentation and procedure

Electrochemical experiments were carried out using the cell assembly with a three-electrode configuration consisting of a carbon paste electrode as the working electrode and saturated calomel electrode (SCE) as the reference electrode. All potentials in this study were applied, measured and reported with respect to the SCE reference electrode. A platinum rod served as the counter electrode. Electrochemical measurements were performed using an Eco Chemie Potentiostat/Galvanostat, Autolab-100; the data acquisition and analysis was carried out by GPES 4.9 software. Experiments were performed at room temperature (298 K). Prior to electrochemical scan, voltammetric solution was purged with high purity nitrogen for 15 min. Digestion of the solid sample was carried out using an Anton

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Fig. 1 Voltammetric response of Hg in (0) blank solution then (1) to (5) with successive addition of $0.16 \mu\text{g L}^{-1}$ of Hg^{2+} . Inset: corresponding calibration plot. The deposition was carried out in 0.1 M HNO_3 solutions and stripping was carried out in $\text{NaNO}_3 + \text{HCl}$ mixture of 0.1 M concentration.

Paar Microwave Digester, Multiwave-3000. An aliquot of 1 g of the solid was taken with 5 ml of concentrated nitric acid and digested at 150°C for 20 min . After complete digestion, the solutions were diluted with nanopure water and made up to the volume of 50 ml . An aliquot of this sample solution was taken into the voltammetric cell and, after suitably adjusting the solution conditions, determination of metal ions was carried out using standard addition methods. The analysis of cold vapor atomic absorption (CVAAS) of mercury was carried out using mercury analyzer Model MA5840 from Electronic Co. of India Ltd. Hg^{2+} from sample solution was reduced using stannous chloride solution and the vapor was automatically collected; the atomic absorption of metallic mercury was measured at 253.7 nm .

Reagents and solutions

All the chemicals used were either E. Merck G. R. grade or BDH Anal R grade. Acids were of high purity BDH Aristar quality. A stock solution of mercury (approx 0.01 M) was prepared by dissolving a weighed amount of high purity HgCl_2 in 0.5 M hydrochloric acid. Appropriate quantities of all these reagents were weighed, dissolved in nano pure water and made up to desired volumes. High purity nitrogen gas of IOLAR grade (from Indian Oxygen Ltd.) was used for removing dissolved oxygen from the voltammetric solution.

Preparation of the carbon paste electrode

The spectroscopic grade carbon powder was heated at 400°C for 4 h in an inert atmosphere, after taking 0.5 g of the powder in a quartz boat. After heating, the powder was transferred to a beaker containing high purity paraffin dissolved in *n*-hexane. The mixture was kept under the fume hood at negative pressure and the *n*-hexane was allowed to evaporate, at the end the mixture was kept under a hot air blower for complete removal of *n*-hexane. Heating removes the adsorbed gases from the surface of the carbon paste; upon paraffin impregnation; the re-adsorption of gases was minimized. In this study, $\sim 1.5\%$ (weight %) of paraffin wax was added to the carbon powder. After paraffin impregnation, a required quantity of silicone oil was added as the binder (25% of the mass of modifier and carbon powder) and ground well to get a homogeneous paste. The carbon paste was filled inside a glass tube with 2 mm diameter at the bottom end; the connection from the carbon paste to the electrode connector of the instrument was made using a platinum wire.

Table 1 Detection limits of some reported methods using similar methods to that of the present case (the unit used to express the detection limit in the original paper has been retained)

Method of determination	Detection limit	Ref.
Stripping voltammetric determination of mercury using multi-walled carbon nano tube film coated glassy carbon electrode	$2 \times 10^{-10} \text{ M L}^{-1}$	19
Stripping voltammetric determination of mercury(II) using lectin-modified carbon paste electrode	0.0474 mg L^{-1}	20
Screen printed electrode modified with gold film and thiols modified magnetic nano particles	$0.08 \mu\text{g L}^{-1}$	21
Stripping voltammetry using modified glassy carbon electrode	$5.0 \times 10^{-9} \text{ M L}^{-1}$	22
Stripping voltammetry using carbon paste electrode	$0.1 \mu\text{g mL}^{-1}$	23
Present method	$0.095 \mu\text{g L}^{-1}$	—

Results and Discussion

The electrochemical response of the carbon paste electrode has been checked by using electrochemical impedance measurements. Well defined capacitive and resistive behavior was obtained with respect to the change in the applied potential (results are not shown). It was observed that, with the increase in the binder and wax concentration, the stability of the electrode material increases but the sensitivity of the electrochemical response decreases drastically. A deposition potential of -0.9 V was applied for the preconcentration process by way of depositing metallic mercury at the carbon paste electrode surface. The deposited tiny mercury droplets provide a sharp oxidation peak for the anodic stripping process. The voltammetric response obtained in the present case is shown in Fig. 1. Deposition was carried out for 600 s in this case. It was observed that the mixture of NaNO_3 and HCl of 0.1 M concentration provided better stripping response of mercury. The presence of Cl^- ions considerably increased the stripping response. This may have been due to the predominant formation of Hg_2Cl_2 and HgCl_2 during oxidation of tiny mercury droplets in the anodic stripping process. A calibration plot is shown in the inset of Fig. 1. Calibration was found to follow the regression equation of $I = 0.06 \times 10^{-9} + 2.18 \times 10^{-9} C$ with a correlation coefficient of 0.9922 and a standard deviation of 6.93×10^{-9} . Here the current I is in A and C in $\mu\text{g L}^{-1}$ unit. A three-sigma detection limit of mercury was obtained as $0.095 \mu\text{g L}^{-1}$. In Table 1 the detection limit of the determination of mercury obtained from a related technique using stripping voltammetry is shown.¹⁹⁻²³ The detection limit of the present method is observed to be better or comparable with the literature reports in similar fields. Additionally, the present method is devoted more to the determination of mercury in the presence of high concentrations of Co^{2+} .

Ayurvedic medicine powder (Triphala) samples were analyzed with this method using carbon paste electrode. Powder samples were digested using microwave digestion process as described in the experimental section. The clear solutions were analyzed for mercury content. The corresponding results are tabulated in Table 2. Results were cross checked using CVAAS method and the values were found from the two techniques agree well.

Table 2 Results of the mercury analyzed in ayurvedic medicine and cobalt sulfate samples

Samples with reference number	Electrochemical method/ng g ⁻¹	CVAAS method/ng g ⁻¹
Triphala (M7204)	511	510
Triphala (M7205)	517	509
Cobalt sulfate (M7300-A)	58.8	Not detected
Cobalt sulfate (M7300-B)	52.5	Not detected

Fig. 2 Cyclic voltammetric plot of 1 mM CoSO₄ with different switching potentials. The switching potential values were written near the corresponding plot.

Analysis of mercury in cobalt sulfate samples

Determination of mercury impurity present in cobalt compounds is an important issue. Cobalt sulfides are used for preparation of an electrochemical supercapacitor²⁴ and the presence of mercury as an impurity might enhance the discharge property of the materials. Mercury impurity is present in cobalt compounds in the range of ng g⁻¹. After solubilization of the solid sample in aqueous media, the concentration of mercury reduces further to sub the $\mu\text{g L}^{-1}$ range. Analysis of mercury in such samples is difficult by the CVAAS method. Electrochemical determination such as described in the present case is particularly important for the determination of mercury in cobalt compounds. Standard reduction potential of Co(II) reduction is -0.29 V (NHE). Though the standard electrode potential was well separated from that of Hg(II) reduction, it was observed that, at higher cobalt concentrations (10^5 times higher than that of mercury), the anodic stripping peak of mercury does not appear clearly at a mercury concentration of less than $\mu\text{g L}^{-1}$. Cyclic voltammetric experiments were carried out using 1 mM CoSO₄ solution on a glassy carbon electrode with varying the switching potential. The corresponding plot is shown in Fig. 2. It was observed that, with a switching potential less negative than -0.8 V , no oxidation peak was observed (cf. inset of Fig. 2). Beyond -0.8 V the oxidation due to the deposited Co metal was observed, this peak current was found to increase with cathodically increasing the switching potential (cf. Fig. 2). Thus in cobalt-containing samples a deposition potential for mercury at around -0.7 V might solve the contamination of the Hg stripping peak due to Co. However, from the effect of deposition potential on the peak current as shown in Fig. 3, it was observed that the Hg stripping peak current increased

Fig. 3 Effect of deposition potential on the mercury stripping process with: (0) the blank, (1) -0.4 , (2) -0.5 , (3) -0.6 , (4) -1.0 , (5) -1.2 V . Deposition time was for 800 s at the Hg^{2+} concentration of $10\text{ }\mu\text{g L}^{-1}$ in the presence of 0.1 mM Co^{2+} . Fig. 4 Effect of deposition time on the mercury stripping process with deposition time of: (0) the blank, (1) 300, (2) 400, (3) 500, (4) 600, (5) 800, (6) 1000 s at a deposition potential of -0.9 V at the Hg^{2+} concentration of $10\text{ }\mu\text{g L}^{-1}$ in the presence of 0.1 mM Co^{2+} . Inset: effect of pH on the stripping peak current for $10\text{ }\mu\text{g L}^{-1}$ of Hg^{2+} with deposition potential at -0.9 V and deposition time for 800 s.

considerably on changing the deposition potential from -0.6 to -0.9 V . So to create a better sensitive method as required in the present case a less negative deposition potential was not advisable.

However, for analyses of samples where the mercury content is more than $100\text{ }\mu\text{g L}^{-1}$, lowering the deposition potential would solve the problem of Co contamination in the Hg stripping peak. In this case the deposition potential was chosen at -0.9 V . The effect of pH on the stripping peak of mercury is shown in the inset of Fig. 4. It was observed at the pH range of 2.5 to 3.5 the response is better. The effect of deposition time was also studied by keeping the deposition potential at -0.9 V . Corresponding results are shown in Fig. 4. Hg stripping currents were found to increase with increase in the deposition time. The base of the peak was found to be broadened at higher deposition time, but the peak heights were clearly increased with deposition time. A higher deposition time was required to determine mercury at the ng L^{-1} range. At higher deposition times, the possibility of deposition of Co also increases. Thus, for successful determination of Hg in cobalt-containing samples

deposition potential and deposition times were very important. In the present case, the deposition potential was optimized at -0.9 V and the deposition time was for 800 s, unlike in water samples the deposition was carried out for 600 s.

Thus under deposition conditions of -0.9 V as deposition potential for 800 s it was not possible to avoid the deposition of Co along with mercury. In order solve the problem, after the deposition step several stripping solutions and conditions were tried to minimize the interference due to the deposited Co. It was observed that, for a stripping solution of $\text{NaNO}_3 + \text{HCl}$ mixture of 0.5 M concentration, a higher concentration of supporting electrolyte was better compared to that in water or ayurvedic medicine samples. After the preconcentration step, the electrode was dipped in the stripping solution and kept there for 300 s under stirring conditions. As a result, the Co interference was reduced considerably. It was observed that the open circuit potential in the stripping solution was -0.14 V; thus, on keeping the electrode in the stripping solution at the open circuit potential with the cell on condition, deposited Co might be oxidized. This might be the reason for the decrease in the Co interference after it was kept at the open circuit condition under stirring conditions. From the cyclic voltammetric measurement results (cf. Fig. 2) it was observed that the reverse peak of Co was well separated from the mercury stripping. Thus, one might ask the reason behind the interference of Co^{2+} with on the determination of mercury. This could be due the fact that, when Co is co-deposited with less content of Hg, the stripping current will be due to the diffusion process of mercury from the Hg-Co solution or inter-metallic compound, where as in absence of Co^{2+} in the solution, metallic mercury will be deposited as fine droplets or as thin films on the carbon paste electrode surface, which will produce very sharp stripping peaks due the oxidation of almost the entire amount of mercury. Thus, the presence of plated Co along with mercury in the deposition process reduces the mercury stripping. The analysis results of two cobalt sulfate samples are tabulated in Table 2. The relative standard deviation (RSD, %) of 4.52% for 6 repeated measurements was obtained for the cobalt sulfate sample No. M 7300-A. Values could not be cross checked by CVAAS method because the concentration was beyond the detection limit of the CVAAS method available in our laboratory.

Conclusion

Parameters for the preparation of the carbon paste electrode have been optimized. Electrochemical behavior of mercury on wax-impregnated carbon paste electrodes has been studied. The carbon paste electrode was found to be an excellent material for determination of mercury. The analytical methodology has been modified in cobalt-containing samples. The reason for the Co interference in the mercury analysis was the formation of a solid solution or intermetallic formation in the presence of Co, which reduced the stripping current.

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