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Diamond Electrochemistry**

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ABSTRACT:

In this project, we have attempted to develop a new technique utilizing Boron-doped diamond (BDD) films to electrochemically detect mercury dissolved in solution via the initial deposition of metallic mercury, followed by anodic linear sweep voltammetry in the range from 10^{-10} M to 10^{-5} M. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques were employed. The extremely low background current for BDD electrodes compared to glassy carbon (GC) provides a strong advantage in trace metal detection. CV peak currents showed good linearity in the micromolar range. A detection level of 6.8×10^{-10} M was achieved with DPV in 0.1 M KNO_3 (pH = 1) for a deposition time of 20 minutes. Reproducible stripping peaks were obtained, even for the low concentration range. A comparison with GC shows that BDD is superior. Linear behavior was also obtained in the mercury concentration range from 10^{-10} M to 10^{-9} M.

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INTRODUCTION:

Mercury is present in coals in the 0.02 to 0.25 ppm range. According to the recent U.S. Environmental Protection Agency's Mercury Study Report to Congress [1], development of cost-effective strategies for the control of mercury emissions from coal-fired power plants is a necessity, since over 30% of the mercury emissions come from these power plants.

It is found that gaseous mercury emissions are about equally divided between elemental mercury (Hg^0) and oxidized mercury (Hg^{2+}) mostly as HgCl_2 , HgO and $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ [2,3]. These different species need to be quantified accurately on-site since each species has a different deposition and transport mechanism in air and may require different control strategies. For example, since Hg^{2+} is about 10^5 times more soluble in water than Hg^0 , it is likely that Hg^{2+} ends up in aquatic ecosystems, which can bioaccumulate as methyl mercury in fish and other aquatic life forms. Recent studies have reported some initial success in the control of mercury emission from power plants using activated/modified carbons as adsorbents [4-8]. It is found that as the carbon content of the coal increases, and flue gas temperature is decreases, the mercury retention in the dust improves [9]. Thus the mercury emissions are dependent on the constituents of a coal, making these emissions to be a complex scientific and environmental problem [9-11].

From the above background, it is clear that rapid on-site speciation and quantification of mercury emission is essential for developing cost-effective control strategies. The methods for the speciation/quantification of mercury that have tried/developed in recent years [11-12]. include: (i) The EPA Method 29 in which impingers ($\text{H}_2\text{O}_2/\text{HNO}_3$ for Hg^{2+} and $\text{KMnO}_4/\text{H}_2\text{SO}_4$ for Hg^0) are used. The problem with this method is that a significant amount of Hg^0 is captured in $\text{H}_2\text{O}_2/\text{HNO}_3$ and therefore reported as Hg^{2+} , making the method unreliable; (ii) The Ontario-Hydro Method is a modification of the Method 29, with $\text{H}_2\text{O}_2/\text{HNO}_3$ replaced by KCl impingers. This method is being tested at a midwestern power plant [12]; (iii) The mercury speciation adsorption method (MESA) is based on using solid absorbers [10]. The difficulty with all these methods is that the turn around time for results is very long (days and weeks). On-line detectors based on spectroscopic methods (e.g. Semtech 2000) are currently being tested; however these detectors only measure elemental Hg and the presence of Co , Fe and Mn interferes with the accuracy of the measurements [10].

Because of the growing awareness of environmental mercury pollution and its high toxicity, it is becoming more urgent to develop highly sensitive techniques for the detection of Hg (13). Spectroscopic techniques such as cold- vapor atomic fluorescence spectrometry (CV-AFS),(14) cold-vapor atomic absorption spectrometry (CV-AAS),(15) and inductively coupled plasma-mass spectrometry (ICP- MS)(16) have been used successfully for the detection of mercury. However,

all of these techniques require relatively large sample volumes for analysis and are also not suitable for on-line monitoring.

EXECUTIVE SUMMARY:

Highly boron doped diamond (BDD) electrode films grown on silicon substrates were used to develop calibration curves for the detection of mercury. Anodic differential pulse voltammetric technique was used for detecting ppb level concentrations of Hg. A comparison with glassy carbon (GC) indicates the extremely low background current and high sensitivity for the BDD electrodes. Further, the presence of ionic species such as chloride and nitrate also influence the sensitivity. Presence of chloride ions improves the sensitivity more than nitrates ions but the formation of mercurous chloride was found to be detrimental to further measurements. We have found that the sensitivity and reproducibility can be improved by co-depositing ppm amounts of gold on the BDD electrodes. Linear calibration method has been developed for 1-10 ppb and 10-50 ppb ranges. Standard addition method has also been used to determine the amount of mercury in flue gas sample obtained from NETL, Pittsburgh. We have also compared our results with cold vapor atomic absorption (CVAA) technique which showed a good correlation indicating that suitability of our method for possible on-line monitoring.

EXPERIMENTAL:

Boron-doped diamond films were deposited on conductive silicon substrates by use of microwave-assisted plasma-enhanced chemical vapor deposition (17). An O-ring type three-electrode electrochemical cell was used. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrodes, respectively. An auxiliary platinum quasi-reference electrode was used along with the SCE to decrease noise. A Hokuto-Denko Model HZ-3000 potentiostat was used for all of the electrochemical measurements. The supporting electrolyte used was 0.1 M KNO_3 , acidified with 0.05M HNO_3 (pH = 1). The mercury solutions were prepared from $\text{Hg}(\text{NO}_3)_2$ (from Fisher and Aldrich) with ultrapure water and ca. 0.05M of HNO_3 . It was found to be unnecessary to remove oxygen from the solutions, due to the high overpotential for oxygen reduction (17). This is also an advantage for trace metal detection using diamond electrode. However, in a series of sequential measurements with increasing Hg concentrations, in which aliquots of Hg^{2+} stock solution were added, the electrolyte was mixed between additions by use of N_2 gas bubbling in order to save time.

RESULTS AND DISCUSSION:

BDD electrode films grown on silicon substrates were used to detect trace metals in laboratory made as well as coal power plant flue gas samples (18,19). We have successfully detected ppb levels of mercury metal ions in standard solutions as well as real samples.

Cyclic voltammetric scans for millimolar concentrations of Hg at a BDD electrode revealed significant anodic oxidation and cathodic reduction peaks at 0.4V vs. SCE and 0.32V vs. SCE respectively in high pure nitrate electrolyte. Figure 1a and 1b show the CVs for the high-purity mercuric nitrate as well as the effect of the addition of 0.14% chloride. As one can see, the addition of chloride significantly shifts the anodic peak to 0.18V vs. SCE and as well as the peak current.

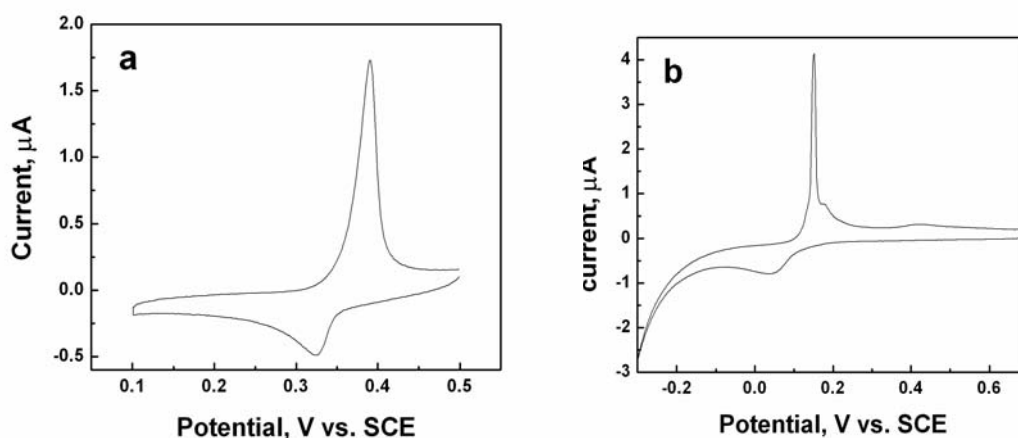
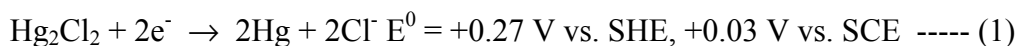


Figure 1. Cyclic voltammetry for $\text{Hg}(\text{NO}_3)_2$ solution ($2 \times 10^{-5} \text{ M}$) in 0.1 M KNO_3 ($\text{pH} = 1$) electrolyte a) without b) with the addition of $0.14\% \text{ KCl}$. The mercury stripping peak appeared at 0.4 V vs. SCE (a) is shifted to 0.18 V vs. SCE (b). This clearly explains the effect of chloride addition

However, if an anion, e.g., chloride, that forms an insoluble mercury compound is present, the reversible potential will be shifted substantially in the negative direction:



It should be noted here that, because the oxidation process involves the formation of highly insoluble product Hg_2Cl_2 (calomel), the electrode must be cleaned carefully with concentrated HNO_3 , followed by rinsing with high-purity water. In order to achieve higher detection sensitivity, we have employed the DPV technique. This technique can increase the sensitivity by isolating the Faradaic response from the associated effects of solution resistance and capacitance especially for mercury. Further, the presence of ionic species such as chloride and nitrate also influence the sensitivity. Presence of chloride ions improves the sensitivity more than nitrates indicating the formation of mercurous chloride which affects the reproducibility. It should be noted that the important observation is the oxidation process that involves the formation of highly insoluble product Hg_2Cl_2 (calomel) which can affect the reproducibility of the experiment unless the calomel is cleaned from the surface. In order to avoid this problem, we followed a new approach in which 1-3 ppm amount of gold was co-deposited on the BDD electrode surface simultaneously. This will be described later.

For comparison with glassy carbon (GC), we have carried DPASV on both BDD and GC electrodes. Fig. 2 shows clear evidence for the observation of the mercury stripping peak at BDD electrode surface whereas no peak was observed for the GC.

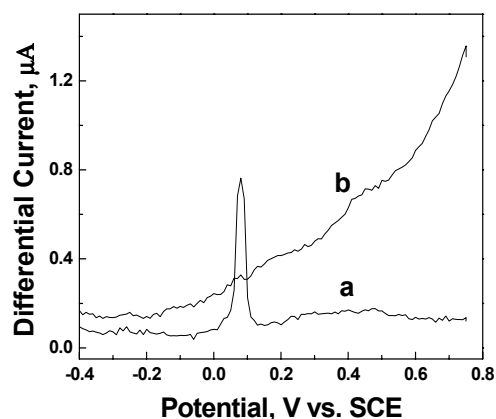
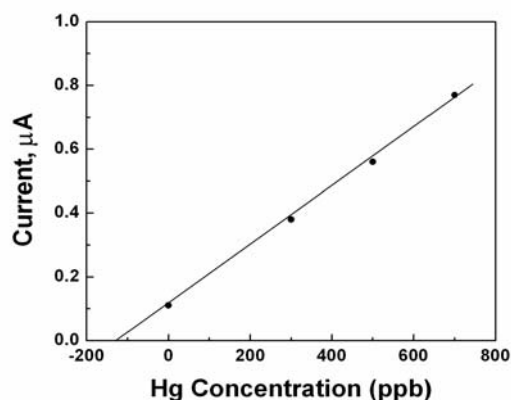


Figure 2. DPV for curves for $\text{Hg}(\text{NO}_3)_2$ solution ($6.4 \times 10^{-7} \text{ M}$) in 0.1 M KNO_3 ($\text{pH} = 1$) electrolyte for a) diamond b) glassy carbon electrodes. Deposition time was 2 minutes at -0.5 V vs. SCE ; pulse amplitude, 50 mV ; sweep rate, 100 mV s^{-1} .

In order to validate our method, a comparison with cold vapor atomic absorption spectrometry (CVAAS) was also carried out using a real sample (KCl impinger solution) obtained from the flue gas coal fired power plant. Figure 3 shows the DPV analysis of the real sample using BDD. The concentration of mercury in the sample was estimated as $120 \pm 7 \text{ ppb}$ using standard addition method. A comparison of the same solution by CVAAS indicated a mercury level of $115 \pm 5 \text{ ppb}$ that agrees well with the value estimated using our diamond electrodes.



We have shown successfully the feasibility of BDD electrodes as electrochemical sensors for the analysis of mercury. The effect of nitrate and chloride ions is very clearly evident from the

cyclic voltammetric analysis. The presence of chloride enhances the stripping peak currents and on the other hand it forms insoluble calomel at the surface of the electrode. In order to avoid this problem, we have successfully utilized a gold co-deposition method. Fig. 4a, 4b shows the calibration plot for 10-50 ppb and 2-10 ppb of mercury in the presence of 3 ppm of gold standard solution.

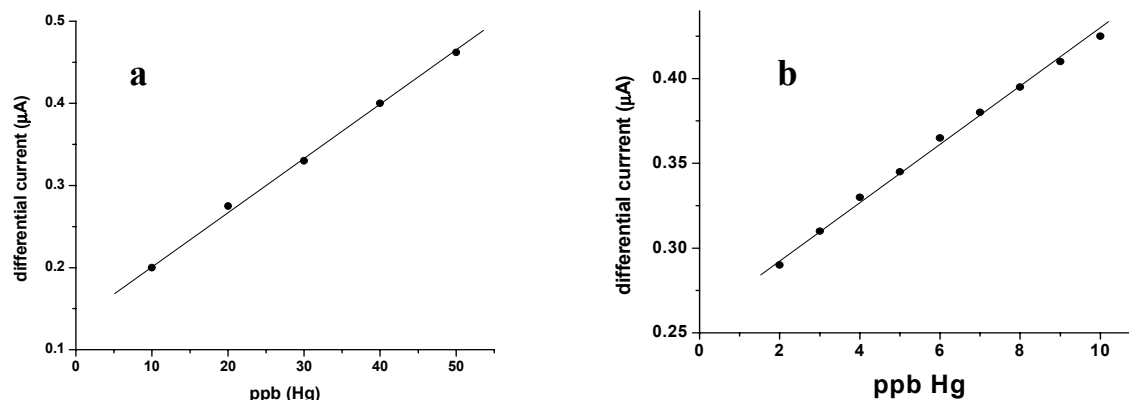


Figure 4. Calibration curve for DPV peak currents for Hg^{2+} concentrations at BDD covering a range from 0-50 ppb (a) and 1-10 ppb (b). 3 ppm of gold standard solution was added to the electrolyte.

The results described above are the proof of concept. For further details and discussions on this work one can refer to our recently published work (18,19). More work is being carried out to analyze new samples from the NETL site during gold co-deposition and compare with CVAA in order to continue our project so that an on-line detector suitable for the power plant can be achieved.

CONCLUSION:

Several other problems need to be solved before this technique becomes useful for practical applications. First is the effect of chloride ions on the detection current since the real samples from coal fired power plants will have significant amount of chloride. Although, the chloride ions enhance the sensitivity, they also form Hg_2Cl_2 at the electrode surface which affects the sensitivity and reproducibility. We are experimenting with different procedures (e.g. co-deposition of gold) to overcome the effect of the chloride problem so that reproducible calibration curves for mercury detection in the presence of chloride ions can be obtained. The co-deposition of gold enhances the nucleation sites for mercury since it has a great affinity to form amalgam with mercury. During this period we have shown the possibility of using diamond electrodes for mercury detection and quantification in the range of 1-50 ppb which can lead to the development of on-line monitors for coal fired power plants.

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